Surface Characterization of Genesis Samples by Total Reflection X-ray Fluorescence Spectrometry: Contaminants and Roughness Variations.

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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 an unexpected 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 containing different degrees of surface contamination. These have to be surface-cleaned thoroughly to enable subsequent analysis of solar wind material embedded within the material. An initial cleaning procedure was developed in coordination with the Johnson Space Center which focused on removing larger sized particulates and a thin film organic contamination acquired during collection in space. [3,4,5]. However, many of the samples have additional residues and more rigorous cleaning steps have to be developed. To aid in this development each sample has to be thoroughly inspected. Total reflection X-ray fluorescence (TXRF) spectrometry is a surface sensitive analysis method capable of analyzing ultra trace elemental concentrations, with small laboratory instruments reaching detection limits in the 10^{10} to 10^{12} atoms/cm^2 range [6]. Different cleaning procedures involving acids and organic solvents are currently tested and surface analysis by TXRF is an important step in evaluating the most appropriate procedure for each sample material.

Experimental: Analysis of Genesis samples has been performed with a PicoTax TXRF spectrometer (Bruker AXS). Excitation current for the molybdenum anode was 1mA and voltage 40kV. Counting time for all samples was 7200 second (2 hours). Since the samples were not uniformly shaped and have different thicknesses adapters were made for each sample. The adapters consist of a standard TXRF polycarbonate disc, which has been altered by removing (i.e. milling) a pocket into it. In this pocket, the Genesis sample is dropped and then presented for analysis. The polycarbonate discs were cleaned with soapy water and ultrasonication before adding the sample. To ensure that no traces are left from the previous samples, the discs were checked each time using TXRF. If no contamination was found, the sample was placed into the pocket of the cleaned polycarbonate disc, mounted into the sample holder and then analyzed by TXRF.

Results: Figure 1 shows the spectra of sapphire (Al_2O_3) sample SAP 50719 after initial UPW and UV/O_3 cleaning at Johnson Space Center (red), after hydrochloric acid only cleaning (green) and after treatment with 6M hydrochloric acid and hydrofluoric acid (1:5) at CalTech (blue).

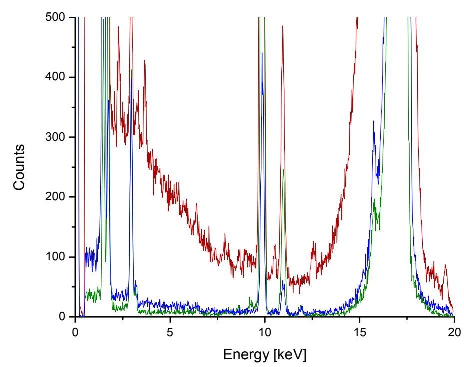

Figure 1: TXRF spectra of Genesis sample SAP 50719 before acid cleaning (red), after HCl only cleaning (green), and HF/HCl cleaning (blue).

The peak at 2.9keV has its origin from air (Ar) in the sample chamber and the one at 17.4keV corresponds to the molybdenum anode material. These two peaks are found in all spectra measured with the PicoTax TXRF. All other peaks are associated with the sample with aluminum at 1.49keV. As can be seen from the spectra, the two acid cleaning steps were able to remove the majority of contaminants with the exception of germanium (Ka at 9.9keV, Kb at 10.9keV). The large background scattering signal was also substantially reduced after HCl only treatment. The reason for the reduced background might be the result of removing organic material deposited on the surface. The additional more aggressive HCl/HF combination treatment appears to have reduced the germanium traces slightly. However, after the last treatment the sample surface seems to have roughened, as indicated by the somewhat elevated background scattering in the blue spectrum. This roughening does not occur to be too severe, thus for surface cleaning of sapphire samples a combination of HCl and HF looks promising, but since the solar wind is implanted at 20nm, this roughening must be evaluated.

Sample SAP 50719 was also inspected by optical microscopy to investigate surface artifacts due to the impact and associated with the germanium contamination present. Figure 2 shows the digital picture of the approximate area analyzed by TXRF at 200 times magnification under transmitted and reflected light. It turned out that on the sample surface quite of few of these metallic streaks and smears were present; moreover, some debris looked embedded in cracks below the sample's surface. Thus for this particular sample, it might be necessary to use very rigorous surface cleaning techniques to remove the embedded material. The progress of removal will be continuously monitored by TXRF.

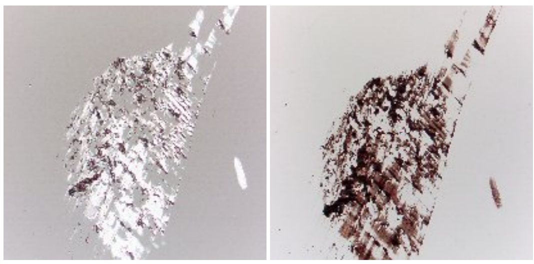

Figure 2: Optical inspection of sample SAP 50719 with 200 times magnification under reflected and transmitted light.

In figure 3 the progressive cleaning of another sample is shown. This sample, SOS 60326, consists of sapphire coated with a thin layer of silicon. Also here the red spectrum shows the surface analysis after UPW and UV/O_3 cleaning at Johnson Space Center.

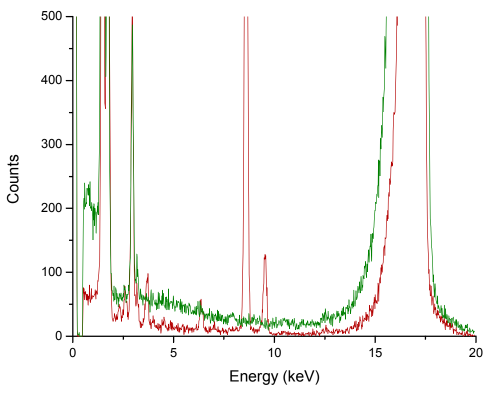

Figure 3: TXRF spectrum of Genesis sample SOS 60326 before acid cleaning (red), after HCl cleaning (green).

The peaks at 1.49keV and 1.74keV are associated with the sample material (aluminum and silicon) whereas the peaks at 9.89keV and 10.98keV originate again from germanium contamination. Small amounts of iron (6.4keV) and calcium (3.7keV) were found as well. This sample was subjected to one additional cleaning step, consisting of hydrochloric acid only (green). The acid cleaning successfully removed the surface contaminants, but the background scatter signal did increase noticeably, as a result of surface roughening. The roughening appears to be more severe than for the sapphire only samples and should be monitored. Accordingly, how much solar wind was removed must be evaluated as well.

Conclusion: Laboratory based TXRF has been used to analyze Genesis flight samples for surface contamination after a set of cleaning steps. It was possible to identify contaminants at the 10^{10} to 10^{12} atoms/cm^2 level using this cost effective approach, which escaped detection by other common non-destructive surface methods. It was found that additional cleaning steps using mineral acids were able to remove most of the contaminants. However, the sample materials behaved differently, with sapphire being less prone to surface roughening than silicon coated sapphire. Currently the effect on surface roughening is investigated with control samples and applying TXRF analysis and compared to the flight samples. The ultimate goal is to find a fine tuned surface cleaning procedure for each sample material used.

References:

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