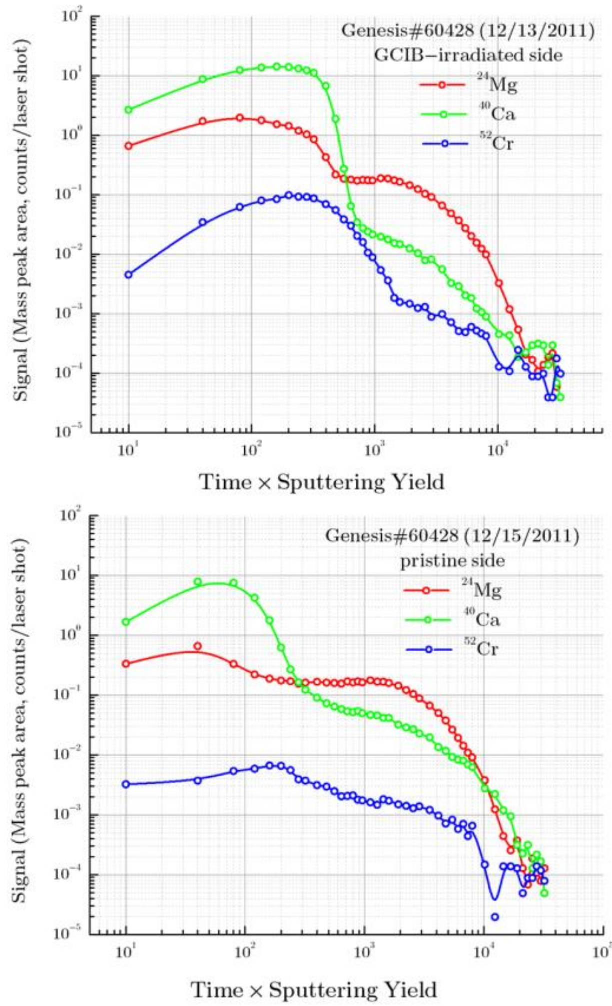
CLEANING GENESIS SAMPLES WITH GAS CLUSTER ION BEAMS: METHOD EVALUATION BY COMPARATIVE STUDIES WITH RIMS, GI-XRF AND OTHER SURFACE CHARACTERIZATION TECHNIQUES. I. V. Veryovkin[1], S. V. Baryshev[1], N. G. Becker[1], D. S. Burnett[2], Y. Choi[3], P. J. Eng[4], J. E. Stubbs[4], M. Schmeling[5], N. Toyoda[6], C. E. Tripa[1], I. Yamada[6] and A. V. Zinovev[1], [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, [3] X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA, [4] GSECARS, University of Chicago, Argonne, IL 60439, USA, [5] Loyola University Chicago, 1032 West Sheridan Rd., Chicago, IL 60660, USA, [6]Graduate School of Engineering, University of Hyogo, 2167, Shosha, Himeji, Hyogo, 671-2280, Japan

Introduction: Solar Wind (SW) samples collected by the NASA Genesis Mission are hard to accurately analyze because their surfaces have been severely contaminated during both the SW collection and the hard landing of the Genesis Sample Return Capsule. Thus SW implants are buried under a "blanket" of contamination, which has the same elements as SW but with orders of magnitude higher abundances. To date, various physical and chemical methods have been tried to clean the sample surfaces. At Argonne National Laboratory, we have recently implemented for this purpose a *quasi-in-situ* CO_2 snow jet technique [1], which showed measurable success with removing surface particulates but apparently was not able to remove film contamination. In this work, we report results of a more systematic (than we previously attempted in Ref. [2]) study of the efficiency of another gas jet based method, the Gas Cluster Ion Beam (GCIB) bombardment, which is capable of addressing this problem.

Experimental: We conducted a series of experiments on comparative and all-round characterization of a subjected to GCIB Genesis Si sample #60428 and one reference ion implant (2 keV/amu, ^{25}Mg, ^{44}Ca, ^{53}Cr) , first non-destructively with Total Reflection X-ray Fluorescence (TXRF at Loyola University) and with synchrotron-based Grazing Incidence X-ray Fluorescence Spectrometry (GI-XRF at GSECARS / Advanced Photon Source), and then with our ion bombardment based technique of Resonance Ionization Mass Spectrometry (RIMS in Argonne MSD). A fraction of the surface of this sample (~ one third) was protected during the GCIB irradiation at University of Hyogo (20 keV $Ar_{2000}^+ \div Ar_{3000}^+$ ions) with a Si wafer shield in order to be able later to perform comparative characterization of two halves of the same sample surface. The GI-XRF studies of Genesis samples at APS have been initiated a few years ago by Kitts et.al. [3] who demonstrated the potential of GI-XRF to non-destructively determine fluences of SW ion implants in Genesis collectors. However, it was difficult to find realistic shapes of the implant depth profiles that would help to improve the accuracy of the GI-XRF data processing algorithm. The rationale for our present GI-XRF vs RIMS studies is that by processing an ion implant sample (both Genesis and reference) with GCIB, we "shave off" a thin layer (~10 nm) from the sample surface and thus create a "truncated" depth profile on the irradiated half so that later we could probe and compare the two halves of the surface, GCIB-irradiated versus pristine, by first using non-destructive X-rays (TXRF and GI-XRF) and then destructive RIMS. We also hypothesized that the "shaved-off" layer would take with it most of the surface film and particle contamination, without affecting the SW implants. The GSECARS GI-XRF setup can distinguish the surface contamination from the SW implants in the bulk by conducting measurements with variable incidence angle of X-rays. Therefore we also expected to see how well the GCIB can remove the surface contamination layer. Before subjecting the sample to the GCIB beam, we probed its surfaces with TXRF. We also did this after the GCIB irradiation. We had experiments at the GSECARS/APS in the beginning of November 2011. The GI-XRF instrument then probed three line-shaped (300 µm × 8 mm) regions on its surface, one on its pristine half, and two on GCIB-irradiated one. After that, we characterized the surface of this sample with white light interferometry, ellipsometry and Atomic Force Microscopy (AFM), and finally performed CO_2 snow jet cleaning and loaded it in the SARISA instrument for RIMS measurements.

Results and Discussion: With this concerted and all-round sample characterization, we were able to observe a number of interesting phenomena that can be better understood only through continuation of these systematic studies. The white light interferometry has shown that the GCIB beam has removed about 12 nm of the sample surface. The AFM in MSD and X-Ray reflectivity measurements at GSECARS showed that, very surprisingly, the roughness of the GCIB-irradiated sample surface region is slightly higher than that of a pristine one (1.4 nm versus 0.9 nm per AFM). We also detected with GI-XRF a thin (~monolayer) Ar layer on top of the GCIB-iradiated surface. This layer served as a surface marker helping to identify the critical (total reflection) angle when X-rays do not penetrate the sample. Overall, the intensities of X-ray fluorescence



from both sample bulk and surface were enhanced for the GCIB-irradiated part. We have also observed the expected "truncation" of the depth profile both on the analyzed Genesis #60428 sample (Figure 1) and on the processed in the same way 2 kev/amu reference ion implant. Our estimates of SW fluences with RIMS indicated that the GCIB-removed 12 nm of material might have been too much because we determined consistently lower SW fluences for the GCIB-irradiated half: ^{24}Mg: 1.2×10^{12} vs 1.7×10^{12} ions/cm^2, ^{40}Ca: 8.5×10^{10} vs 4.1×10^{11} ions/cm^2, ^{52}Cr: 2.1×10^{10} vs 6.1×10^{10} ions/cm^2. Finally, the level of contamination on the surface after the GCIB processing did not go down as seen in Figures 1 (RIMS) and 2 (GI-XRF). It seemed that the GCIB beam might have been sputter-coating the irradiated surface with some material from the vicinity of the sample. Some results of these studies have yet to get fully processed. At the Conference, we will show more pieces of this puzzle and will provide our more detailed interpretations of the results.

Conclusion: With their depth of detail, the results of these tests of the GCIB technology applied to cleaning Genesis samples are still *inconclusive*. It is clear that more studies are needed, trying different variants of GCIB (noble gas versus CO_2 molecules, normal versus oblique incidence angle) and different sample preparation and handling procedures.

References: [1] I. V. Veryovkin et al., (2011) *LPSC XLII*, Abstract #2308, [2] B. V. King et. al. *LPSC-XLI* (2010), Abstract #1975, [3] K. Kitts et. al., (2008) *LPSC XXXIX*, Abstract #1296

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Figure 1. Comparison between RIMS sputter depth profiles measured with ultra-high resolution dual beam method (250 eV ion milling vs 5 keV pulsed analysis beams) for GCIB-irradiated and pristine surfaces.

Figure 2. Comparison between GI-XRF spectra measured at near-critical angle (corresponding to surface composition) for for GCIB-irradiated and pristine surfaces.