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Analysis of Genesis Sample 60234 by Laboratory Total Reflection X-ray Fluorescence Spectrometry and Synchrotron Grazing Incidence X-ray Fluorescence

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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 a crash landing, shattering the samples into small fragments and exposing them to desert soil and other debris. Only small fragments of the original collectors are available with each of them having a different degree of surface contamination. Thorough surface cleaning is necessary to allow for subsequent analysis of solar wind material embedded within. Initial cleaning is carried out at Johnson Space Center mainly removing larger sized particulates and a thin film organic contamination acquired during collection in space [3]. Additional cleaning steps consisting of acid and organic solvent application are done for most samples to remove smaller particulates and the most notorious contaminants. To aid in the development of appropriate cleaning procedures and classify a sample as clean for subsequent analysis the sample is thoroughly inspected by conventional laboratory total reflection X-ray fluorescence (TXRF) spectrometry [4,5]. The ability of TXRF to distinguish between surface deposits and material in the bulk is well known and documented [4,6]. This is done by carefully changing the incident beam angle and penetrating into the bulk material. In an effort to extend the use of TXRF for Genesis mission samples from a surface control tool to a more versatile method, its ability to distinguish qualitatively between elements present at the surface and within the bulk was tested. For this, a cleaned Genesis sample and an implant standard were subjected to conventional laboratory TXRF analysis and to synchrotron grazing incidence X-ray fluorescence (GI-XRF). The latter one is a closely related, but much more sensitive X-ray fluorescence method than TXRF and has been already successfully applied for analysis of fluences in selected Genesis samples, mainly first row transition metals [7,8].

Experimental: Analyses of Genesis sample 60234 and a Fe implant of 5×10^{14} atoms/cm², both silicon on sapphire, was performed with a) S2PicoFox TXRF spectrometer (Bruker AXS, Germany) and b) at the GeoSoilsEnviro Consortium for Advanced Radiation Sources (GSECARS) 13-ID-C undulator beamline in grazing incidence X-ray fluorescence set-up. Experimental conditions for the S2PicoFox were: excitation energy 17.4 keV (Mo- Anode) and counting time 3600

seconds (1hour). A special polycarbonate adapter to accommodate the sample was used as described in [5]. The 13-ID-C beamline of the GSECARS at the Advanced Photon Source at Argonne National Laboratory is equipped with a cryogenic Si (111) double crystal monochromator, a Vortex® Si-drift detector and a reflectivity detector. The samples were mounted in a He-flow chamber with a Kapton® window [7,8].

Results and Conclusion: Figure 1 shows the TXRF surface spectrum of sample 60234 after cleaning with hydrochloric acid. The most prominent peaks are Ca and Fe, but also Ba, Cr and Pb were detected. Previous data obtained with GI-XRF suggested that Fe is present in the Si layer of the bulk and relatively close to the surface, thus the Fe peak might originate from this.

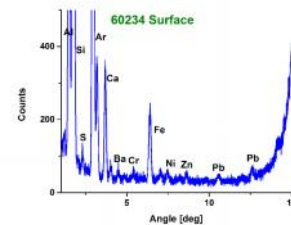


Figure 1: TXRF surface spectrum of Genesis sample 60234 (silicon on sapphire) taken in total reflection mode.

Figure 2 shows an angle scan of the same sample acquired with GI-XRF. The black line represents beam reflectivity, which is at its highest at small angles before the beam penetrates below the surface. Silicon (blue) and aluminum (red) are the collector materials and its signals increase substantially with beam penetration into the bulk. Note the oscillating wave pattern for Si (blue line), which arises from the interaction of incident and reflected beam within the material and is used to determine the presence and concentration of an element in this layer. Barium (magenta) is present as a surface contaminant where it displays its highest fluorescence yield and follows a comparable pattern as reflectivity. Fe (green) and Ni (aqua) are within the Si layer of the sample and part of solar wind. Both elements trace the fluorescence yield pattern of Si.

To test the feasibility of using TXRF to determine qualitatively whether an element is present at the surface or within the bulk, sample 60234 was subjected to an angle scan with the S2PicoFox. Figure 3 shows the

data obtained from this scan. Whereas the resolution is far below that of GI-XRF, Ba (magenta) is still clearly recognizable as a surface contaminant with highest fluorescence yield there. Fe (green) is most likely present within the bulk as its fluorescence yield increases with increasing angle. The sensitivity of the method is not sufficient to identify Ni, and Ca is difficult to characterize due to decreased fluorescence yields for lighter elements. However, the data indicate the potential of conventional laboratory TXRF to discriminate between surface contaminants and material present in the bulk.

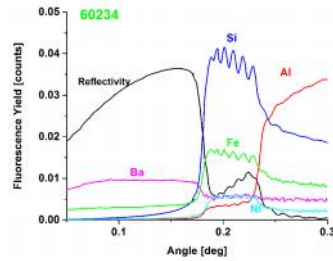


Figure 2: GI-XRF angle scan of Genesis sample 60234. The black line shows beam reflectivity, blue and red lines represent collector materials, green, magenta and aqua are elements either at the surface (Ba) or in the bulk (Fe, Ni). The critical angle is at 0.17 degree. Please note individual fluorescence yields have been scaled for presentation purpose in all graphs.

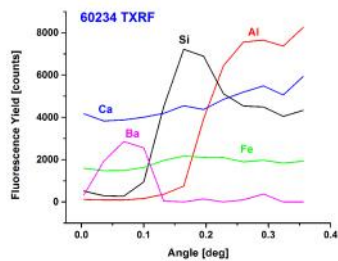


Figure 3: TXRF angle scan of Genesis sample 60234. The black and red lines represent collector materials, blue (Ca), green (Fe) and magenta (Ba) show elements found. Ba is present at the surface, Fe within the bulk and for Ca the sensitivity of the method is not sufficient to determine its location. The critical angle is at 0.1 degree.

To investigate this ability further an implant sample containing 5×10^{14} atoms/cm² Fe implanted at $395 \pm 130 \text{ \AA}$ in epitaxially grown silicon (1000 \AA) on a sapphire substrate was measured by both TXRF and GI-XRF. Figure 4 shows the data obtained by conventional TXRF and figure 5 the GI-XRF results. Fe clearly traces the Si fluorescence yield for both methods and thus is present within the Si layer. Calcium was found to be a surface contaminant by TXRF in total reflection mode (spectrum not shown), which is confirmed by GI-XRF data. Again, TXRF is not sensitive enough to locate Ca clearly.

The results indicate that it should be possible to employ conventional TXRF to qualitatively distinguish between surface contaminants and bulk material for

selected elements, when employing both angle scan and surface analysis at the critical angle. This ability will be very useful as it aids in selection of the most promising samples for GI-XRF quantification of solar wind by eliminating heavily surface contaminated samples.

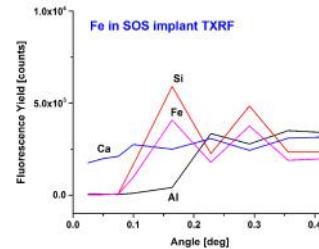


Figure 4: TXRF angle scan of 5×10^{14} atoms/cm² Fe (magenta) implanted at $395 \pm 130 \text{ \AA}$ in epitaxially grown silicon (red, 1000 \AA) on a sapphire (black) substrate. Ca (blue) was detected as surface contaminant by surface analysis. The critical angle is at 0.1 degree.

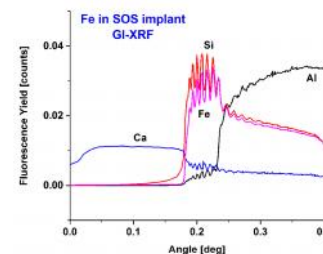


Figure 5: GI-XRF angle scan of 5×10^{14} atoms/cm² Fe (magenta) implanted at $395 \pm 130 \text{ \AA}$ in epitaxially grown silicon (red, 1000 \AA) on a sapphire (black) substrate. Ca (blue) is clearly detected as surface contaminant having highest fluorescence yields there. The critical angle is at 0.17 degree.

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