Analysis of Genesis Sample Surface Contamination by Total Reflection X-ray Fluorescence Spectrometry .
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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 Septermber 8, 2004 was less smooth than anticipated and a crash landing shattered the samples not only in small fragments but also exposed them to desert soil and other debris. As a result only small sample fragments are available, which contain different degrees of surface contamination and have to be cleaned thoroughly. A cleaning process removing substantial amounts of particulate and thin film contaminations was developed at Johnson Space Center [3,4,5]. However, many of the samples still have residual contamination. The contaminants have to be identified to develop more rigorous cleaning steps.

Total reflection X-ray fluorescence (TXRF) spectrometry is a surface sensitive analysis method capable of analyzing ultra trace concentrations. It is used in various fields of science and reaches detection limits in the 10^{10} to 10^{12} atoms/cm^2 range [6]. Its surface sensitivity makes TXRF perfectly suitable for analysis of Genesis samples and a small number of them have been characterized using TXRF before and after implementation of an additional cleaning step.

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 for each sample were made. 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 each time before adding the sample. Cleaning consists of an intial step with soapy 18MOhm water and ultrasonication for 10 minutes and a second step of ultrasonication for 10 minutes in pure 18MOhm water. After each cleaning session the disc was checked for potential contamination. 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. Figure 1 shows the spectrum of a cleaned polycarbonate disc.

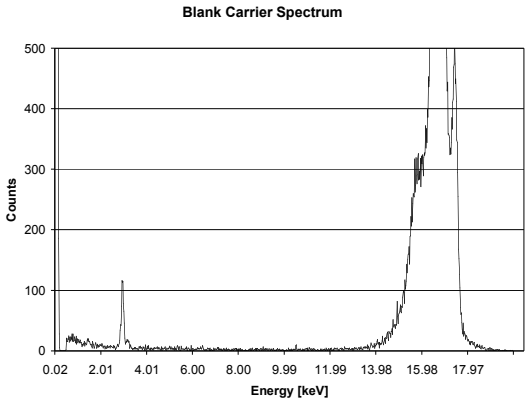

Figure 1: TXRF spectrum of a clean polycarbonate carrier. The peak at 2.9keV belongs to argon (air) and the one at 17.4keV corresponds to the molybdenum tube.

To estimate the range of contaminations, detection limits were determined using multielement standard solutions and can be found in table 1.

Element	Atoms/cm^2
Ca	1.76×10^{12}
Ti	4.80×10^{11}
Mn	3.35×10^{11}
Fe	1.65×10^{11}
Ni	9.66×10^{10}
Cu	1.41×10^{11}
Zn	5.76×10^{10}
Ga	8.76×10^{10}
Ge	3.35×10^{10}
Pb	4.44×10^{10}

Results: Figure 2 shows the spectra of Genesis sample SAP 60679 after initial UPW and UV/O_3 cleaning at Johnson Space Center (black) and after additional acid cleaning with HCl and HF at Jet Propulsion Laboratory (blue). The peak at 2.9keV has its origin from air 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. It is obvious that the initial cleaning step did not remove all contaminants and substantial contaminations of gallium (Ka at 9.2keV, Kb at 10.2keV) and germanium (Ka at 9.9keV, Kb at 10.9keV) are still present besides iron (Ka at 6.4keV, Kb at 7.1keV) and zinc (Ka at 8.6keV, Kb at 9.6keV). After acid cleaning,

most of the major contamination has been removed, however elements, which were masked by the large gallium and germanium peaks do appear now. Among those are osmium (La at 8.9keV, Lb at 10.3keV) and lead (La at 10.6keV, Lb at 12.6keV) as well as hafnium (La at 7.9keV). Traces of iron and germanium are also still noticeable. Both osmium and hafnium are very uncommon, but have been verified by measuring standards of each element and comparing those with the spectra.

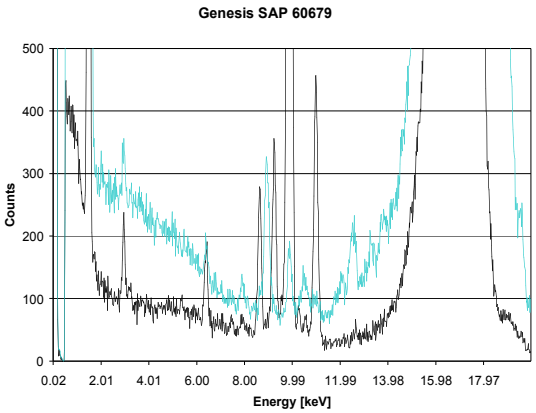

Figure 2: TXRF spectrum of Genesis sample SAP 60679 before acid cleaning (black) and after acid cleaning (blue).

Sample SOS 60324 was analyzed for surface contamination after UPW and UV/O_3 cleaning at Johnson Space Center. Two different spots were measured on this sample and the combined spectra are shown in figure 3. The comparison of the two spectra in figure 3 shows that contamination is not evenly distributed on the sample surface and differences in contamination type exist. The blue spectrum in the figure shows a much higher background signal than the black one. Common reasons for high background scattering are increased surface roughness of the sample or organic deposits on the sample surface. Assuming that the surface of the sample is evenly smooth the increased background is most likely caused by some surface deposits. Contaminants present in SOS 60324 are: Hf (La at 7.9keV) and Pb (La at 10.6keV, Lb at 12.6keV) in both spots and additionally zinc at 8.6keV in the blue spectrum.

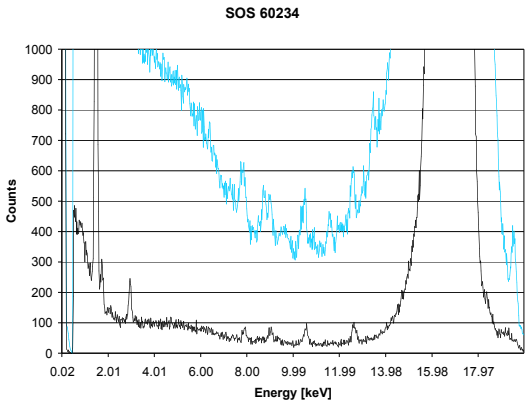

Figure 3: TXRF spectrum of Genesis sample SOS 60234. The blue and black spectrum show different spots analyzed.

Conclusion: Laboratory based TXRF has been used to analyze Genesis flight samples for surface contamination. It was found that after an initial cleaning step at Johnson Space Center substantial contaminations remain, especially of germanium and gallium. An additional acid cleaning step could remove most of the germanium and gallium, but other contaminants appear now. The degree of contamination varied between different spots on the same sample measured.

References:

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