

ANALYZING GENESIS DIAMOND COLLECTORS BY TOFSIMS: DEVELOPMENT OF A METHOD FOR THE SIMULTANEOUS DETECTION OF MANY SOLAR WIND IMPLANTED ELEMENTS. J. L. Claydon¹, I. C. Lyon¹, T. Henkel¹, D. Rost¹, A. King¹ and S. Davies^{1,2}, ¹SEAES, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK, ²present address, Hiden Analytical, Warrington, UK. Jennifer.L.Claydon@student.manchester.ac.uk

Introduction: The Genesis spacecraft returned collectors with implanted solar wind atoms to Earth in October 2004, but the crash landing of the capsule resulted in contamination and fragmentation of the ultra-pure collector materials requiring the development of new analytical procedures [1,2]. We describe here the development of Time-of-Flight Secondary Ion Mass Spectrometry (TOFSIMS) analysis of a diamond collector fragment to attempt the simultaneous detection and quantification of implanted solar wind atoms.

TOFSIMS: The instrument used for these analyses was a new Time of Flight Secondary Ion Mass Spectrometer built to the same design as the 'IDLE' (Interplanetary Dust Laser Explorer) instrument [3], the major difference being the use of a high current duoplasmatron primary ion source delivering pulses of oxygen ions to the sample. The technique of 'delayed extraction' of secondary ions [4] was used to obtain high sensitivity secondary ion detection whilst retaining high mass resolution. Briefly, a long primary ion pulse of oxygen ions (typically ~50ns) was used to sputter the collector surface. Secondary ions were allowed to leave the surface for a short time (~100ns) and then the sample voltage was rapidly switched on. The secondary ions that left the surface earlier from the primary pulse were given less energy than those sputtered later. After following a trajectory through a reflectron time of flight mass spectrometer, the initial long pulse of ions was time focused by the pulsed extraction to give high mass resolution at the detector. An area of ~200 μ m wide was cleaned for a short length of time using a dc primary ion beam to sputter some of the surface, removing up to a few nm in depth and then pulses of primary ions were rastered over the surface of the sample in an area ~50 μ m wide to analyze the atoms found at that depth in the surface. The process was repeated numerous times to depth profile through the depth where the solar wind atoms should be implanted.

Diamond and TOFSIMS: The principal elements desired for analysis by TOFSIMS were Na, Mg, Al, Si, K, Ca and Fe because these elements form positive ions efficiently during secondary ionization and the solar wind abundances of these elements are expected to be in the ppm–0.1ppm abundance range in the top few 10s of nm of the collectors. (K was expected to be present at only 0.01ppm levels but it has a secondary

ionization efficiency an order of magnitude greater than most of the other elements listed making it still potentially detectable). It was hoped that the simultaneous detection of elements would allow the exact comparison of implantation depth profiles for different elements and hence derivation of relative implantation velocities for the different elements as well as quantification of abundances of the different elements. Analysis of standards with ²⁵Mg implanted to ppm abundance levels showed that these detection levels could be attained by TOFSIMS. Carbon by contrast forms positive secondary ions very inefficiently and as the diamond collector material was extremely pure, the signal rates acquired from the diamond were extremely low. This gives diamond a considerable advantage over other collector materials because a drawback of SIMS is the formation of isobars from any combination of atoms found in the sample matrix and the primary ions (e.g. see [4] where this problem was much more pronounced for Si). The predominant peaks observed in the mass spectrum of analyzed diamond were therefore C⁺, C₂⁺, CO⁺ and hydrocarbons from CH⁺ upwards. Of the elements identified above, the most serious isobar is C₂⁺ which has a mass of 23.99945 whereas ²⁴Mg⁺ has a mass of 23.98449, requiring a mass resolution in excess of 2000 to adequately separate the peaks since the C₂⁺ peak was 2 orders of magnitude larger than the ²⁴Mg⁺ peak. Other likely isobars because of either, major abundance (from the diamond, C, N) or primary beam (O), CO⁺ with ²⁸Si⁺, ²⁷Al¹²C⁺ with ³⁹K⁺, ²⁴MgO⁺ and ²⁸Si¹²C⁺ with ⁴⁰Ca⁺. Although some of the latter require higher mass resolution (~3000), none of these interferences were quite as problematic as C₂⁺ with ²⁴Mg⁺ because of the high abundance of C₂⁺ relative to ²⁴Mg⁺. A mass resolution of >3000 (FWHM) was used throughout these series of measurements.

Quantification: A major goal following the detection of any solar wind element profiles is the accurate determination of element abundances. Secondary ionization gives fairly reproducible ionization efficiencies under stable conditions but ones that can vary by many orders of magnitude depending upon the ionization potential of the element under analysis and the primary ion beam species. Quantification therefore requires accurate calibration from standards where the element abundances are known accurately within a matrix of the same composition as the sample under analysis.

These factors are usually expressed as a relative sensitivity factor (RSF) for a particular element relative to a major component of matrix material (carbon in this case). RSFs used here are taken from [5] who used 4keV oxygen primary ions to sputter elements from silicon, almost identical to the conditions used here.

Results: A depth profile obtained after sputter-cleaning the surface using a DC ion beam followed by pulsed beam analysis in a repeating cycle is shown in figure 1.

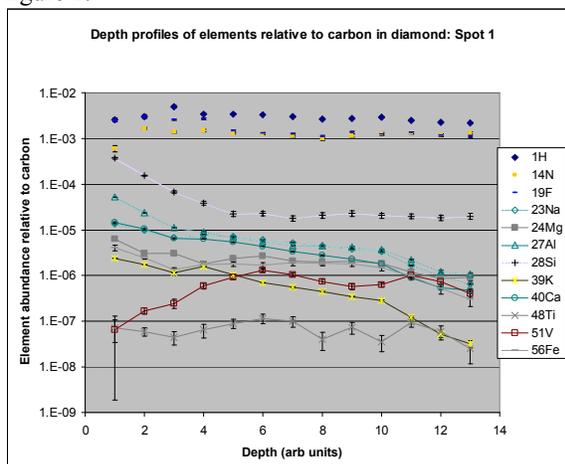


Figure 1. Depth profiles of multiple elements in Genesis 60235 diamond. Depth scale not calibrated at time of abstract.

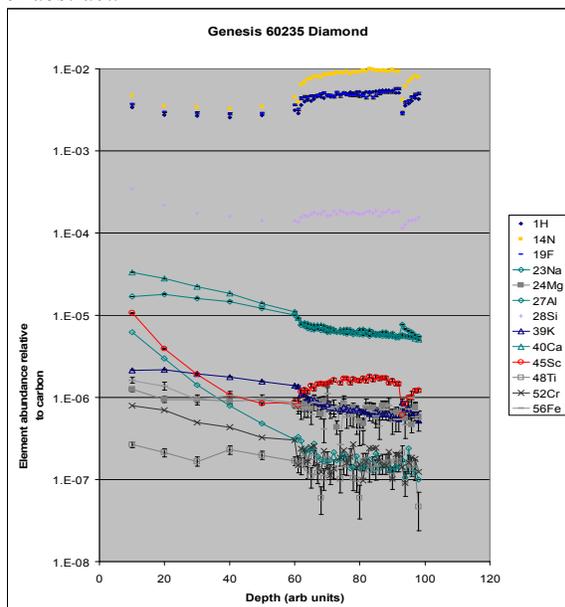


Figure 2. Depth profile obtained by using sputter cleaning alternated with analysis for the first 6 points followed by analysis only for the remaining points.

Discussion: Contamination levels of Si, Na, Al, K and Ca are too high to show solar wind abundances and show only a decreasing abundance from the surface

value. Nitrogen, hydrogen and fluorine are very high and rise when there is not aggressive sputtering of the area (figure 2). This suggests that these elements result from the vacuum and RSFs used here may not be appropriate, considerably overestimating abundances.

Magnesium and iron are at about the correct abundance expected for solar wind implantation and both show a decreasing abundance from the surface followed by a small rise and then a decrease – suggestive of an implantation profile.

A curious observation is a peak in the mass spectrum exactly at the mass of ^{51}V that is low at the surface, rises to a maximum and then tends to fall again with depth. Whilst strongly suggestive of an implantation profile, if it were to be ^{51}V from the solar wind, the abundance of this element would be approximately 2 orders of magnitude higher than anticipated. No other element or molecular interference has the same profile indicating that it is unlikely to result from an isobar derived from another element. The interpretation of this feature is thus unclear at this stage.

Conclusion: There is evidence that solar wind Mg and Fe are being detected but surface levels of Si, Na, Al, K and Ca are too high and contaminate the depth profiles. Better cleaning prior to analysis may result in lower background limits sufficient to reliably detect the solar wind implanted atoms and more accurate and quantifiable depth profiles for solar wind implanted elements will be available in the near future.

Acknowledgements: This work was supported by the Science and Technology Facilities Council, through its UKCAN programme and through a rolling grant. The University of Manchester is thanked for major SRIF and other funding for equipment. The authors express their gratitude to D. Blagburn, B. Clementson and B. Gale for essential construction and maintenance work. We are grateful to D. Burnett and A. Jurewicz for the provision of samples and considerable discussion.

References: [1] Burnett D. (2005), *Eos Trans. AGU*, 86(52), Fall Meet. Suppl., Abstract SH32A-01. [2] Burnett D. et al. (2003) *Space Science Reviews*, 105, 509–534. [3] Henkel T. et al. (2007) *Rev. Sci. Instrum.*, 78, 055107. [4] Lyon I.C. et al. (2008) *LPSC XXXIX submitted*. [5] Wilson R.G. (1995) *Int. J. Mass Spec. Ion Process.*, 143, 43–49.