FINE STRUCTURE OF NEAR-SURFACE SOLAR WIND DEPTH PROFILE BY SNMS/SEM IMAGING.

S. V. Baryshev[1], A. V. Zinovev[1], C. E. Tripa[1], M. J. Pellin[1], D. S. Burnett[2] and I. V. Veryovkin[1], [1]Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA, [2]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA (sbaryshev@anl.gov)

Introduction: NASA Genesis Mission samples made of a number of ultrapure materials, which captured the solar wind (SW), pose a serious challenge for analytical approaches to reveal solar elemental and isotopic abundances at high precision and accuracy. The difficulties are generally known to be (i) surface contamination due to brown stain and/or the crash landing and (ii) ultralow/trace concentrations of the implanted elements (~1 ppb/parts of ppb) which are distributed within the first 100 nm depth from the collectors surface.

Mass spectrometry (MS) based on ion sputtering proved to be an inestimable method in the Genesis project [1]. The combination of factors (i) and (ii) requires of MS approaches to have the highest possible depth resolution (in addition to the highest possible sensitivity) to accurately distinguish between surface terrestrial contamination and the implanted SW. For a number of SW elements having high terrestrial abundances, this is possibly the only way to restore the correct depth profile curves yielding to correct fluence calculations.

In this work, we report results on Genesis Si flight samples obtained by laser post-ionization secondary neutral mass spectrometry (LPI SNMS) based on dual beam depth profiling with low energy normal incidence sputtering (*lenis*DB). Being an approach of ultimate depth resolution, coupled with preliminary Genesis sample surface SNMS mapping and secondary electron microscopy (SEM) imaging, *lenis*DB allowed us to (i) resolve the SW depth profile from the surface contamination and (ii) find analytical cleaner (*sweet*) spots, i.e. surface areas of lowest initial contamination levels, and so uncover a fine structure of the near-surface SW depth distribution (essentially pronounced in Mg), which we attribute to radiation enhanced diffusion towards the surface.

Experimental: In SARISA [2] we combined two separate ion beams; one of low energy and normal incidence for ultimate depth resolution (~0.5 nm) ion milling and another for elemental analysis with high lateral resolution (~10 μm). This arrangement is an advanced version of known dual beam depth profiling [3] and should be called in our case *lenis*DB (Fig.1).

The principle of LPI SNMS is as follows. Sputtered neutrals are converted into photo-ions for further time-of-flight (TOF) MS analysis by resonantly enhanced multi-photon ionization with tunable Ti-

sapphire lasers by the scheme as reported in [4]. Such a scheme allows us, in general, to detect simultaneously Mg, Ca and Cr.
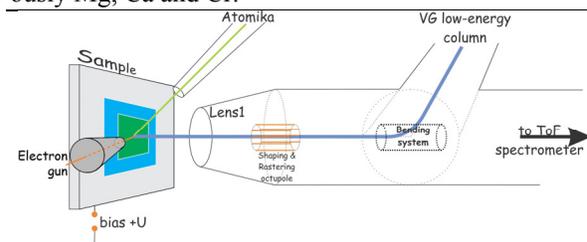

Figure 1: The *lenis*DB system. The sputtering Ar+ beam comes from the VG low energy column and is deflected into the front TOF column by the Bending System optics. Being focused with Lens1, it impinges at normal incidence on the sample surface. Normal incidence gives a way to vary the sputtering beam energy down to 0 eV by biasing the target (+U), and hence to achieve sub-nm depth resolution. The separate Atomika ion gun probes the surface with 10 μm lateral resolution. Sputtered species are then analyzed by the TOF spectrometer. The electron gun images surface topography. Ionizing lasers beams are not shown in this cartoon, one can imagine them intercepting neutrals right between sample surface and Lens1.

Elemental depth profiles of SW were obtained by a sequence of alternating cycles of ion milling by a raster scanned primary direct current Ar+ ion beam at 250 eV (VG gun in Fig.1) and TOF SNMS analysis using a raster scanned primary pulsed Ar+ ion beam at 5 keV (Atomika gun in Fig.1).

Since analytical techniques that use beams of either electrons or ions as probes are often the methods-of-choice for demanding tasks, scanning electron microscopy (SEM) protocol was developed in SARISA to make it versatile [5].

Results and Discussion: Figure 2 demonstrates depth profiles of [24]Mg in a Genesis Si bulk SW collector fragment. The black dashed depth profile is a typical result of all our previous measurements. There are 2 regions attributed to surface contamination, followed by SW fall starting from a somewhat short plateau (due to the sum of the slow and the fast solar wind components, as shown in Ref.6). However, at a closer look, it unravels unexpected results. We combined the advantages of SEM imaging protocol with trace-sensitive surface-only SNMS chemical mapping using the pulsed analytical Atomika beam only on the pristine surface, prior to our standard *lenis*DB depth profiling. It is important to note, that the chemical SNMS

imaging with a pulsing ion gun is quasi-nondestructive and has a much higher relative sensitivity than, for example, x-ray microanalysis. This imaging combination allows one to store a three dimensional array of chemical and topographical information (X-, Y- coordinates and elemental signal intensities). An example of an imaging array is shown in Fig.3 revealing *sweet* spots (marked by #), which were used later for acquiring 3 depth profiles depicted in Fig.2 in red, olive and cyan. In essence, it appears that it is possible to get detailed near-surface distributions of all three elements, Mg, Ca and Cr, as shown in the inset in Fig.2.

The most interesting and pronounced features are revealed in the case of ^{24}Mg depth distribution within first 10 nm in a distinct and reproducible manner. It is observed that instead of 2 mentioned regions there are 3 ones: first peak corresponding to the surface contamination, followed by a second one proceeding the SW plateau. We interpret the second peak (at ~6 to 8 nm) as a manifestation of proton radiation induced diffusion towards the collector's surface. To qualitatively demonstrate it, we simulated depth distribution of Si vacancies, produced under singly charged hydrogen of 1 keV/amu bombardment, which then serve as interstitial traps for implanted SW at a concentration ~10^3 times higher that of implanted SW [7]. In general, there are several driving forces that should be taken into account in a real experiment. Nevertheless, the simplified view of SW trapped at defects conserves the existing condition of a peaking impurity within the first ~10 nm of the matrix [8].

Conclusions: The ultimate depth resolution of *lenis*DB at 250 eV sputtering due to the shallow ion penetration depth into the solid, which results in an ultra-short range of crystal lattice disturbance, together with preliminary SEM and SNMS mapping/imaging represents a powerful approach for detailed reconstructing SW elemental depth distributions within the first 20 nm. This depth accuracy is beneficial for understanding physics behind the SW itself, including precise calculations of implanted fluences, and processes taking place in the collector material.

References: [1] McKeegan K. D. et al. (2011) *Science, 332*, 1528-1532. Marty B. et al. (2011) *Science, 332*, 1533-1536. [2] Veryovkin I. V. et al. (2004) *Nucl. Instr. Methods Phys. Res. B, 219-220*, 473-479. [3] Iltgen K. et al. (1997) *J. Vac. Sci. Technol. A, 15*, 460-464. [4] Veryovkin I. V. et al. (2010) *LPSC XLI*, Abstract #2579. [5] Veryovkin I. V. et al. (2011) *LPSC XLII*, Abstract #2790. [6] Veryovkin I. V. et al. (2012) *LPSC XLIII*, Abstract #2296. [7] King B. V. et al. (2008) *Appl. Surf. Sci., 255*, 1455-1457. [8] Yacout A. M. et al. (1989) *Nucl. Instr. Methods Phys. Res. B, 42*, 49-60.
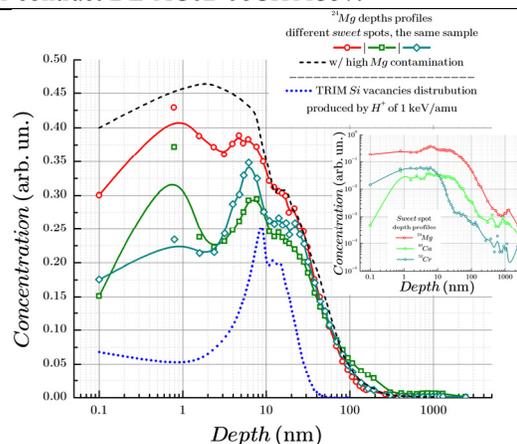
Fig.2. ^{24}Mg depth profiles in a Genesis Si bulk SW collector fragment: the black dashed line is a typical results without preliminary SEM/SNMS imaging; red, olive, cyan (solid lines + open circles, squares, diamonds, respectively) are three measurements without pronounced surface contamination (i.e. starting, in some cases, from surface concentrations lower than SW ones. The blue dotted line is a TRIM calculation of Si vacancies distribution produced by protons of 1keV energy. The inset: an example of depth distributions of all three ^{24}Mg, ^{40}Ca, ^{52}Cr detected simultaneously for one of the *sweet* spots found.
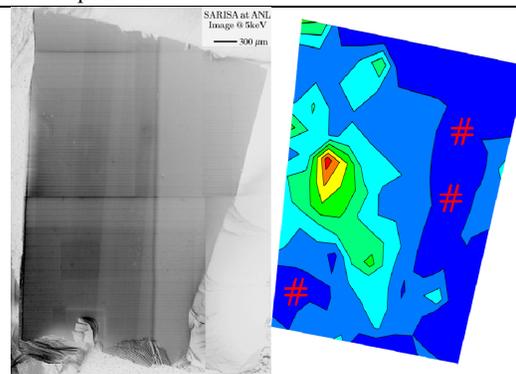

Fig.3. The principle of combined mapping/imaging by SNMS/SEM. The left side is the topographical view of a Genesis Si coupon in secondary electrons contrast obtained by SEM (vertical and horizontal lines are artifacts due to slight charging of the sample under the electron beam). The right side introduces a map of ^{24}Mg lateral distribution on the fragment surface. The chart of colors is as follows: blue is the lowest Mg abundance up to a maximum value colored in red. Places marked by # are the *sweet* spots analyzed by depth profiling.