MULTIELEMENT RIMS ANALYSIS OF GENESIS SOLAR WIND COLLECTORS – RECENT PROGRESS TOWARDS BETTER ACCURACY. I. V. Veryovkin[1], C. E. Tripa[1], A. V. Zinovev[1], S. V. Baryshev[1], M. J. Pellin[1], and D. S. Burnett[2], [1] Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA, verigo@anl.gov [2] Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA

Introduction: Solar wind (SW) samples collected by the NASA Genesis Mission present a serious challenge for analytical techniques. Firstly, the solar wind implants are low concentration and are distributed within 200 nm of the collector material surfaces. Secondly, the initial depth distribution of SW implants has been altered by a radiation-enhanced thermal diffusion process, which is not well understood. Thirdly and *most importantly*, there is significant terrestrial contamination on collector surfaces, which occurred during the hard landing and breach of the sample return capsule (SRC), causing most of collectors to fracture, and be contaminated by Utah soil particles and the SRC debris. Thus, an optimal combination of efficient surface cleaning methods and advanced analytical techniques capable of distinguishing between the surface contamination remaining after cleaning and the low concentration SW implants is needed to perform quantitative analyses of the Genesis SW collectors with high accuracy and precision. In this paper, we report on progress in the simultaneous measurements of Mg, Ca and Cr fluences in Genesis samples by Resonance Ionization Mass Spectrometry (RIMS). Our evolved analytical approach allowed us *for the first time* to clearly distinguish these SW elements from terrestrial contamination.

Experimental: Sputtered neutral atoms were converted into photoions for time-of-flight mass spectrometry (TOF MS) analysis by Resonantly-Enhanced Multi-Photon Ionization (REMPI) with tunable Ti-sapphire lasers by the same scheme as reported at LPSC 2010 [1]. Using a combination of three tunable lasers allowed us to simultaneously detect Mg, Ca and Cr. Concentration versus depth profiles of SW implants were obtained by a sequence of alternating sessions of ion milling (sputtering), using a raster scanned primary ion beam in direct current (DC) mode, and TOF MS analysis, using raster scanned primary ion beam in pulsed mode. Two significant recent innovations in our analytical approach aiming at minimizing artifacts that originate from the terrestrial surface contamination are described below.

CO_2 snow jet cleaning and sealed sample transfer: During our earlier work on advanced analytical instrument facility for analysis of Genesis SW collectors, we have developed a sealable container, which allowed sample transfer from a cleanroom environment into SARISA instrument through its loadlock. Aiming at improved accuracy of our RIMS analyses, we came to a conclusion that not only Genesis SW collectors needed to be cleaned from particulate contamination, but the reference samples too. Therefore we designed and built a sample cleaning station (Fig. 1) comprised of (1) a CO_2 snow jet cleaning system, with its nozzle mounted on two-axis translation stage, (2) a sealed chamber identical to SARISA's loadlock, which is purged by dry nitrogen, and equipped with a viewport and camera for monitoring the cleaning process, and (3) the sample transport container to transfer all samples between the cleaning station and the analytical instrument. Thus CO_2 snow jet cleaned samples never again "see" the lab environment where they could be contaminated again. As described below, this implementation helped remove many surface contamination related artifacts such as those caused by micron-sized particulates and resulted in drastic improvement of the reproducibility of depth profiling analyses, for all ion implants.

We conducted a series of experiments to compare this approach with the sample cleaning by an ion beam of giant gas clusters, GCIB (20 keV Ar_{5000}^{+}), which was performed in the laboratory of Prof. I. Yamada at the University of Hyogo (Himeji, Japan) [2]. From Fig.2 summarizing these results for ^{24}Mg, it is apparent that the (surface) concentration of Mg *does* change after exposure to GCIB while the shape of the SW Mg implant *does not*. The best results in our RIMS measurements were obtained when the GCIB irradiated samples were extra cleaned with CO_2 snow jet.

The preliminary conclusion from these tests is that

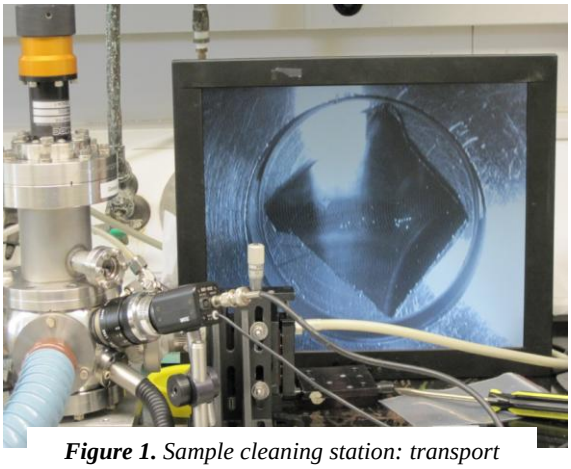

Figure 1. *Sample cleaning station: transport container mounted on loadlock-like chamber with CO_2 snow jet nozzle and nitrogen purging*

the snow jet does remove most of larger particulates from sample surfaces, a crucial first step for accurate depth profiling. However, there is still some contamination remaining, possibly in the form of a film, which can be removed by the GCIB technique, or by low energy ion milling. Films in the form of a "brown stain" on Genesis sample surfaces are well known.

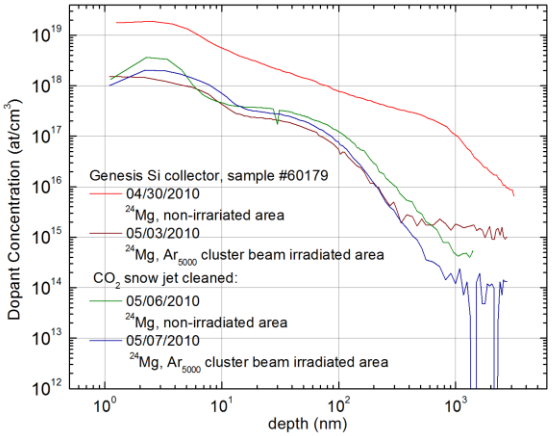

Figure 2. *Comparison of sample cleaning approaches: CO_2 snow jet and Gas Cluster Ion Beam*

The presence of Ca and Cr as surface contaminates remaining after the CO_2 snow jet cleaning, prevented resolving the corresponding SW implant peaks from the "tails" of ion beam mixed surface contamination when we used the "mesa" depth profiling approach [1]. Given the high concentrations of surface contaminates on the Genesis spacecraft samples, it was necessary to take steps to significantly improve the resolution of our depth profiling techniques, as described below.

Dual beam sputter depth profiling: In order to successfully perform sputter depth profiling of the shallow, trace-level solar wind ion implants buried under abundant surface contamination, the alteration of the near-surface composition by ion beams must be minimized. This can be done in a dual beam sputter depth profiling regime, which is achieved in the SARISA instrument by a combination of normally incident raster scanned low energy Ar^+ ion beam for material removal (DC mode sputtering, 500 eV impact energy tested here) and an obliquely incident (60° from normal) pulsed and raster scanned 5 keV Ar^+ ion beam 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 (thus *dramatically reducing ion mixing depths*) while gently removing the samples topmost layers. Thus analysis of underlying layers without mixing in the terrestrially contaminated upper layers becomes possible. We have conducted a series of measurements in dual beam mode (Fig. 3) and were able, *for the first time*, not only to identify the concentration peak of the SW Ca implant but also to resolve the SW Cr peak from the surface contamination. Taking into account the logarithmic scale depth, depth profiles of each element clearly show two separate "bands" of elemental concentration enhancement. Such a profile structure is typical for thin films on solid substrates. In this case, the (film of) terrestrial surface contamination exhibits a peak near the surface due to its roughness, and an interface between the film and the substrate can be clearly seen. The second "band" peaking near 30-40 nm into the sample is presumed to be the solar wind. Interestingly, the Cr contamination "tail" appeared to penetrate deeper into the substrate that those of Mg and Ca, by some 20-30 nm. Two possibilities for this behavior are: (1) chemical cleaning of the sample # 60178 has in some way altered its surface composition or (2) the terrestrial Cr coming from the outgassing spacecraft is embedded in the "brown stain" film. Additional test samples will be needed to decide on the actual mechanism.

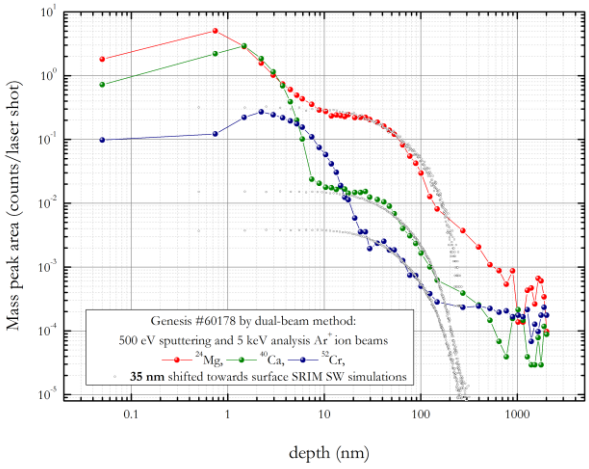

Figure 3. *Dual beam sputter depth profiling experiment on Genesis sample #60178, The estimated depth resolution for Mg in Si with 500 eV beam is about 1 nm.*

The estimates of the SW fluences for Mg, Ca and Cr obtained from these first dual beam depth profiling experiments are in a very good agreement with results obtained by Secondary Ion Mass Spectrometry (SIMS):

fluence, at/cm^2	Mg	Ca	Cr
RIMS	2.24×10^{12}	9.4×10^{10}	3.3×10^{10}
SIMS (ASU, UCLA)	2.15×10^{12}	1.0×10^{11}	3.0×10^{10}

References: [1] I. V. Veryovkin et al., (2010) *LPSC XLI*, Abstract #2579. [2] King, B. V. et al. (2010) *LPSC XLI*, Abstract #1975.

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