Trace Elemental Analysis of Genesis Samples: Progress in Developing RIMS with Laser Ablation Probe

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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 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 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.

We respond to this challenge [5] *with our development of an improved RIMS instrument described in this presentation.*

The Approach

RIMS instrument is a combination of TOF-MS with a laser post-ionization ion source. Extracted material must be neutral atoms (not ions as in SIMS) from the solid sample produced by either an ion- or a laser beam acting as analysis probe. Each sub-system of the RIMS, **(1)** the analysis probe, **(2)** the REMPI lasers and **(3)** the TOF-MS, contributes to the SNR (which is crucial for detection of trace SW elements) and therefore must be thoroughly optimized.

For Genesis, the optimization process is driven by experience obtained in experiments with different types of SW collector materials subjected to the actual analysis probe so that elemental species extracted from these materials are post-ionized by actual REMPI lasers and analyzed by actual TOF-MS. To be truly useful for the improved design of RIMS for Genesis, this experimental information must be very extensive and multifaceted.

Thus, our development [6] is step-by-step process such that key instrument components (1), (2) and (3) are constructed and tested with SW collector materials using an intermediate "testbed" RIMS instrument. The most important and time-consuming part of these tests is the analytical method development – i.e. figuring out how to analyze Genesis SW samples in most accurate and precise fashion. Results of experiments with the "testbed" RIMS guide our continuing optimization of the design of the dedicated Genesis RIMS, whose TOF-MS component is being currently constructed.

Our analysis probe **(1)** is 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. Using ultrafast lasers with femtosecond or picosecond pulses dramatically reduces heating (a "cold" ablation regime) during extraction of material from the sample and is 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-bottomed craters enabling high resolution depth profiling can be obtained with laser beams that have specially shaped power density profiles. Depth profiling will allow efficient discrimination from surface contaminants, which is what we need for accurate analyses 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.

Our tunable REMPI laser system **(2)** features three Ti:sappire lasers designed for multi-element RIMS analysis with simultaneous detection of two SW trace elements (Rb + Sr) and one reference SW element (Mg).

For the TOF-MS **(3)**, we introduced a concept of mass analyzer with slit spectroscopy capability, which can efficiently filter out noise from direct/secondary ions with minimal influence on signals of photo-ions. We called it Right-Angle Ion Mirror-Prism (RAIMP). We upgraded the operational TOF-MS instrument at UIC with RAIMP. Based on results of the experiments with this RIMS "testbed", we further developed this concept to synergize the RAIMP and reflectron for ultimate combination of high SNR and high MRP – exactly what is needed for analyses of trace elements in Genesis SW samples

Accomplishments

Combined operation of all three subsystems of RIMS at UIC was optimized in a "testbed" instrument, which is applied to three different SW collector materials (Si, DOS and sapphire). We used 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. We have demonstrated multi-element RIMS analysis for Rb +Sr. The laser for Mg is near completion: its ability to generate 3[rd] harmonic (~285nm) of tunable Ti:sapphire radiation is currently being optimized.

Our progress in depth profiling with RIMS using 800 nm femtosecond laser probe was very substantial: from LPSC 2019 to LPSC 2020, we improved dynamic range by optimizing the laser ablation probe and demonstrated *sub-nanometer depth resolution* of the laser probe was sufficient to resolve surface contamination from the ion implant.

Thus, to date, our testing and optimization resulted in having components **(1)** and **(2)** close to completion in terms of optimal performance, and we achieved considerable progress in development of most efficient methods for depth profiling analysis of Genesis samples with RIMS.

Finally, the optimized TOF-MS (i.e. component **(3)**) has been designed and a vast fraction of its components purchased or fabricated. The remaining pieces awaiting completion of fabrication are ion optics: because our entire series of test experiments aimed at their optimization, minor design changes and "tweaks" were introduced at the last moment. The construction of the new dedicated RIMS instrument is going in parallel with continuing optimization of the analytical methods using the "testbed" RIMS instrument.

Continuing and future effort

Our ongoing efforts using the testbed RIMS are focused on: (1) further 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.

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.

References

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Acknowledgements

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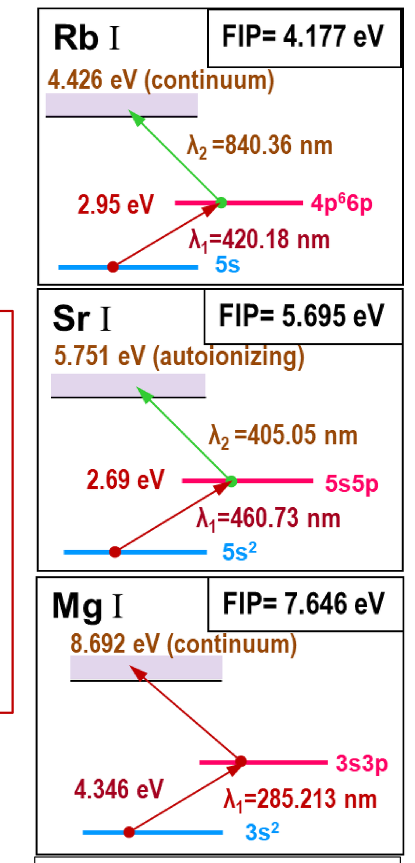
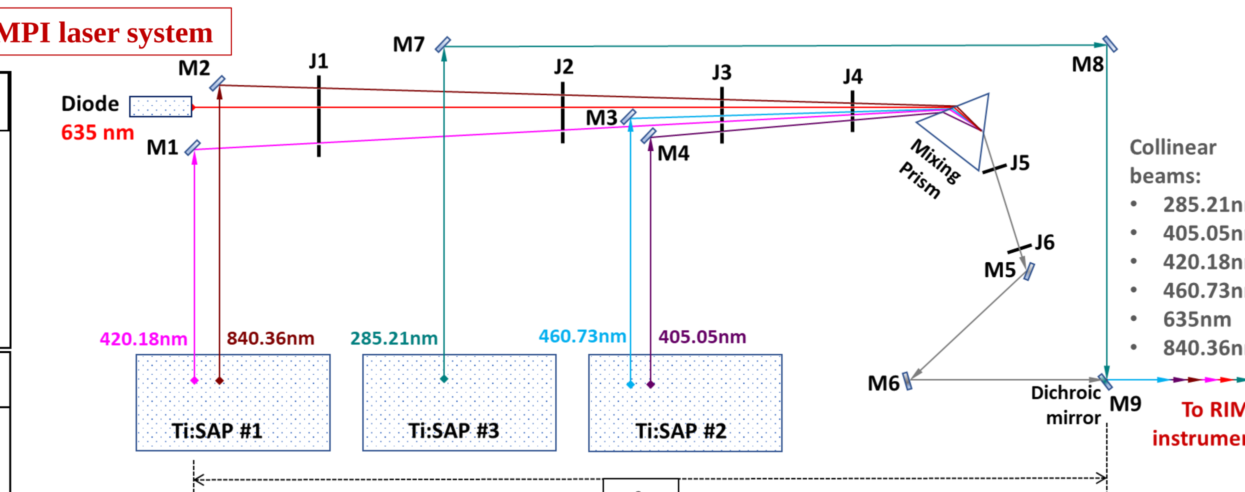
Improved RIMS for Genesis = Synergy of
(1) Femtosecond IR and Picosecond UV Laser Ablation Probes with Flat-Top Power Profile
(2) Optimized Tunable Laser System for Resonantly-Enhanced Multiphoton Ionization (REMPI)
(3) Time-Of-Flight Mass Spectrometer (TOF-MS) with high Signal-to-Noise (SNR) and Mass Resolving Power (MRP)

(2) Operational REMPI laser system

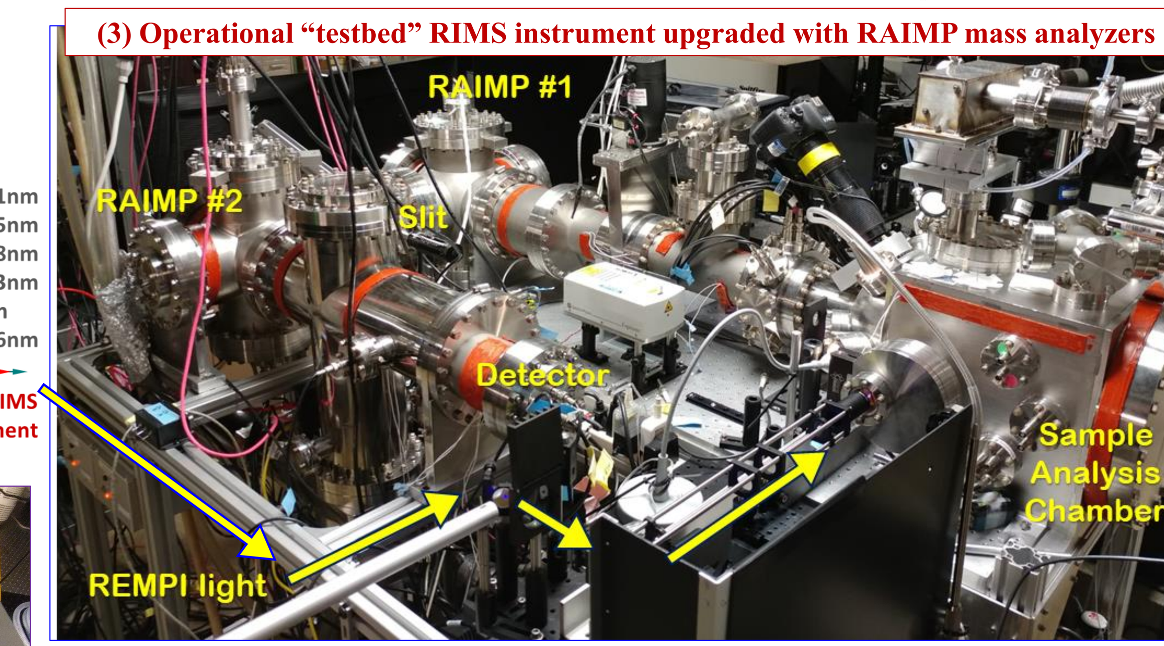


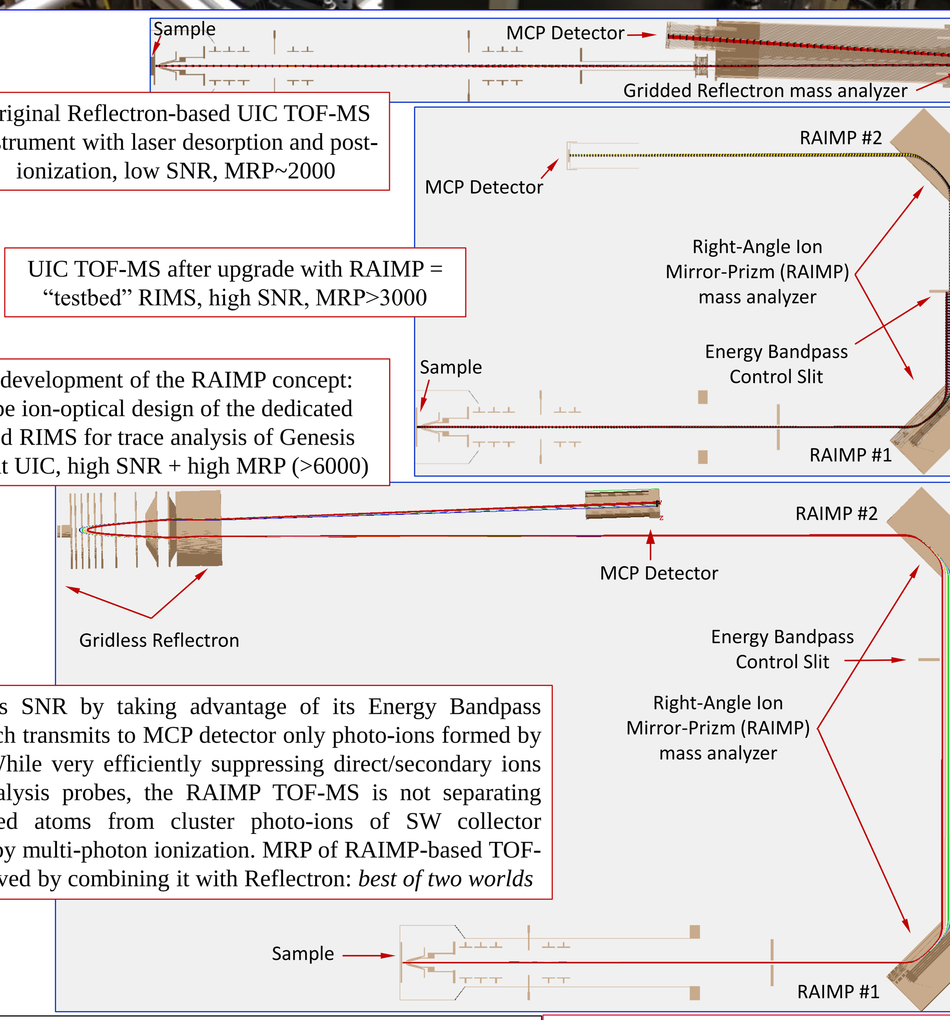
REMPI schemes for Rb, Sr and Mg



Schematic layout of the optical beamline for collinear combination of several tunable laser beams for REMPI generated by Ti:sapphire lasers (Ti:SAP #1 / Rb, #2 / Mg and #3 / Sr) and a reference red 635 nm beam generated by a diode laser (needed for visualization of the position of REMPI beams with respect to the analyzed sample surface). Mirrors M1 - M4 direct beams from Ti:SAP #1 and #3 into the Mixing Prism (fused silica), and a combined set of four beams (fundamental 840nm, and second harmonics 460nm, 420nm and 405nm) is steered by mirrors M5 and M6 towards the RIMS instrument viewport (for REMPI of Rb and Sr). Alignment jigs J1-J6 with precisely machined aperture holes assure that these beams enter and exit the mixing prism with correct angles. During RIMS experiments, these jigs are removed. Mirrors M7 and M8 steer the tunable third harmonic beam (285nm) towards dichroic mirror M9 (transparent for 400-800 nm and reflecting for 285nm), which brings this beam onto the same axis as the other five (four tunable + red). After the mirror M9, the six beams are directed and conditioned by another optical setup installed on the frame of the "testbed" RIMS instrument.

(3) Operational "testbed" RIMS instrument upgraded with RAIMP mass analyzers



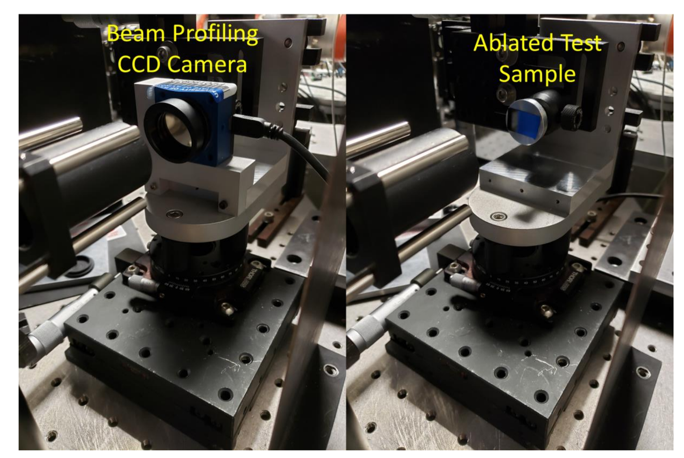


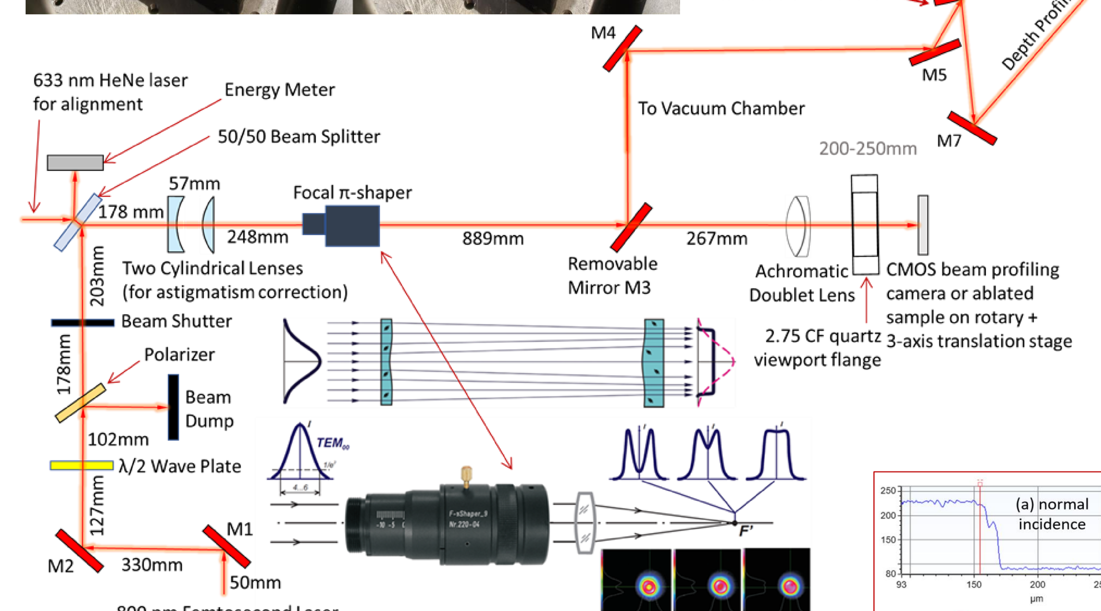
Original Reflectron-based UIC TOF-MS instrument with laser desorption and post-ionization, low SNR, MRP~2000

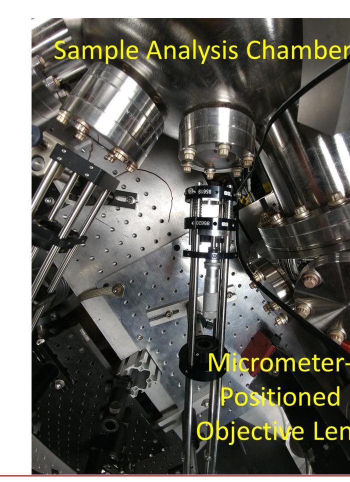
UIC TOF-MS after upgrade with RAIMP = "testbed" RIMS, high SNR, MRP>3000

Further development of the RAIMP concept: prototype ion-optical design of the dedicated improved RIMS for trace analysis of Genesis samples at UIC, high SNR + high MRP (>6000)

RAIMP improves SNR by taking advantage of its Energy Bandpass Control Slit, which transmits to MCP detector only photo-ions formed by REMPI lasers. While very efficiently suppressing direct/secondary ions generated by analysis probes, the RAIMP TOF-MS is not separating resonantly ionized atoms from cluster photo-ions of SW collector material formed by multi-photon ionization. MRP of RAIMP-based TOF-MS can be improved by combining it with Reflectron: *best of two worlds*





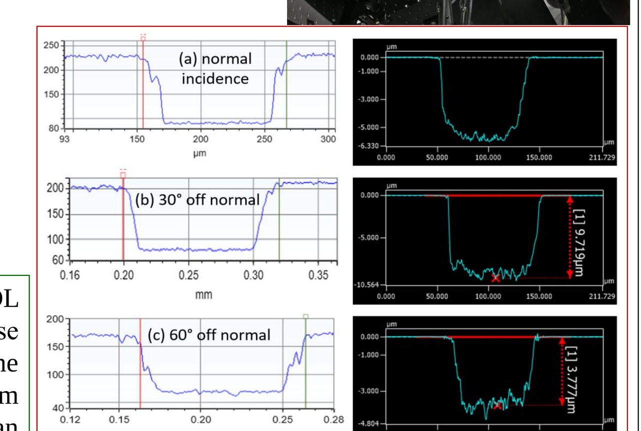


(1) Operational femtosecond 800nm Laser Probe with flat-top beam profile

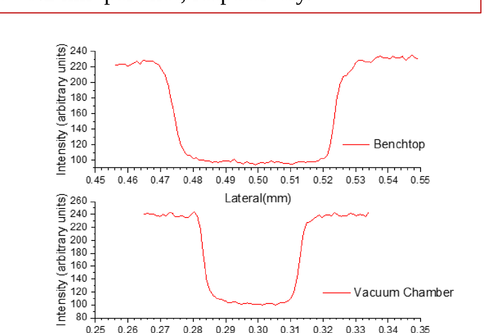
To shape the profile of our analysis probe, we use special refractive optics (ADL Optica Pi-shaper), which allows choosing between Gaussian, Flat-top, "Inverse Gauss" and "Doughnut" profiles. The schematic layout of the optical beamline for the laser probe is shown above. It features a flexible setup with beam profiling camera such that the shape of the beam going into vacuum chamber can be precisely aligned under ambient conditions.

Using Pi-shaper optics allows obtaining laser ablation craters with nearly-flat bottom and steep nearly-vertical walls for a wide range of irradiation angles, from normal to oblique. We also experimentally demonstrated that the diameter of a crater obtained with flat-top profile changes slowly while the number of adsorbed laser shots increases quickly. On the contrary, a crater formed by Gaussian beam profile quickly widens with increase of the number of laser shots, making accurate depth profiling virtually impossible.

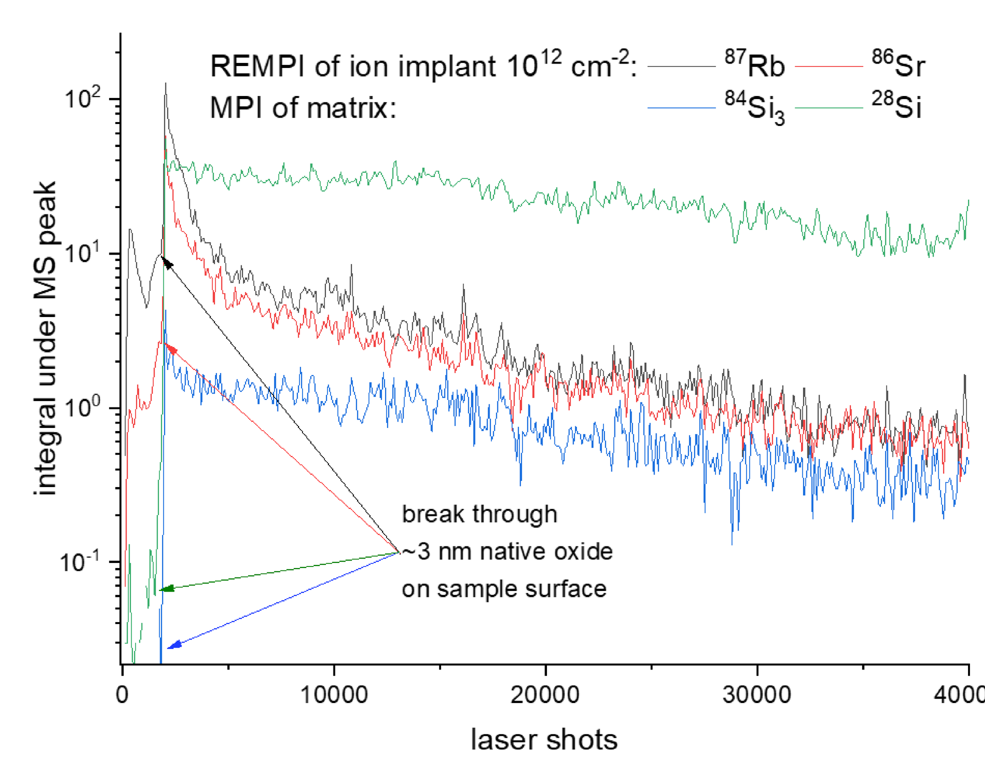
We demonstrated sub-nm depth resolution with the flat-top laser ablation probe



Ablation of Si with flat-top laser probe. Craters represent 20000 laser shots. Characterization used: Left: Bruker-Nano Contour GT-K optical profilometer, Right: Keyence VK-X1000 3D laser scanning confocal microscope.
(a), (b) and (c) – normal incidence, 30° and 60°, respectively. Crater depths: from ~6 μm for normal ablation to <4 μm for 60°, yielding depth resolutions from ~0.3 nm to ~0.2 nm per shot, respectively.

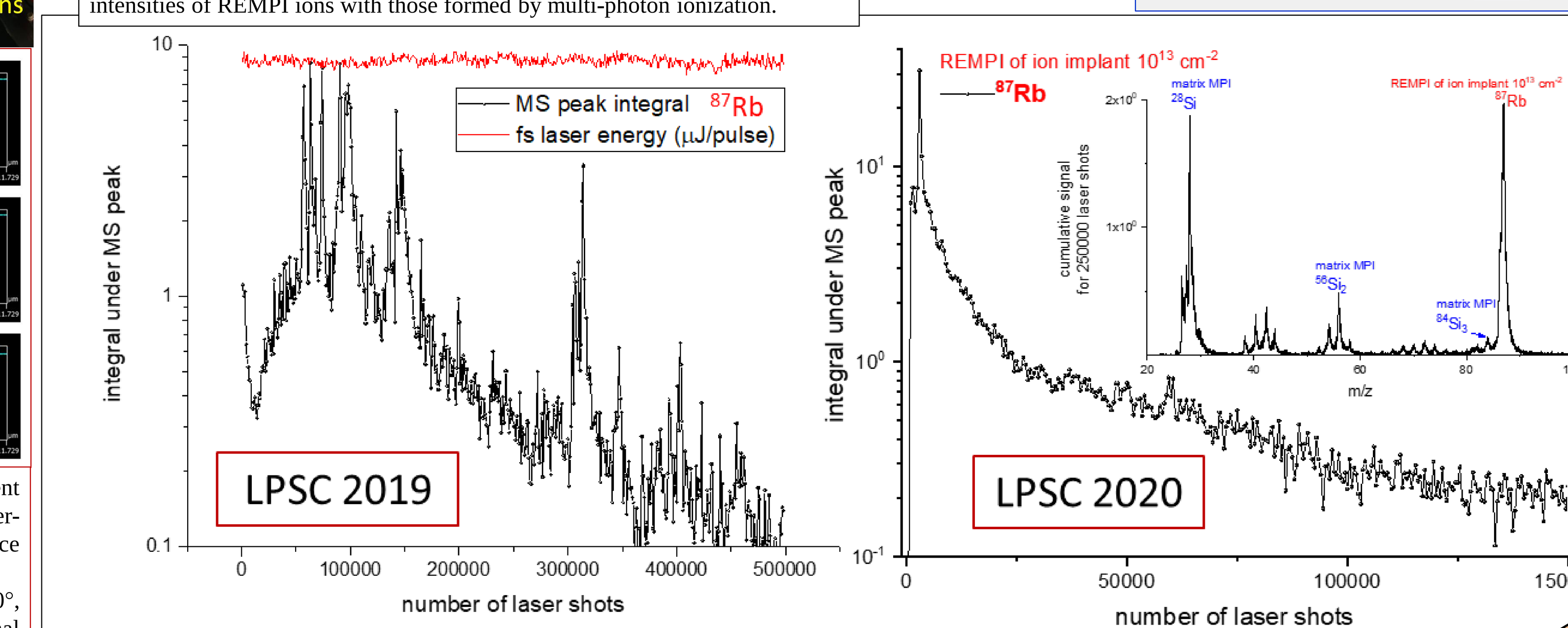


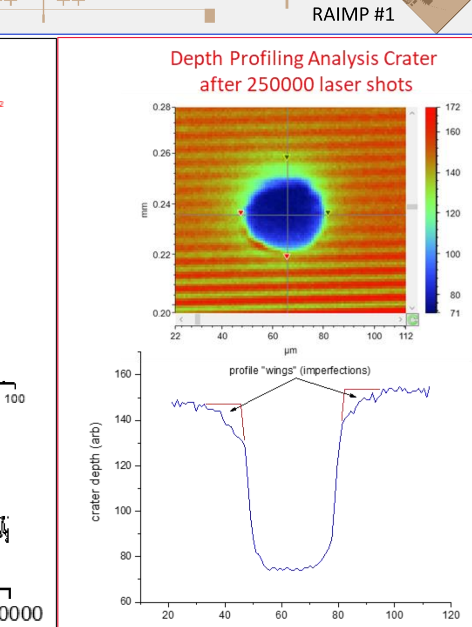
Shapes of the laser ablation craters after switching from optimization under ambient conditions to ablation in vacuum



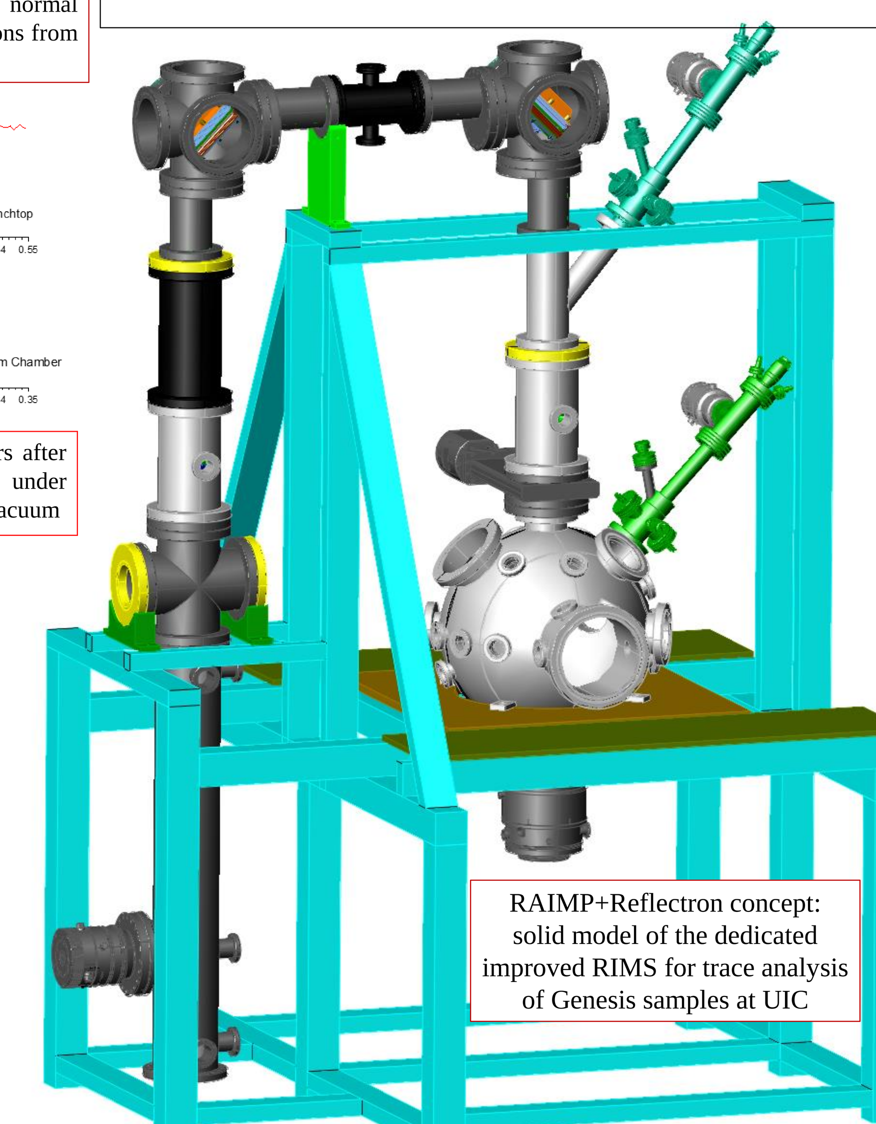
Dual-element RIMS depth profiling of ^{87}Rb/^{86}Sr ion implants in Si (90 keV @ 10^{12} cm^{-2}) with flat-top 800nm fs laser probe (100 shots per point average). Note the very clear distinction between the surface contamination + native oxide region (about 3 nm thick according to the literature) and the bulk Si. The sharp interface measured here has no mixing artifacts in the interfacial region that are observed with ion beam sputtering probes. This clearly proves that the depth profiling with flat-top laser probe has sub-nm depth resolution.

Depth profiling analysis of ion implants with testbed RIMS
LPSC-2019: Tests of RIMS depth profiling with the flat-top shaped fs laser probe on ^{87}Rb ion implants in Si (10^{13} cm^{-2} @ 180 keV). Each data point corresponds to an average of 1000 laser shots. Pulse energy of the fs ablation laser ≈9 μJ/pulse was just above the ablation threshold yielding sub-nm depth resolution but a lot of signal fluctuation. **LPSC 2020:** RIMS depth profiling of the same sample, 500 laser shots per point. Somewhat higher fs laser ablation fluence was optimized for a compromise between depth resolution and signal-to-noise. The inset shows the corresponding mass spectrum comparing intensities of REMPI ions with those formed by multi-photon ionization.

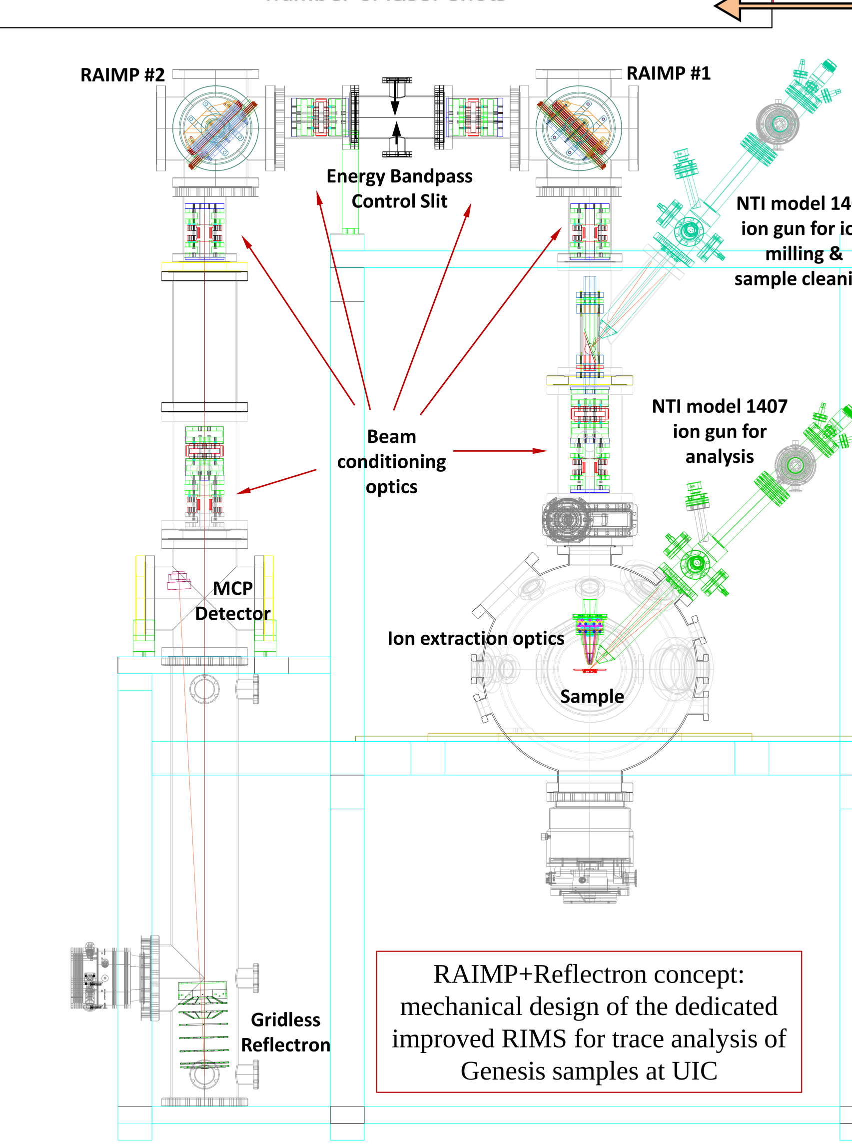




Shape of the laser ablation crater for the RIMS depth profiling experiment from LPSC 2020 on the left – measured by Bruker-Nano Contour GT-K Optical Profilometer



RAIMP+Reflectron concept: solid model of the dedicated improved RIMS for trace analysis of Genesis samples at UIC



RAIMP+Reflectron concept: mechanical design of the dedicated improved RIMS for trace analysis of Genesis samples at UIC

In contrast to the "testbed" RIMS, the dedicated Genesis RIMS has vertical design. Its ion optics instrument will permit operation with both laser and pulsed ion probes. Moreover, an additional ion gun can be used for sample cleaning by low energy ion sputtering, which can be combined with either analysis probe. High SNR will be assured by using RAIMP in combination with energy bandpass control slit. High MRP will be assured by combining RAIMP with a Reflectron. For high useful yield, optimized ion extraction and beam conditioning optics is used + gridless reflectron design.