Study of Genesis Solar Wind Samples by Laboratory Based Total Reflection X-ray Fluorescence Spectrometry and Synchrotron Based Grazing Incidence X-ray Fluorescence

M. Schmeling[1], D.S. Burnett[2], Y. Choi[3], P.J. Eng[3], J.E.. Stubbs[3], C.E. Tripa[4] and I.V. Veryovkin[4]
[1]Loyola University Chicago, Chicago, IL 60660, mschmel@luc.edu; [2]California Institute of Technology, Pasadena, CA 91125; [3]GSECARS, University of Chicago, Argonne, IL 60439; [4]Material Sciences Division, Argonne National Laboratory, Argonne, IL 60439

Introduction: The Genesis mission was the first mission returning solar material to Earth since the Apollo program [1,2]. Unfortunately the return of the space craft on September 8, 2004 resulted in a crash landing, which shattered the samples into small fragments and exposed them to desert soil and other debris. Thus only small fragments of the original collectors are available, each having different degrees of surface contamination. Thorough surface cleaning is necessary to allow for subsequent analysis of solar wind material embedded within. An initial cleaning procedure was developed in coordination with Johnson Space Center which focused on removing larger sized particulates and a thin film organic contamination acquired during collection in space [3]. However, many of the samples have additional residues and more rigorous cleaning steps might be necessary. These cleaning steps must affect the surface only to avoid leaching and/or redistribution of solar wind material from the bulk of the collectors. To aid in the development of appropriate cleaning procedures each sample has to be thoroughly inspected before and after the cleaning steps. Laboratory based total reflection X-ray fluorescence (TXRF) spectrometry is non-destructive and surface sensitive permitting analysis of elements present at and near the surface of a flat substrate [4]. Synchrotron based grazing incidence X-ray fluorescence (GI-XRF) enables the analysis of materials not only at or close to the surface, but also allows for identification of materials deeper in the bulk of a sample via manipulation of the incident angle of the X-ray beam [5]. Three samples (two flown samples and one implant) were investigated by TXRF with respect to surface cleaning and presence of elements near the surface. One sample was also analyzed by GI-XRF to distinguish between surface contamination and solar wind.

Experimental: Analysis of Genesis samples 60326 and 60966 (both silicon on sapphire) and a 1kV Mg Ca Cr implant in silicon was performed with a PicoTax (2000) and a S2PicoFox (2011) TXRF spectrometer (Bruker AXS, Germany). Excitation energy was 17.4 keV using a Mo- Anode. Counting time for all samples was 7200 seconds (2 hours) for PicoTax and 3600 seconds for S2PicoFox measurements. A special polycarbonate adapter to accommodate the sample was used as described in [6]. Sample 60966 and the 1kV implant were analyzed before and after CO_2 snow cleaning (K4-10, Applied Surface Technologies, New Providence NJ), whereas sample 60326 was analyzed before and after concentrated HCl cleaning. Sample 60326 was also analyzed by GI-XRF at 13-ID-C of the GSECARS at the Advanced Photon Source at Argonne National Laboratory before and after concentrated HCl treatment.

Results and Conclusion: Figure 1 shows the spectra for sample 60966 acquired by TXRF before (black) and after CO_2 snow cleaning (red).

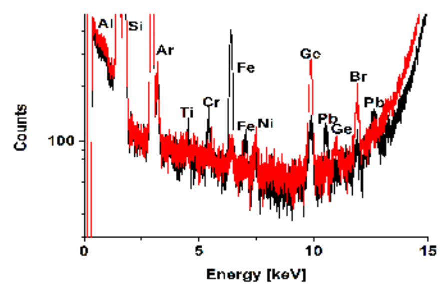

Figure 1: TXRF spectra of Genesis sample 60966 (silicon on sapphire) before CO_2 snow cleaning (black) and after CO_2 snow cleaning (red).

CO_2 snow is a gentle cleaning method that removes contaminant particles located at the surface of a sample and does not penetrate into the bulk of the material. For sample 60966 the results appear to be mixed: some elements decreased, whereas others were unaffected or even seem to have increased in concentration after the cleaning. The peaks for Ti, Cr, and Fe for example did decrease substantially after cleaning, whereas Ni did not show any noticeable changes, and Ge and Br signals increased. More samples have to be investigated to demonstrate the effectiveness of CO_2 for surface cleaning.

Figures 2 and 3 show data obtained for sample 60326. The sample was analyzed before and after concentrated HCl cleaning with both TXRF and GI-XRF. The TXRF analysis (Fig. 2) does indicate that acid cleaning did remove some of the contaminants, most noticeably Zn, but other elements like Fe and Ni are still present. Figure 3 shows the fluorescence yield (red) dependency on incident angle for Si, Fe and Ni before and after acid cleaning together with total reflectivity (black). In Figure 3(a), the vertical dashed line indicates the total external reflection angle for Si, below which the incident x-ray barely penetrates into the Si layer. Thus, high fluorescence intensity below the angle suggests its fluorescing element is located above the Si layer. While Ni maintains this profile after acid cleaning, high Fe fluorescence intensities at low angles indicate the relative fraction of near/above-surface Fe atoms increases. Interestingly the TXRF data also show Fe and Ni as still remaining contaminants and based on the GI-XRF results Ni is present in the silicon layer as solar wind. Both TXRF spectra show besides Si also an Al peak suggesting that the X-ray beam penetrates deeper than near the surface.

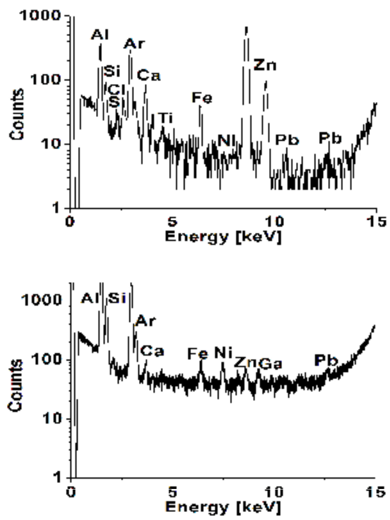

Figure 2: TXRF spectra of sample 60326 before cleaning with concentrated HCl (left) and after (right).

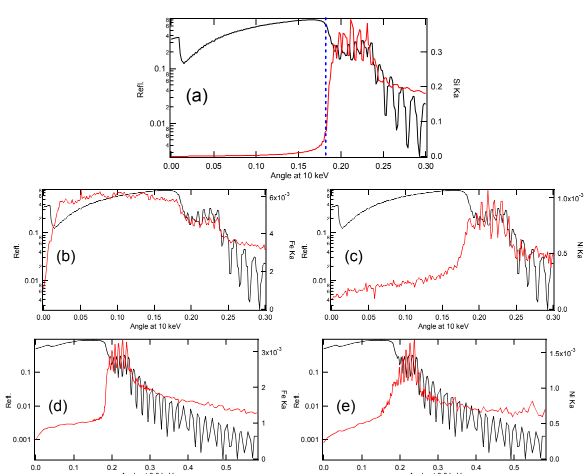

Figure 3: Total reflectivity of X-ray beam (black) and fluorescence yield (red) as a function of incident X-ray angle in degrees. Si Kα(a), Fe Kα (b), and Ni Kα (c) after HCl cleaning. Fe Kα (d) and Ni Kα (e) before HCl cleaning.

In order to obtain a rough estimate of beam penetration with TXRF, two standards containing Mg, Ca and Cr implanted into silicon bulk with different energies were analyzed. Both samples were CO_2 snow cleaned to remove loosely bound surface contaminants. Since TXRF is relatively insensitive in the light element range Cr seems to be the most feasible implanted element to observe. Figure 4 shows the results of this experiment and indeed Cr is present in both spectra besides Fe and also Ni (as contaminants). This data suggest even the current laboratory based TXRF set-up permitting for only very limited angle manipulation might allow for discrimination of elements present at/near the surface or within the bulk of a sample. This can be achieved by using implants and surface deposited materials as standards to align the angle of the incident X-ray beam with two slightly different positions one penetrating deeper (implant) than the other (surface).

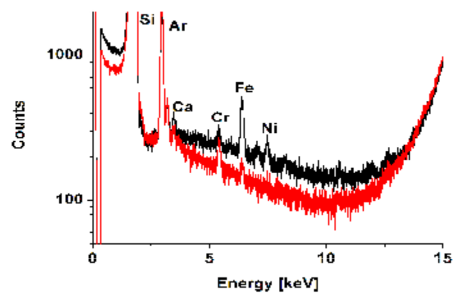

Figure 4: Spectra of a 1kV (black) and 2 kV (red) Mg Ca Cr implants in silicone after CO_2 snow cleaning.

References:

[1] Burnett D.S. et al. (2003), *Space Science Reviews,* 105, 509-534.

[2] Jurewicz A.J.G. et al. (2003) *Space Science Reviews*, 105, 535-560.

[3] Calaway M.J. et .al. (2009), *LPSC XXXX*, Paper #1183.

[4] Kitts K. et al. (2008), *LSPC XXXIX*, Paper #1296.

[5] Schmeling M., (2005), *Elsevier Encyclopedia of Analytical Science,* 440-448.

[6] Schmeling et .al., (2011), *LPSC XXXXII*, Paper #2041.

Acknowledgements: The authors would like to thank the Genesis sample curators at Johnson Space Center for their sample cleaning efforts and help provided in characterizing the samples. This research was supported by NASA grant NNX10AH05G.