UPGRADES TO SARISA: AIMING AT QUANTITATIVE THREE-DIMENSIONAL MASS SPECTROMETRY ON NANOMETER SCALE. I. V. Veryovkin, C. E. Tripa, A. V. Zinovev, S. V. Baryshev, M. J. Pellin, Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA, verigo@anl.gov

Introduction: Chemical analyses of samples returned to Earth by space exploration missions, even if they are carried out using different analytical techniques, have one common feature: these samples are unique, irreplaceable, and *atom-limited.* In other words, the amount of sample material available is finite, and once it is consumed, the analysis cannot be repeated. This is particularly true for particulates samples delivered by Stardust and Hayabusa missions. To perform sensitive, precise and accurate quantitative elemental and isotopic analysis of such samples with mass spectrometric methods, a combination of high sensitivity, mass resolving power, lateral and depth resolutions is extremely important because it permits to minimize the sample consumption. These are the features of the upgraded SARISA [1] Laser Post-Ionization Secondary Neutral Mass Spectrometry (LPI SNMS) instrument, which was originally developed and constructed to conduct analyses of Genesis solar wind samples. In this work we will outline the upgrades and explain how they are expected to enable new analytical capabilities in the nearest future.

Experimental: SARISA, which stands for Surface Analysis by Resonant Ionization of Sputtered Atoms, belongs to the new generation LPI SNMS instruments developed at Argonne National Lab. Neutrals are the predominant species in ion sputtering and laser desorption, two most efficient microprobe methods that convert sample surface material into analyzable gas phase atoms and molecules. The LPI method efficiently converts these ion sputtered or laser desorbed neutrals into photoions that can undergo mass analysis for identification and quantification.

Ion optics upgrades: In order to improve mass resolving power of SARISA, the nominal ion extraction voltage has to be increased. In the first approximation, the resolving power is going to grow as a square root of the increase in the ion energy. We verified this hypothesis by three-dimensional computer simulations with SIMION software and confirmed that an increase from 1 kV to 4 kV would result in about a factor of two improvement in mass resolution. Moreover, we expect the useful yield of the instrument also to improve due to better extraction of photoions. To make this possible in the existing instrument, we have modified the design of its ion optics and rebuilt it using larger ceramic insulators, polished 6.35 mm Al_2O_3 balls instead of 4.76 mm balls. This allowed us to stretch the effective length of insulators separating the electrodes in the optics from 4 mm to 6.7 mm, which will permit stable operation at nominal extraction voltage of at least 4 kV instead of the present 1 kV. The recent installation of these upgraded ion optics is expected to make LPI SNMS analyses with a mass resolution greater than 3000 possible.

Another important upgrade of the ion optics was a complete redesign of the target electrodes assembly, which (1) assured minimal changes in the instrument ion optics transmission when samples have to laterally move by as much as 10-15 mm in any direction, (2) increased the analyzable sample region from 5 mm to about 25 mm in diameter, (3) made the samples com-

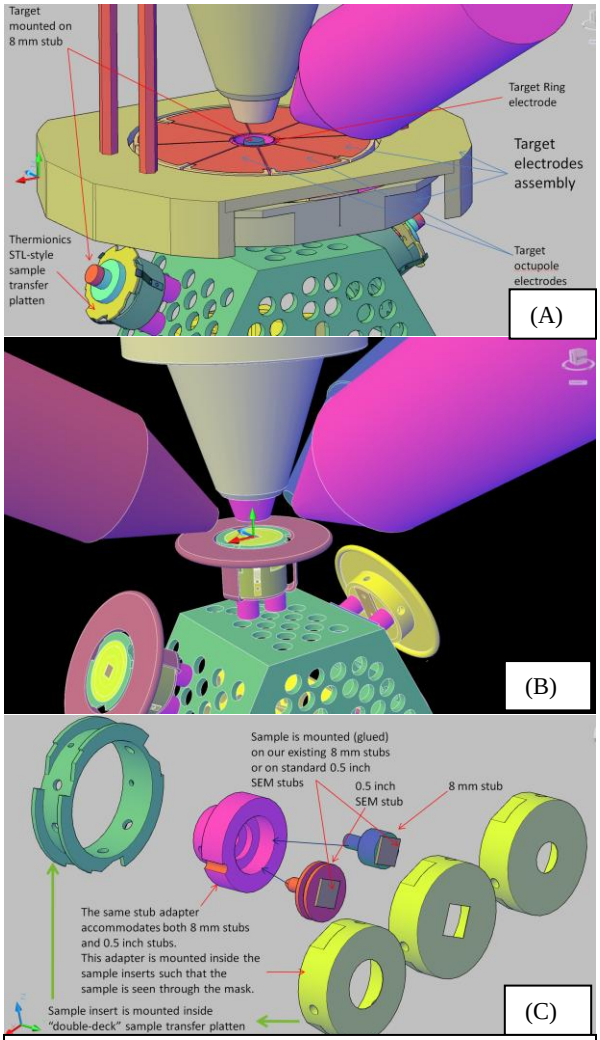

Figure 1.Modifications of ion optics of SARISA: (A) the original target electrodes asembly, (B) the redesigned target electrodes assembly; (C) the new sample holder design compatible with most commecrial SEM and SIMS instruments

patible with most commercial SEM and CAMECA SIMS instruments (Figure 1), and (4) made the near-target region less crowded and permitted installation of new microfocused ion and electron probes at manufacturer specified working distances.

High resolution ion and electron guns: The redesign of the ion optics and ultra-high vacuum hardware allowed us to install on SARISA two new probes, an FEI Magnum liquid metal ion gun and an FEI 2LE field emission electron gun that will enable LPI SNMS analysis with lateral resolution of up to 5 nm and Scanning Electron Microscopy with comparable lateral resolution. This is a key requirement for analyses of ultra-small samples such as presolar grains and interstellar dust particles.

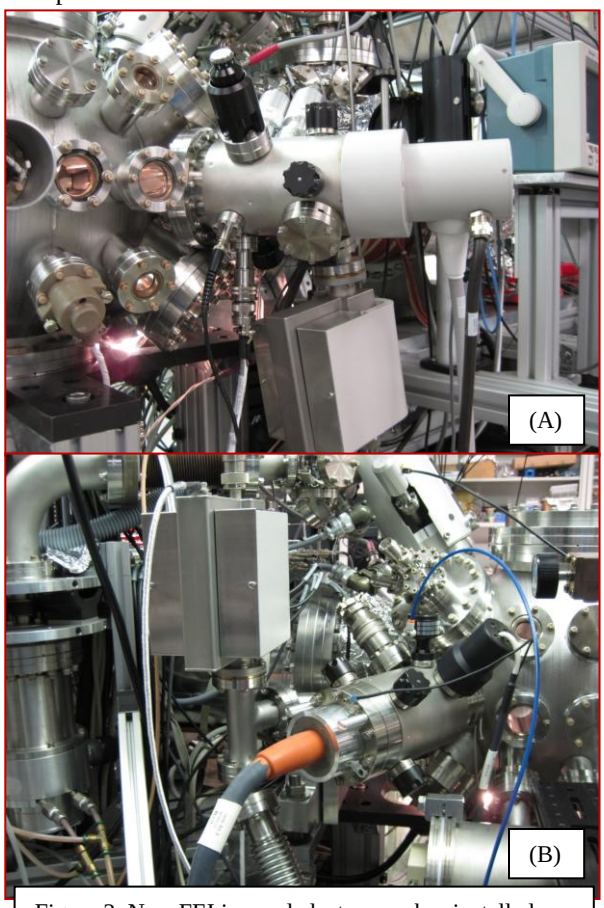

Figure 2. New FEI ion and electron probes installed on SARISA: (A) – Magnum ion gun; (B) 2LE electron gun

Dual beam sputter depth profiling: High lateral resolution of the above FEI probes can be combined in SARISA with sub-nanometer depth resolution to perform three-dimensional mass-spectrometric analyses on small samples or sample features. This can be done in a dual beam sputter depth profiling regime, which is achieved in SARISA by a combination of normally incident raster scanned low energy Ar^+ ion beam for material removal (DC mode sputtering, 250 eV impact energy demonstrated) with obliquely incident (60° from normal) pulsed and raster scanned 30 kV keV Ga^+ ion beam from the FEI Magnum ion gun for TOF MS analysis. Under such conditions, the vast fraction of the primary ion beam fluence corresponds to low energy ions that do not penetrate deep into the sample (i.e. *no ion mixing*) but, instead, gently remove ("*shave"*) its topmost layers thus opening new layers to analyses. These areas can also be imaged in the SEM regime using the 25 keV electron beam generated by the FEI 2LE gun. The initial tests of the dual beam sputter depth profiling in SARISA were done using pulsed 5 keV Ar^+ ion beam generated by Atomika WF421 ion gun for TOF MS analyses. A depth resolution of 0.4 nm was demonstrated for a test sample representing a stack of sixteen 5.5 nm layers of MgO and ZnO grown by Atomic Layer Deposition. We have also performed first dual beam sputter depth profiling analysis of the Genesis solar wind collectors [2] and were able to clearly distinguish between the surface contamination and solar wind implants.

Conclusion: The recent upgrades of the SARISA instrument will significantly enhance its analytical capabilities and widen the range of samples of cosmochemical interest that can be characterized with an unprecedented combination of sensitivity, mass, lateral and depth resolutions.

References: [1] Veryovkin I. V. et al. (2004) *Nucl. Instr. and Meth. B, 219–220,* 473–479. [2] Veryovkin I.V. et al. (2011) *LPSC XLII*, Abstract #2308.

Acknowledgements: This work is supported by is supported by NASA through grants NNH08AH761 and NNH09AM48I, and by UChicago Argonne, LLC, under contract No. DE-AC02-06CH11357.