TOFSIMS studies of Genesis standards and samples.

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Introduction: The Genesis spacecraft returned implanted solar wind in collectors of pure materials such as silicon, germanium and diamond-like-carbon to Earth in September 2004 (1). However, the crash landing of the capsule shattered and mingled the fragments of most of the collectors and exposed them to water and Utah desert soil, exacerbating the difficulties of obtaining accurate analyses of implanted solar wind in the collector materials. Even under favorable circumstances these were going to be challenging measurements to make but contamination issues made their analysis even harder.

We have undertaken Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) analyses of various Genesis collector materials and standards to help understand how to overcome these issues and bring additional capabilities to the task of measuring implanted solar wind profiles.

Analytical Technique: All analyses reported here were obtained using the 'IDLE' time of flight secondary ion mass spectrometer (2,3). Briefly, a focused, pulsed Ga^+ ion beam was fired at the sample target and secondary ions released to be accelerated and detected with high mass resolution in a time of flight secondary ion mass spectrometer. The primary ion beam was rastered over the surface in a rectangular pattern to sputter uniform craters in the sample. Ion beam sputtering removes atoms from the sample so layers of material were removed from the crater during each analysis. A sequence of analyses therefore formed a depth profile into the sample. The procedure followed here was to raster the primary ion beam over a rectangular area of dimensions ~100x200μm using the dc Ga^+ beam to sputter away a desired depth into the surface and then an ion image was obtained from the central 50x100μm area (avoiding edge effects from the crater walls). The sputtering rate from the central area from which data was acquired was almost negligible compared with the sputter rate during dc sputtering of the larger crater. The relative depth at which each measurement was obtained was calculated by carefully recording the sputtering times, areas and primary ion current of each analysis. An absolute depth calibration was then obtained by measuring the final crater depth using AFM.

Issues: The issues we wished to address with the analyses reported here concern (1) the calibration and uniformity of ^{25}Mg implant samples used as standards and (2) the nature and distribution of contaminant particles and atoms on the Genesis samples acquired both from the crash landing and during space exposure.

Results:

Calibration and uniformity of standards. Two standards were studied, a pure Si wafer with 25keV ^{25}Mg ions implanted and a 'Sandia' diamond standard with 43keV ^{25}Mg ions implanted.

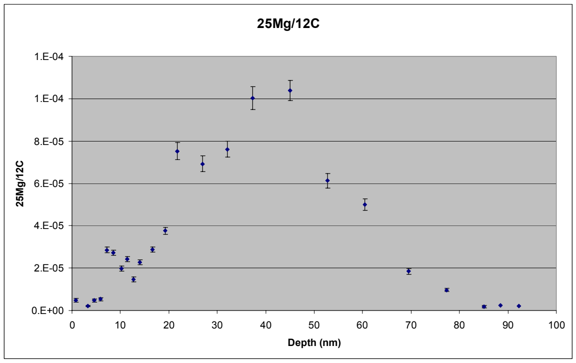

Figure 1. ^{25}Mg depth profile in Sandia diamond standard, $^{25}Mg/^{12}C$ is the measured atomic ratio of these species obtained by using measured total counts of these species at each measured depth and relative sensitivity factors of these elements.

The measured depth profile reported here (depth of peak ^{25}Mg ~40nm) agrees well with depth of the maximum of the profile obtained using a Cameca 6f ion microprobe (Jurewicz pers. comm.)

Suspicions have also been raised concerning the lateral uniformity of the ^{25}Mg implant standard so we obtained high mass resolution images of ^{25}Mg within craters of both the Sandia and Si standards made by both the Cameca 6f ion microprobe and craters we sputtered using 'IDLE'. The beam was rastered over an area selected to give about 1μm per pixel (the spot size was $\leq$1μm). The number of discrete ^{25}Mg counts in each pixel were summed and compared with a Poisson distribution. The low abundance of the ^{25}Mg implant relative to the diamond matrix meant that the number of counts in each pixel was quite low. Figure 2 shows these data for the Sandia standard which has been more strongly suspected of ^{25}Mg implant heterogeneity.

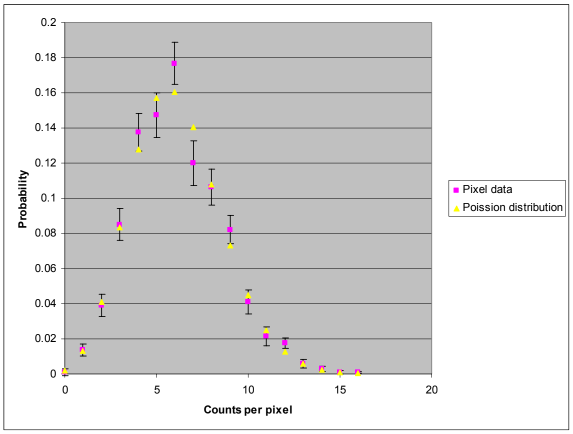

Figure 2. Comparison between the number of counts per pixel against proportion of pixels with that number of counts as a fraction of the total number of pixels (data points with error bars). Also shown is a Poisson distribution with a mean value equal to the pixel data.

The fit between the measured counts distributed between pixels and a Poisson distribution is extremely good. This implies that the distribution is random. Repeat analyses on both the Si and Sandia diamond standard were all consistent with this conclusion. Nor was there any evidence that counts between neighbouring pixels were correlated leading us to conclude that the ^{25}Mg implantation standards used as calibration standards for the Genesis samples were not subject to systematic errors due to heterogeneous implantation.

Contamination of collector surfaces. Analyses of Si, Ge and diamond-like-carbon collector materials from Genesis showed particulates on or just under the surface to a depth of a few nm. These were mostly removed by cleaning in a reduced-power ultrasonic using a series of organic solvents followed by a Micro-90 and UHP-water rinses, but depth profiles of several elements showed declining values from the surface to still measurable quantities at depths of tens of nm. Of particular surprise were very significant quantities of Cs which can only have come from earlier analyses using a Cameca 6f ion probe. Although O^- primary ion beams were used in these analyses, Cs deposition in ion columns over the history of the instrument must have been resputtered and deposited onto the samples. Indeed since the primary ion beam is of high energy, the ions will be implanted to some depth. This is likely true of other elements in primary ion columns too which may include Fe and other elements found in the metals used to fabricate the ion columns.

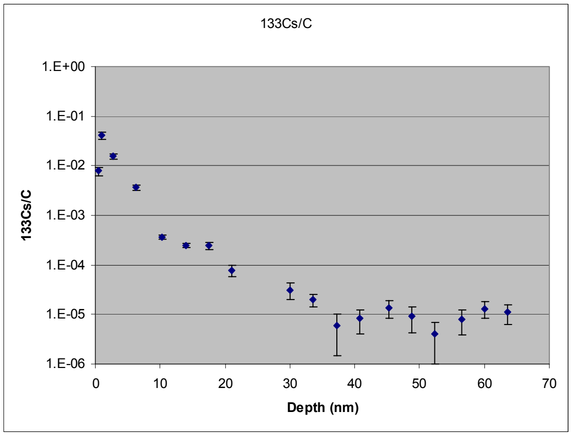

Figure 3. Measured ^{133}Cs depth profile in Genesis diamond sample 20732,2. The apparent depth to which Cs was measured may be due to real implantation of the Cs but also to artifacts such as primary ion beam mixing of the surface layers which may fold in an abundant surface element deeper and deeper into the material as depth profiling progresses.

Discussion: TOFSIMS offers complimentary capabilities to other SIMS techniques and can accurately obtain depth profiles to detect very low abundance elements with sufficient sensitivity to analyse solar wind profiles. Extreme care will be needed however in obtaining such profiles as they are prone to artifacts that may obscure solar wind elemental profiles.

References: (1) Burnett D. (2005), *Eos Trans. AGU, 86*(52), Fall Meet. Suppl., Abstract SH32A-01, (2) Henkel et al., (2006) App. Surf. Sci. 252, 7117-7119, (3) Henkel et al., (2007) in review, Rev. Sci, Inst.

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