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Differentiation of Surface Contaminants and Implanted Material on Genesis Solar Wind Samples Using Total Reflection X-Ray Fluorescence Spectometry and Grazing Incidence X-Ray Fluorescence

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DIFFERENTIATION OF SURFACE CONTAMINANTS AND IMPLANTED MATERIAL ON GENESIS SOLAR WIND SAMPLES USING TOTAL REFLECTION X-RAY FLUORESCENCE SPECTROMETRY AND GRAZING INCIDENCE X-RAY FLUORESCENCE

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ABSTRACT

During the Genesis mission solar wind was implanted in collector materials for analysis by various instrumental methods. Unfortunately the space craft crash landed upon return to Earth shattering the collectors into small fragments and exposing them to desert soil and spacecraft debris. Thus only small fragments are available for analysis with each having different degrees of contamination present at and embedded within the surface. Cleaning procedures were developed and applied to remove the contamination. To aid in this process bench top total reflection X-ray fluorescence spectrometry (TXRF) was used to characterize a sample surface before and after various cleaning steps. In contrast to TXRF, synchrotron grazing incidence X-ray fluorescence spectrometry (GI-XRF) is capable of probing at the surface and below the surface thus providing information about surface deposits as well as implanted material. A number of samples were subjected to both, TXRF and GI-XRF analysis and it was observed that some elements detected by TXRF were present not on top of but below the surface of the collector fragment. This suggested the possibility of using laboratory TXRF to distinguish between surface deposits and ion-implanted subsurface material. The feasibility of this approach was tested with a surface deposited and an ion implanted control sample. In addition a careful TXRF angle scan was also executed with one Genesis flight sample and compared to GI-XRF measurements, confirming the ability of bench top TXRF to distinguish between surface and subsurface material.

INTRODUCTION

Solar wind material originates from the outer layer of the sun, the corona, and provides information about initial solar nebular composition and how differences in planetary composition came about. Current data suffer from large uncertainties as they are derived either by optical spectroscopy or by means of meteoritic analysis. (Anders and Grevesse, 1989). In order to obtain more accurate data and model initial solar composition more precisely, the NASA Genesis mission collected solar wind material at LaGrange point 1 for 854 days from November 30, 2001 to April 1, 2004. (Burnett *at al*,. 2003, 2011; Reisenfeld *et al*., 2005). The solar wind was embedded in a variety of high purity collector materials including silicon, sapphire (Al_2O_3) and silicon on sapphire. (Jurewicz *et al*., 2003). Unfortunately, the spacecraft crash landed upon return to Earth, which not only shattered all collectors into small fragments, but also exposed them to desert soil and space craft debris. As a result only small and contaminated samples are available, which have to be cleaned individually as contamination is not uniform. Moreover contamination is not only present at the surface, but also embedded within it dislodged in small crevices and pits, presenting additional challenges. Different cleaning procedures, mostly of chemical nature, were developed and are continuously improved to address these challenges. (Allton *et al*., 2007; Calaway *et al*., 2009; Kuhlman and Burnett, 2007). To aid in the cleaning process bench top total reflection X-ray fluorescence spectrometry (TXRF) is used to characterize the surface before and after a cleaning step. (Schmeling, 2010; Schmeling *et al*., 2011, 2012, 2013). This includes checking for removal of contaminants and monitoring whether the sample surface has been altered during a cleaning process.

In contrast to TXRF synchrotron grazing incidence X-ray fluorescence (GI-XRF) can discriminate between material present at and below the surface of a smooth sample. Thus GI-XRF analysis is suitable for analysis of solar wind which is embedded well below the surface. (Kitts *et al*., 2009a,b). However, high concentrations of surface contaminants may impact GI-XRF data by creating sum peaks, which can interfere with peaks of ion implanted solar wind species. To reduce such peak interference, bench top TXRF is used as a pre-selection tool of samples suitable for subsequent GI-XRF analysis.

In this study we demonstrate the capability of bench top TXRF to determine whether a cleaning method is appropriate in removing surface contaminants from a Genesis flight sample. We also show that it is possible to employ bench top TXRF to distinguish between surface contaminants and implanted material by using standards and a Genesis flight sample.

EXPERIMENTAL

Sample preparation

Control Samples

20 µl of a standard solution containing 100ng/g Ti, Fe, Ni, Zn and Se and pipetted onto a cleaned quartz reflector and dried at 60°C served as a surface deposited control sample. A reference ion implant with $5x10^{14}$ Fe atoms/cm^2 implanted at a depth of 395±130Å in epitaxially grown silicon (1000Å) on a sapphire substrate was used as a subsurface control sample. (Jurewicz, 2012)

Genesis Flight Samples:

Two Genesis flight samples were cleaned initially using a routine procedure of megasonication in ultrapure water and UV/ozone at Johnson Space Center (Allton *et al.,* 2007; Calaway *et al*., 2009). The next cleaning steps varied for the samples. In case of sample 60966 the subsequent steps consisted of a) CO_2 snow jet b) ultrapure concentrated hydrochloric acid and hydrogen peroxide and c) ultrapure concentrated nitric acid at California Institute of Technology (Burnett, 2011, Lin, 2010). As a last cleaning step an organic cellulose acetate film was placed over the sample, wetted with acetone and the dried residue was peeled off later at the Planetary Sciences Institute. (Kuhlman and Burnett, 2007)

Genesis flight sample 60234 was cleaned with ultrapure concentrated hydrochloric acid at California Institute of Technology (Burnett, 2011).

Instrumentation and Analysis

Bench top TXRF analysis of Genesis and control samples was carried out with a PicoTax® and S2 PicoFox® TXRF spectrometer (BrukerNano, Berlin, Germany) in 90 degree tilted position to load the sample horizontally at Loyola University Chicago. Operating conditions were 1mA, 40kV for the PicoTax and 600µA and 50kV for the S2 PicoFox. Counting times were 7200 seconds (PicoFox) and 3600 seconds (S2PicoTax), respectively.
GI-XRF analysis was done at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) at the Advanced Photon Source of Argonne National Laboratory. The 13-ID-C undulator beamline features a cryogenic Si(111) double crystal monochromator and a Vortex® Si drift detector. The samples were mounted in a He flow chamber with a Kapton® window.

RESULTS AND DISCUSSION

In order to demonstrate the capability of bench top TXRF in gauging the suitability of a cleaning step, Genesis flight sample 60966 was selected. The sample consisted of epitaxially grown silicon on a sapphire substrate and underwent multiple cleaning steps, which are listed in table 1 along with the color of the spectra shown in figure 1a and b. Please note that the initial and the CO_2 data of the sample were recorded with the PicoTax TXRF spectrometer (figure 1a).

Table 1: Cleaning procedures applied to Genesis flight sample 60966.

Cleaning Process	**Spectrum Color**	**TXRF Instrument used**
UPW/O_3	Green	PicoTax
CO_2	Magenta	PicoTax
HCl/H_2O_2	Black	S2PicoFox
HNO_3	Red	S2PicoFox
Cellulose Acetate Peel	Blue	S2PicoFox

The initial sample (figure 1a, green) showed only germanium on the surface, originating from germanium collectors, which were pulverized as a result of the crash landing. In the second step a new cleaning approach was tested on the sample by using CO_2 snow shown in figure 1a in magenta. (Lin, 2010). It is evident that this cleaning step introduced contaminants instead of removing them. Upon further investigation it was found that the sample was held with a stainless steel tweezers during the CO_2 application process, which accounts for the chromium, iron and nickel. The next two cleaning steps involving concentrated mineral acids were able to reduce the added metal contaminants (figure 1b, black and red) as well as the germanium. Nitric acid (red) appears also to have a smoothing effect on the surface, which manifests itself in the lower background signal. The last spectrum (blue) was collected after application of a cellulose acetate peel procedure, which was found to be successful in removing organic particles on other collector materials (Kuhlman and Burnett, 2007). In this case, it appears that some material from the peel remained on the surface accounting for the substantially elevated background signal. Also the concentrations of contaminants did increase, which might have been due to different reasons. The sample itself showed scratches and surface damage so that some material which was dislodged in the scratches might have been dissolved by the liquid organic film. It was then re-deposited at different locations when dried. Another possibility is that the film itself contains

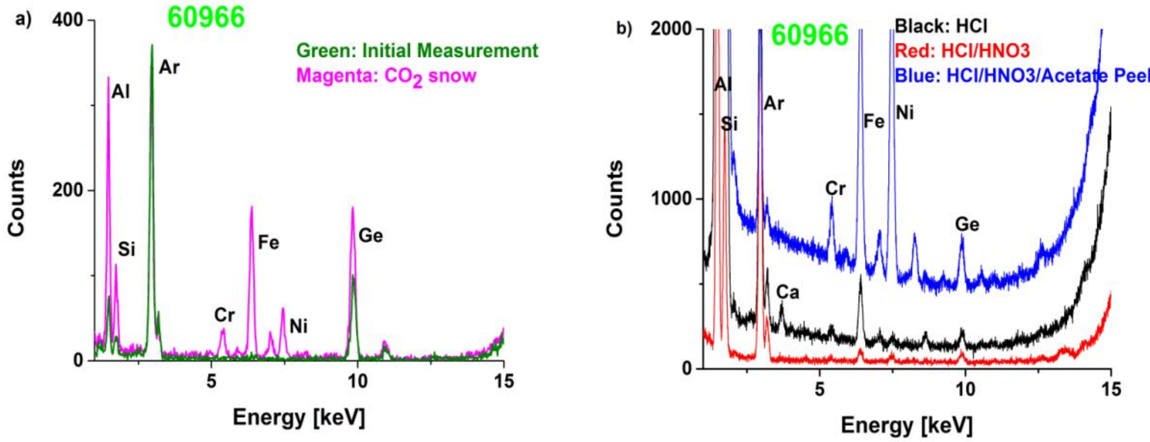

Figure 1: TXRF spectra a) collected with PicoTax after routine UPW/O_3 cleaning (green) and after CO_2 snow cleaning (magenta) and b) collected with S2PicoFox after HCl/H_2O_2 (black), HNO_3 (red) and acetate peel (blue) treatment.

inorganic impurities. In conclusion the cellulose acetate peel does not seem to be effective in removal of contaminants as is the CO_2 snow when using stainless steel tweezers. Later studies using a specially designed CO_2 snow cleaning set-up at Argonne National Laboratory showed more successful results for this cleaning method. (Schmeling *et al*., 2013).

Due to its capability of probing at and below the surface, synchrotron GI-XRF measurements are employed to calculate concentrations of embedded solar wind in a variety of collector materials. (Kitts *et al*., 2009a,b.). A number of samples were pre-selected for GI-XRF measurements using TXRF to avoid highly contaminated ones and maximize beam time for relevant samples. During this process it was noticed that some elements detected with TXRF were present below the surface and not on top of it according to GI-XRF data. This suggested the possibility of using simple bench top TXRF to discriminate between the surface deposits and the implanted material (solar wind) by careful recording of fluorescence intensity (count rate) as a function of incident X-ray beam angle. To test the feasibility of such measurements manual angle scans of a surface deposited multi-element standard (100ng/g per element) and an implant of known concentration were executed with the bench top TXRF spectrometer. Figures 2 and 3 show the results for surface deposited standard and implant with the critical angle of total reflection indicated as a dotted line. The substrate of the standard was quartz (SiO_2) and the implant consisted of a 100nm silicon layer on a sapphire (Al_2O_3) substrate with $5x10^{14}$ atoms/cm^2 of iron implanted in silicon. Two critical angles exist for the latter sample, one for Si at 0.1degree and one for aluminum at about 0.2degree and Ca can be identified as a surface contaminant. Hence the angle scans of both samples follow the behavior described in deBoer *et al*. (1995) and Schwenke *et al*. (1999) suggesting that simple bench top TXRF indeed can be used to differentiate between the surface dirt and the implanted solar wind in Genesis flight samples.

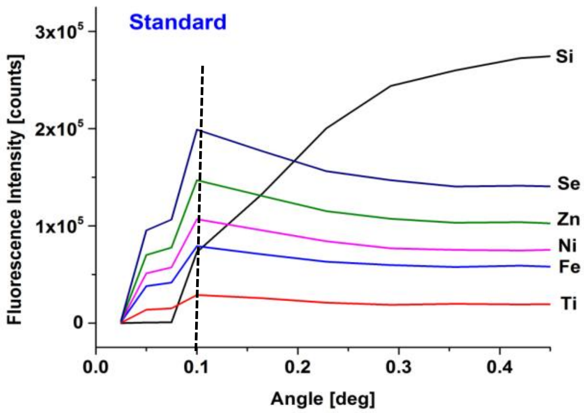

Figure 2: Fluorescence Intensity as counts in dependency of incident X-ray beam angle for a surface deposited standard containing 100ng/g Ti, Fe, Ni, Zn and Se.

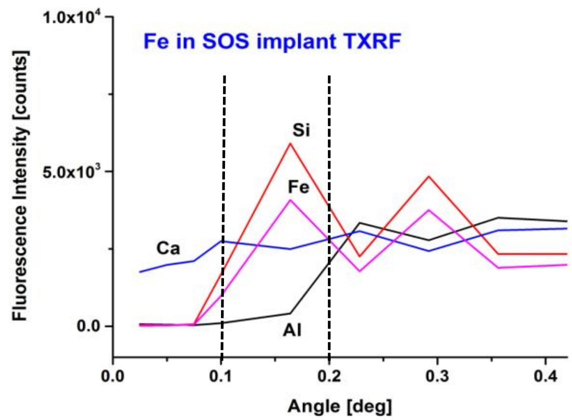

Figure 3: Fluorescence Intensity as counts in dependency of incident X-ray beam angle for a $5x10^{14}$ atoms/cm^2 Fe implant. Implanted depth at 395±130Å (Kitts *et al*.,2009a,b).

To check this hypothesis, Genesis flight sample 60234 was measured with both TXRF and GI-XRF. In Figure 4, fluorescence intensity versus incident beam angle is graphed for bench top TXRF and in figure 5 - for synchrotron GI-XRF of the same sample (60234). Not surprisingly bench top TXRF is far less sensitive than GI-XRF when probing below the surface, but it was possible to clearly identify barium as a surface contaminant with TXRF. The data on iron are less conclusive, and iron might be present on and also below the surface. The two critical angles for the layered sample are well noticeable. GI-XRF measurements confirm barium as a surface contaminant and show that iron is below the surface confined to the silicon layer, but some iron is also on the surface.

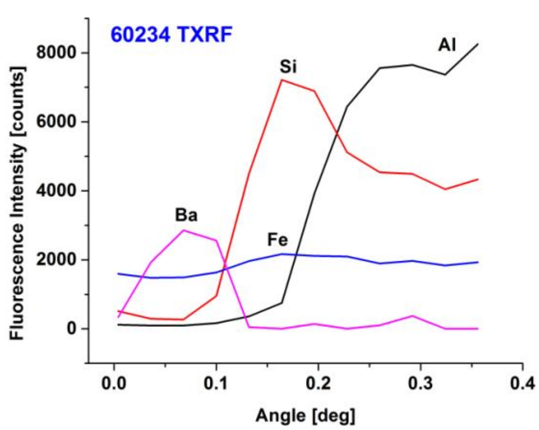

Figure 4: Fluorescence Intensity versus incident beam angle recorded with bench top TXRF for Genesis flight sample 603234.

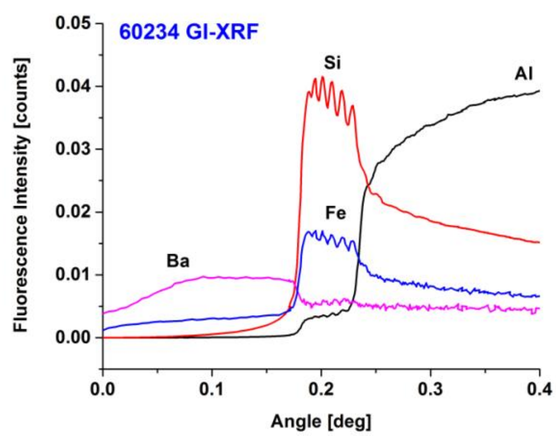

Figure 5: Fluorescence Intensity versus incident beam angle recorded with synchrotron GI-XRF for Genesis flight sample 60234.

In summary simple bench top TXRF is a very powerful analytical tool, which enables evaluation of efficiency of a surface cleaning procedure for Genesis flight samples when used in surface analysis mode at the critical angle. Moreover, it is also capable of discrimination between surface deposited material and subsurface material by employing manual angle scans, which further enhances its utility in Genesis surface cleaning studies.

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REFERENCES

Allton, J.H.; Wentworth, S.J.; Rodriguez, M.C.; Calaway, M.J.; (**2007**).“ Cleaning Genesis solar wind collectors with ultrapure water residual analysis”, Lunar and Planetary Science **XXXVII**, Paper #2138.

Anders, E.; Grevesse, N. (**1989**), “Abundances of the elements: Meteoritic and solar”; Geochimica and Cosmochimica Acta **53**, 197-214.

Burnett, D.S.; Barraclough, B.L.; Bennett, R.; Neugebauer, M.; Oldham, L.P.; Sasaki, C.N.; Sevilla, S.; Smith, N.; Stansberry, E.; Sweetnam, D.; Wiens, R.C.; (**2003**). “The Genesis discovery mission: return of solar matter to Earth”, Space Science Reviews, **105**, 509-534.

Burnett, D.S., Personal communication (**2011**).

Burnett, DS; and Genesis Science Team; (**2011**). “Solar composition from the Genesis Discovery Mission” Proc. Nat. Acad. Sci., **doi: 10.1073/pnas**.1014877108.

Calaway, M.J.; Rodriguez, M.C.; Allton, J.H.; Stansberry, E.K.; (**2009**). “Decontaminating solar wind samples with the Genesis ultrapure water megasonic spin cleaner”, Lunar and Planetary Science **XXXX**, Paper #1183.

DeBoer, D.K.G.; Leenaers, A.J.G.; van den Hoogenhof, W.W.; (**1995**). “Glancing-incidence X-ray analysis of thin –layered materials: a review”; X-ray Spectrometry **24**, 91-102.

Jurewicz, A.J.G.; et al. (**2003**). “The Genesis solar-wind collector materials”, Space Science Reviews, **105**, 535-560.

Jurewicz, A.J.G. (**2012**). Personal communication.

Kitts, K.; Choi, Y.; Eng, P.J.; Ghose, S.K.; Sutton, S.R.; Rout, B.; (**2009a**). “Application of grazing incidence X-ray fluorescence technique to discriminate and quantify implanted solar wind” J. App. Phys. **105**:6, 064905.

Kitts, K.; Choi, Y.; Eng, P.; Sutton, S.R.; (**2009b**). "X-ray standing wave based internal reference method for quantification of implanted Fe in Genesis samples", Lunar Planetary Sciences **XXXX**, paper # 1439.

Kuhlman, K.R.; Burnett, D.S.; (**2007**), "Extraction replica cleaning of Genesis AuOS and AlOS", Lunar Planetary Sciences **XXXVIII**, paper #1920.

Reisenfeld, D.B.; Wiens, R.C.; Barraclough, B.L.; Steinberg, J.E.; De-Koning, C.; Zurbuchen, T.; Burnett, D.S.; (**2005**). "The Genesis mission solar solar wind samples: collection times, estimated fluences, and solar wind conditions,", Lunar Planetary Sciences **XXXVI**, paper # 1278.

Schmeling, M.; (**2010**). "Analysis of Genesis Sample Surface Contamination by Total Reflection X-ray Fluorescence Spectrometry"**,** Lunar Planetary Sciences **XXXXI**, paper #1682.

Schmeling, M.; Burnett, D.S.; Jurewicz**,** A.J.G.; (**2011**)**.** "Surface characterization of Genesis solar wind samples by TXRF", Lunar and Planetary Sciences **XXXXII**, paper #2041.

Schmeling, M.; Burnett, D.S.; Jurewicz, A.J.G.; Veryovkin, I.V.; (**2012**). "Steps toward accurate large area analyzes of Genesis solar wind samples: evaluation of surface cleaning methods using total reflection X-ray fluorescence spectrometry, Powder Diffraction **27**:2, 75-78.

Schmeling, M.; Burnett, D.S.; Allton, J.H.; Rodriguez M.C.; Tripa, C.E.; Veryovkin, I.V.; (**2013**). "Application of CO_2 snow jet cleaning in conjunction with laboratory based total reflection X-ray fluorescence spectrometry for Genesis solar wind samples", Lunar and Planetary Sciences **XXXXIV**, paper #2465.

Schwenke, H.; Beaven, P.A.; Knoth, J.; (**1999**). "Applications of total reflection X-ray fluorescence spectrometry in trace element and surface analysis", Fresenius J. Analytical Chemistry **365**, 19-27.