Grazing Incidence X-ray Fluorescence Measurements of Genesis Sample 30580 for Determination of Manganese and Nickel Fluences

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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 and 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 (JSC), but typically removes only larger sized particulates and a thin film organic contamination acquired during collection in space [3]. Some contaminants like those embedded within the scratches or crevices of the samples require more aggressive cleaning methods. These additional cleaning steps consist of acid and/or organic solvent treatment and typically reduce or at best remove the notorious contaminants. Total reflection X-ray fluorescence analysis (TXRF) is then used to identify remaining contaminants and select the most suitable samples for further analyses [4].

After pre-selection by TXRF some samples are analyzed using grazing incidence X-ray fluorescence (GIXRF), a non destructive method capable of identifying first row transition metals below the surface quantitatively even when only minor surface contaminants are present. GIXRF analysis was already successfully employed for determination of Fe fluences in silicon samples [5,6]. Unfortunately other transition metals of interest for the Genesis mission specifically Mn and Ni cannot be determined in silicon collectors due to peak overlap of remaining surface contaminants and bulk material sum peaks. The most suitable material to analyze those two elements appears to be sapphire (Al_2O_3) and several sapphire flight samples were TXRF screened and cleaned to obtain a promising sample for GIXRF analysis. Flight sample 30580 showed the least surface contaminants left and was selected.

Experimental: Analyses of Genesis sample 30580, a sapphire flight control, and a sapphire implant containing $3x10^{13}$ atoms/cm^2 Mn and Ni, were performed at the GeoSoilsEnviro Consortium for Advanced Radiation Sources (GSECARS) 13-ID-C undulator beamline in grazing incidence X-ray fluorescence set-up. All three samples underwent surface inspection by TXRF analysis prior to GIXRF measurements: S2PicoFox, excitation energy 17.4 keV (Mo- Anode), counting time 3600 seconds (1hour) [4]. The 13-ID-C beamline of the GSECARS at the Advanced Photon Source at Argonne National Laboratory where GIXRF analysis was performed 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 and data acquisition time was adjusted for expected fluences i.e. longer acquisition times for 30580 than for control and implant. [5,6].

Results and Conclusion: Figure 1 shows the surface spectrum of sample 30580 after cleaning with a water, hydrochloric acid, and nitric acid (1:1:1) solution. Cr, Mn, Fe, Ni, and Br are the most prominent elements recognizable as surface contaminants left with Br stemming from the hydrochloric acid cleaning. In addition Si can be seen as well.

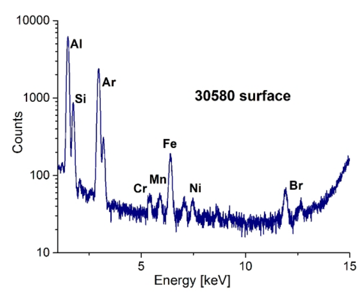

Figure 1: TXRF spectrum of Genesis sample 30580 showing elements present at the surface.

Figure 2 shows a normalized angle scan of the same sample acquired with GIXRF. The black line represents beam reflectivity, which is at its highest at small angles before the beam penetrates below the surface. Aluminum (red) is the collector material and increases with beam penetration depth. Ni (magenta) and Fe (green) appear to be present at and slightly below the surface whereas Mn (blue) seems to be slightly below the surface. In contrast to layered materials such as silicon on sapphire collectors, data for single crystalline materials are more difficult to interpret and X-ray standing wave calculations will be necessary to identify how much material is embedded below the surface.

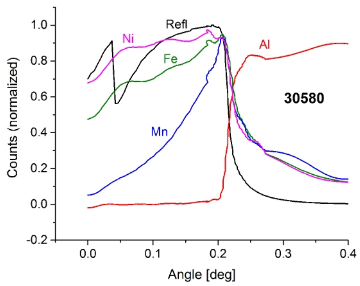

Figure 2: GIXRF analysis of Genesis sample 30580. The black line shows beam reflectivity, the red line the Al collector material, green, magenta and blue are elements either at the surface or in the bulk (Mn, Fe, Ni).

To aid in this process a sapphire implant sample containing $3x10^{13}$ atoms/cm^2 ^{55}Mn and ^{60}Ni implanted at 55kV and 60kV, respectively, and a flight control sample were measured by GIXRF as well. The latter one was hand cleaved and cleaned at JSC prior to analyses. TXRF measurements showed only minor traces of Cr, Fe and Ni as surface contaminants left. The implant had only some Fe on the surface, but was otherwise clean and was used as standard for discriminating between material at or below the surface. Figure 3 shows the normalized GIXRF spectrum of the control sample and figure 4 the normalized GIXRF spectrum of the implant.

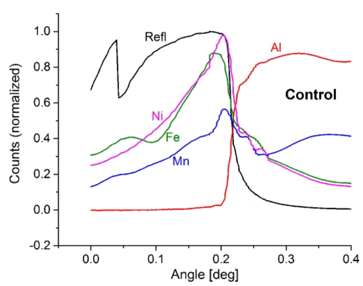

Figure 3: GIXRF data for sapphire flight control sample.

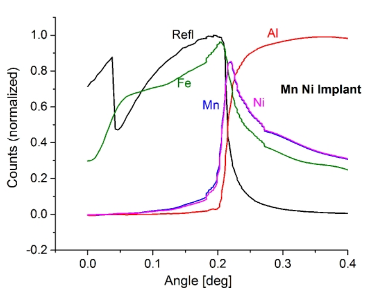

Figure 4: GIXRF data for $3x10^{13}$ Mn and Ni implanted in sapphire.

As seen in figure 3, Mn, Fe and Ni show a distinct peak structure with a maximum at maximum reflectivity for the control sample. This is an indication that all three elements appear to be particle like contaminants present at the surface. Mn shows a similar pattern for the flight sample, but slightly shifted towards higher incidence angles, possibly indicating its presence below the surface.

The implant sample shows almost identical signals for Mn and Ni, clearly below the surface and roughly at the intersection between reflectivity and Al bulk material signal. Fe on the other hand is present mostly at the surface following approximately the shape of the reflectivity curve.

Figure 5 shows the normalized spectrum of flight sample 30580 again, but this time only for Si and Fe besides Al bulk signal and reflectivity. This graph indicates that the Fe peak is shifted slightly into the bulk as compared to Si, indicating that Fe is also present slightly below the surface.

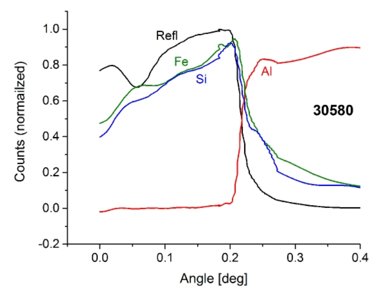

Figure 5: GIXRF analysis of Genesis sample 30580 showing Si and Fe.

As discussed above the graphical interpolation of the different elements is not sufficient to clearly identify the location and concentration of each element. For this X-ray standing wave calculations have to be performed, which will be the next step for this sample [5,6].

References:

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