

**TOFSIMS ANALYSIS OF SOLAR WIND IMPLANTED ELEMENTS INTO GENESIS COLLECTORS: DEVELOPMENT OF HIGH SENSITIVITY ‘DELAYED EXTRACTION’ AND APPLICATION TO THE ANALYSIS OF SILICON COLLECTORS** I. C. Lyon<sup>1</sup>, J. L. Claydon<sup>1</sup>, T. Henkel<sup>1</sup>, D. Rost<sup>1</sup>, A. King<sup>1</sup> and S. Davies<sup>1,2</sup>, <sup>1</sup>SEAES, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK, <sup>2</sup>present address, Hiden Analytical, Warrington, UK. [Ian.Lyon@manchester.ac.uk](mailto:Ian.Lyon@manchester.ac.uk)

**Introduction:** The Genesis spacecraft returned ultra-pure detectors with solar wind implanted atoms to Earth in 2004. The integrated fluxes of atoms over the 2 year mission were predicted to yield typically ppm and sub-ppm atomic abundances of atoms from the solar wind implanted into the surface layers of collectors of silicon, diamond and germanium. [1] Progress in analyzing solar wind atoms implanted into diamond using TOFSIMS (Time-Of-Flight Secondary Ion Mass Spectrometry) is described in an accompanying abstract [2]. Here we describe a method for improving the sensitivity of TOFSIMS analyses so that sub-ppm abundances of elements in samples may be analyzed in short-times (<1hr) and its application to the analysis of silicon flown on the Genesis mission to detect and quantify the level of implanted solar wind atoms.

**TOFSIMS and ‘delayed extraction’:** The instrument used here for analyses is a new instrument built to a very similar design to the ‘IDLE’ instrument [3], the major difference being the use of a duoplasmatron primary ion gun to provide high currents of oxygen ions.

TOFSIMS is a well established analytical technique in which a short time period (~ns) pulse of energetic primary ions is fired at a sample. Secondary ions generated by sputtering are accelerated by passing them through a large potential difference (typically by biasing the sample to a large potential relative to ground) and passing the energetic secondary ions through a reflectron time-of-flight mass spectrometer. The secondary ions have an initial spread of energies due to the sputtering process but the reflectron time-focuses the ions so that high mass resolution may be achieved if a short time primary ion pulse is used to sputter the sample. To obtain mass resolving powers of >2000, however, requires short primary ion pulse lengths (~few ns) and the resulting integrated primary ion current is very small. The poor duty cycle of TOFSIMS  $10^{-4}$ – $10^{-5}$  (primary ion pulse ~few ns repeated at a frequency of up to a few kHz) results in poor signal rates for low abundance atoms in samples. If higher mass resolution is required then even shorter primary ion pulses are necessary which result in even poorer detection sensitivity. We have therefore been exploring an alternative method of achieving high mass resolution without sacrificing primary ion current. This technique is known as ‘delayed extraction’ and in it, a long (~50ns) primary pulse is fired at the surface whilst the

surface is at ground potential. After the conclusion of the primary pulse when the ~50ns long secondary ion pulse has left the surface but is still within about 1mm of it, the sample potential is rapidly switched on (1.5kV in a ~10 ns) thus establishing an accelerating field for the secondary ions. Those ions sputtered from the surface near the start of the primary ion pulse will have moved furthest away from it and gain less additional energy than those ions sputtered later by the primary ion pulse. By suitably adjusting the time delay of the sample pulse and the energy focusing properties of the reflectron, high mass resolution (3000–5000 FWHM) can be obtained despite being generated by a long primary ion pulse. Drawbacks to the technique are that the time focusing is only optimal over a restricted mass range (although a mass resolution >2500 has been achieved from masses 12 to 70) and the relationship between mass and time can be more complex than the simple time of flight relationship  $t \propto \sqrt{m}$  making mass calibration more difficult.

**Genesis Silicon collector:** A problem with secondary ionization is that molecular combinations of the primary ion with any atom from the sample, surface contamination or from residual gas near the sample surface, can be formed as long as the resulting molecule or cluster is stable enough to last at least a few microseconds and survive long enough through the time of flight mass spectrometer to be detected. Although the silicon collector was composed of very pure silicon, nevertheless, sufficient molecular and cluster interferences are formed to prevent this material being suitable for detection of certain solar wind implanted elements. These isobaric interferences are  $^{28}\text{Si}^{2+}$  with  $^{14}\text{N}^+$  and  $^{30}\text{Si}^{2+}$  with  $^{15}\text{N}^+$ ,  $^{30}\text{SiH}^+$  with  $^{31}\text{P}^+$ ,  $^{28}\text{SiC}^+$  with  $^{40}\text{Ca}^+$ ,  $^{28}\text{SiO}^+$  and  $^{28}\text{SiOH}^+$  (and all variants with  $^{29}\text{Si}$  and  $^{30}\text{Si}$ ) with masses in the range 44–47 and  $^{28}\text{Si}_2^+$  with  $^{56}\text{Fe}^+$ .

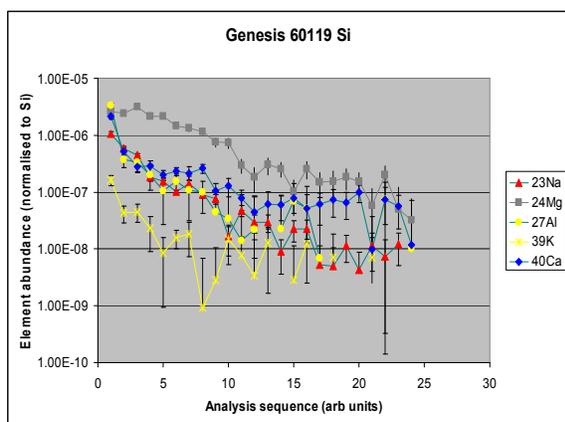
Although there is sufficient mass resolution to nominally resolve some of these interferences, they are ruled out here because the interferences, such as  $^{28}\text{Si}_2^+$ , are sufficiently abundant to affect or even hide low abundance elemental peaks.

An additional problem that plays a large role in the interpretation of depth profiles acquired here is the mixing of surface contamination atoms into the surface. Relatively high surface contamination can therefore give rise to spuriously high abundance values for any

specified element at depths below the surface, carried into the surface by primary ions. Surface contamination can therefore mask the low abundance solar wind atoms.

**Quantification:** Silicon, giving a major peak at  $^{28}\text{Si}^+$ , can be used for quantification of elements within the sample rationed against Si. Relative sensitivity factors used here to normalize ionization efficiencies of the different elements against Si are taken from [4] who published relative sensitivity factors for elements in silicon obtained using 4keV oxygen ions, almost identical to the experimental configuration here. Further quantification of RSFs will be undertaken from standards in the near future.

**Results:** Depth profiling was undertaken by sputtering an area of  $\sim 200\mu\text{m}$  across with a DC ion beam for a period of 55 seconds and then mass spectra acquired from an area  $< 100\mu\text{m}$  within the sputtered crater. This sequence was repeated for each step in the depth profile. Element ratios relative to Si dropped fairly rapidly with depth and the  $^{24}\text{Mg}$  depth profile does initially drop followed by an increase below the surface indicating that solar wind Mg may have been detected. More detailed depth profiles with lower surface contamination by these elements are needed.



**Figure 1:** Simultaneous depth profiles of Na, Mg, Al, K and Ca obtained in a Genesis 60119 silicon collector fragment. The depth scale at the time of this abstract is uncalibrated but will be in the near future.

For comparison, estimated abundances, in ppma for these elements following 2 year exposure to the solar wind [1] are: Na 0.22ppma; Mg 4.1ppma; Al 0.32ppma; K 0.014ppma and Ca 0.23ppma. The most abundant element, Mg, shows a profile that is consistent with implanted solar wind at the few ppma level. Na, Al and Ca are expected to be more in the low 0.1ppma level and although there is a little evidence for flattening of the profiles at about the predicted levels,

any identification as an implanted atom profile is not secure. Surface contamination levels are too high and mixing of the surface contamination atoms to lower depths is affecting the measured profiles. The sample analyzed here was not cleaned after receipt and further analyses will be now undertaken with pre-cleaning of the surface.

**Conclusion:** There is evidence that solar wind Mg may have been detected in the silicon collector material but surface contamination levels of Na, Al, K and Ca are too high (albeit in the ppm range) and mixing of surface atoms is affecting the measured depth profiles. Better cleaning prior to analysis may result in lower background limits sufficient to reliably detect the solar wind implanted atoms and should result in more accurate and quantifiable depth profiles for solar wind implanted elements in the near future.

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