SW Mg FROM GENESIS: NEW METHOD OF DATA REDUCTION AND IMPLICATIONS

A. J. G. Jurewicz[1], C. Olinger[2], D. S. Burnett[3], K. D. Rieck[2], and D. S. Woolum[4], [1]ASU/CMS P.O. 6004, Tempe AZ 85287 (Amy.Jurewicz@asu.edu), [2]LANL Los Alamos NM 87545, [3]GPS Caltech 1200 E. California Blvd Pasadena CA 91125 and [4]Physics, CSUF, Fullerton CA 92831

Purpose

To quantify the fluence of solar wind (SW) in DoS collectors. Fluences from Si collectors can then be compared with fluences from DoS to assess the risk of diffusive addition or loss of ions in silicon during radiation-induced segregation.

Background

Genesis Mission: Use & Collection of Solar Wind

A preponderance of evidence suggests that the composition of our solar nebula has been preserved (with a few exceptions) in the outer layers of the sun for almost 5 billion years. Thus, the solar elemental and isotopic composition is a baseline for modeling solar system formation.

To sample pristine solar material to accurately measure this compositional baseline, GENESIS, NASA's 5th Discovery Mission, collected solar-wind atoms in high-purity collectors for laboratory analysis *[1]*. Collection was successful, but an engineering design problem resulted in an inglorious landing. Scientists now need to work with fragments of collectors, many sized beautifully for SIMS.

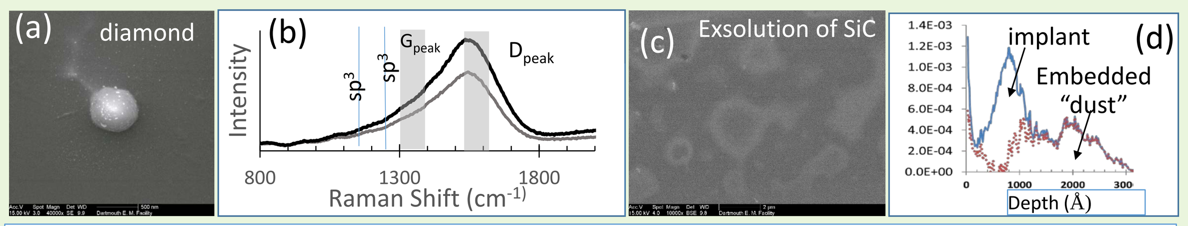
Genesis DoS Collectors: Retentive of SW, but Variable Properties Make Accuracy by SIMS Difficult

Sandia makes diamond-like carbon on silicon (DoS) for:

"electron-emitting materials for flat-panel displays, dielectrics for interconnects, diffusion barriers, encapsulant, and nonvolatile memories, and tribological coatings that reduce wear and friction in integrated micro-electro-mechanical devices" [2].

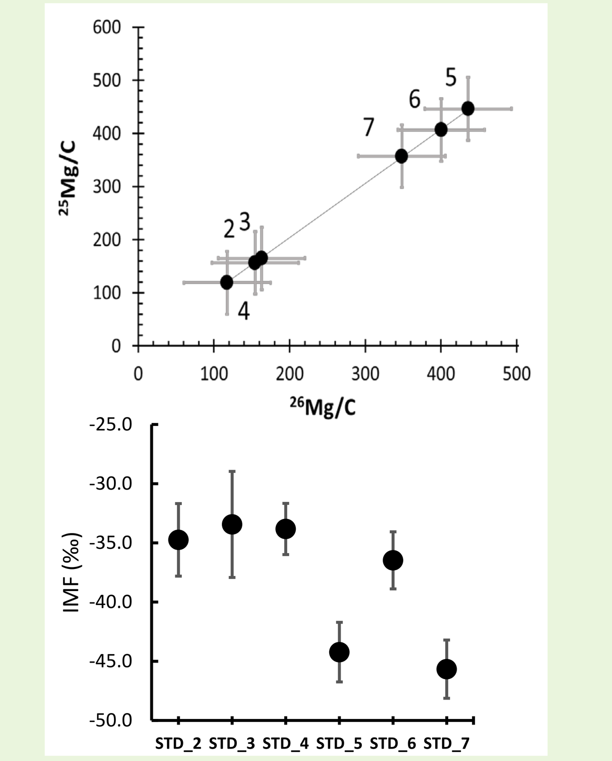
where high levels of structural and chemical homogeneity are not required.

In Genesis DoS wafers, the diamond-like carbon (DLC) coating collects solar wind, and silicon supports the coating. DLC is carbon (sp^3>sp^2 bonds) with minor silicon and trace matrix impurities. The texture and distribution of both carbon bonding and Si are variable, which causes issues for SIMS analysis *[3,4,5,6]*.

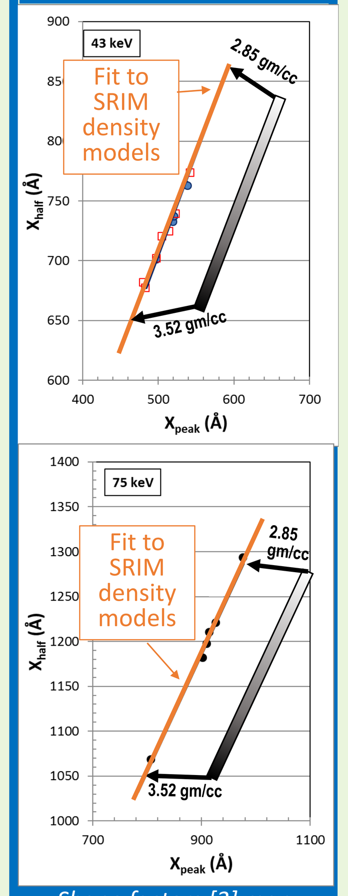


Variations in bonding and texture observed in Genesis DLC in fragments used in this study. (a) micro and nano-diamonds, (d) an embedded particulate of dust, and (c) exsolving SiC. Raman spectroscopy in (b) shows variations in bonding in the flight sample. Similar features and more have been seen in all samples of DoS analyzed [3,4,5,6].

Below: SIMS matrix effects on relative (Mg/C) ion yield (~4x) and instrumental mass fractionation (~10‰) in a DLC standard. Density variation (lower right) is modeled at 3.4-2.8 gm/cc. The diamond photo (lower left, (a)) is from the pit giving the high-density measurement. These data are from one SIMS session, constant conditions, and O_2^+ Ion beam [3].



Density variations in DLC



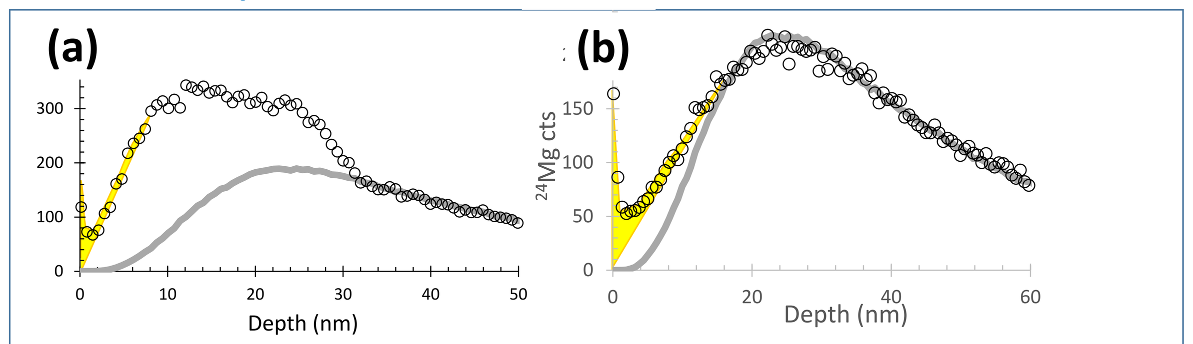
Shape factors [3] map model density to individual depth profiles, multiple Dos Fragments, multiple analysis session.

Quantifying Solar Wind Fluences from SIMS depth profiles into DLC

What is different about this data reduction technique?

Assumption:

SW does not segregate or otherwise diffuse after implantation in DLC; i.e., when: the depth of each duty cycle in the depth profile is known, and the density of the DLC is known, then the SW implant can be calculated using TRIM plus the distribution of energies determined from spacecraft data.



Example SRIM surface fits: (a) particulate at surface; (b) minor "thin film" surface contamination. Note: area in yellow is what past fits would have assumed was surface contamination.

Specifically, surface corrections use a SRIM model-fit of the SW depth profile that varies with density. In addition, standardization by minor ion implant now uses a correction for the (%-level), variable IMF. For details on SRIM and its applications, see www.srim.org and references therein.

Procedural Details

Collection of SIMS Data

Two pieces of DoS were analyzed on the Cameca 6F at ASU. (1) An IMF/RSF standard: DLC having an implanted $^{25}Mg/^{26}Mg$ at a ICPMS-calibrated ratio of 0.975, with a ^{25}Mg fluence of 8.2E13 at/cm² as determined by SIMS analysis of co-implanted silicon. (2) sample: Genesis DoS #20732,2. For details of standard calibration and SIMS conditions see *[3]*.

When sputtering with O_2^+ two matrix ions ($^{12}C^+$ and $^{12}C_2^+$) were sufficient to track variations in matrix bonding using $^{12}C^+/^{12}C_2^+$ because the intensity of $^{24}Mg^+/^{12}C^+$ varied strongly with Si content. Sputtering with Cs^+, changes the dynamics: there is less O to cause chemical etching or to influence ion yield. Although sputtering rate and ion intensity vary weakly with Si under Cs^+ sputtering *[6]*, a direct measurement a Si ion (e.g., Si, SiC) is needed.

Conversion to Depth Profiles

Our SIMS data was collected as ion yields as a function of time, but our SW data reduction used ion intensity as a function of depth. The primary beam was nominally stable, so a constant sputtering rate was assumed. Then, the times given in each duty cycle was converted to a depth scale by defining the ***depth of ion collection*** as (***time reported in duty cycle***)*(***total pit depth***)/(***total time of analysis***) *[3]*.

Background Corrections

Standards were run overnight, and the observed backgrounds were all <1 cps. However, for SW measurement, even a background of 0.5 cps (e.g., the tail of a particularly large C_2^+ peak) results in a %-level change in the calculated SW fluence. Our SW profiles did not measure the entire low-intensity tail of the SW implant (the deep <1% of SW). Although the truncated SW was negligible to the fluence, the final cps of the profile were higher than background by these SW counts. Therefore, a minimum and maximum value for the background was estimated and the difference was incorporated into the error. The surface-correction by SRIM fit was not significantly affected by an elevated background (illustrated in under Surface Corrections below). But non-uniform background (e.g., particles embedded at depth), could influence calculations if not observed and separately corrected.

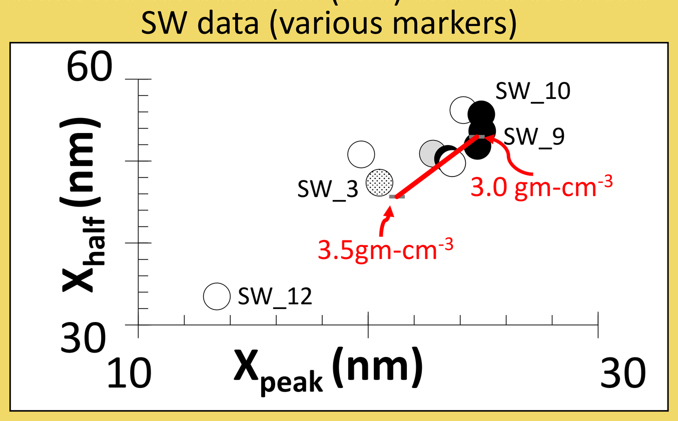
Surface Corrections

To fit the SRIM model to the data, first the local density of the DLC is estimated using the peak of the SW profile (see plot below left) which is relatively insensitive to background and small compositional changes (see schematics below right). The SRIM model corresponding to that density is then scaled to the correct intensity. Then, both density and intensity can be tuned to find a fit that minimizes the equation:

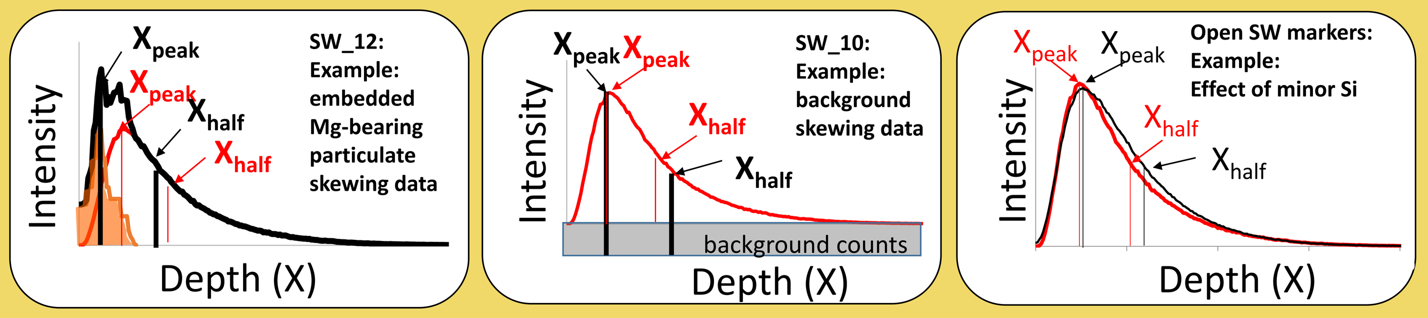
$$\Psi^2 = \Sigma((\text{SIMS-SRIM})^2)/\text{SRIM})$$

where the SIMS data is deeper than the surface contamination. The choice of data (the reasonableness of fit relative to the data and the choice of "uncontaminated" data) were be validated visually in plots. Illustrations of fits are given below as well.

SRIM model densities (line) and uncorrected SW data (various markers)

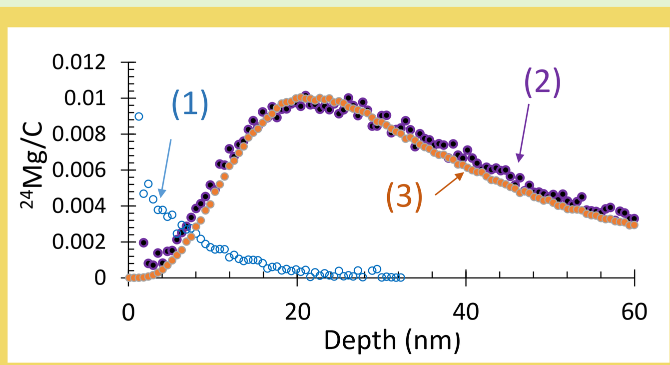


Below: Schematics of how particulates, uncorrected constant background , and small amounts of Si in DLC effects the shape of the SW data. This accounts for some of the scatter of SW vs. SRIM-calculated density in the plot at left.



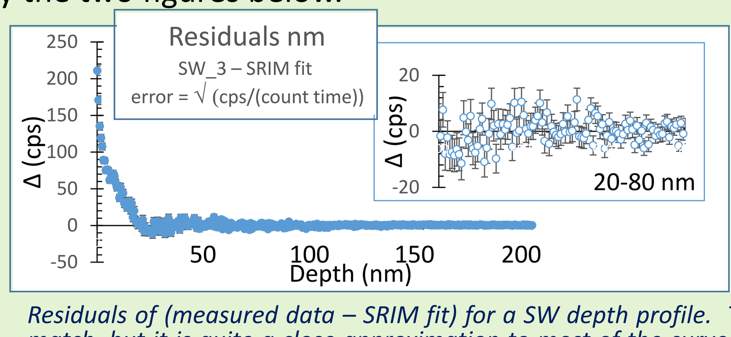
Legend: SRIM (red curve); measured data (black curve – under red if not observed); X_{peak} and X_{half} (depth of peak and depth after peak to half height [3] color coded to SRIM and data); brown ("particulate").

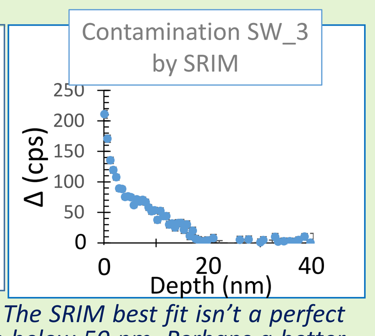
Reasonableness of using SRIM to fit the depth profile in DLC is illustrated by the two figures below.



Profiles (left): (1) surface contamination profile measured for a standard and scaled in density and intensity; (2) measured SW data (SW_3) from which (1) has been subtracted; (3) SRIM fit for the measured SW data.

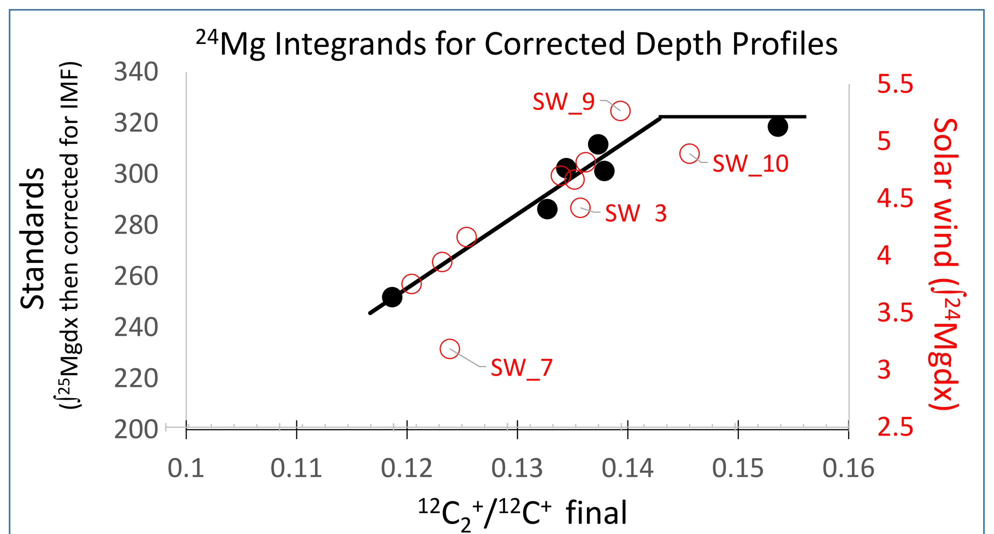
(3) And (2) "match" because, in this instance, the surface contamination of both standard and SW collector can be modeled as a thin film.





Residuals of (measured data – SRIM fit) for a SW depth profile. The SRIM best fit isn't a perfect match, but it is quite a close approximation to most of the curve below 50 nm. Perhaps a better fit could be obtained by trying to account for ion mixing by the SIMS primary ion beam. The deviation from SRIM in the first ~30 nm is the estimated surface contamination.

Results



In DLC, both integrals and IMF vary with the matrix bonding and composition. To match the SW analysis with a matrix-appropriate standard, the $^{12}C_2^+/^{12}C^+$ ratio was used*. Standards are precisely corrected with respect to the contamination and background; the corrections to the trace SW are not as precise. SW analyses 7, 3, and 10 probably have an insufficient background correction (the tail of $^{12}C_2^+$); although shifted to the right of the calibration curve, the corresponding standard is correct. Theoretically, SW_ 9 could be over corrected for background $^{12}C_2^+$; but, more likely, a small terrestrial particulate is present in the DLC.

* The sloped portion of the calibration curve primarily reflects the changing Si content; the flat portion reflects variations in electrical conductivity (i.e., the voltage of the sample is changing as sp^3 is an excellent electrical insulator) *[3]*. This parametrization (based on an O primary) will change with SIMS conditions and must be calibrated for each SIMS session.

$$F_{SW} = (F_{STD})/(\int^{24}Mg^*/C)_{STD} \times (\int^{24}Mg/C)_{SW}$$

where F= ^{24}Mg fluence, $\int^{24}Mg^*/C)_{STD} = (\int^{25}Mg^*/C)_{STD}$*(correction for IMF_{std}).

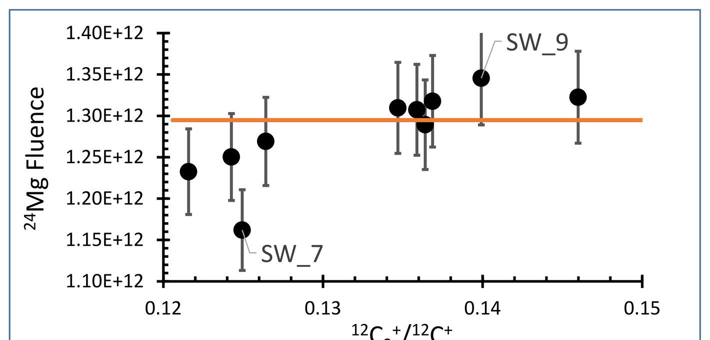
analysis	Estimated ^{24}Mg Fluence (F_{sw})	1σ error in Surface + bkg fits	Δ new correction *
SW_2	1.31E+12	1.3%	4.5%
SW_3	1.29E+12	1.5%	5.9%
SW_5	1.32E+12	1.3%	4.7%
SW_6	1.31E+12	1.2%	5.0%
SW_7	1.16E+12	1.3%	6.6%
SW_8	1.27E+12	0.8%	6.8%
SW_9	1.35E+12	0.9%	5.8%
SW_10	1.32E+12	1.9%	5.6%
SW_11	1.25E+12	1.5%	7.6%
SW_12	1.23E+12	1.6%	36.0%
Average	1.28E+12 at/cm² (1σ = 4.2%; 1 SE=1.3%)		

* % change over entire profile, old method – new method of surface correction.

Total Mg fluence from DoS:

$$F_{sw(total)} = F_{sw(24Mg)} /0.78 = 1.64(0.07)E+12$$

Discussion with Implications



Individual ^{24}Mg fluence results vs. $^{12}C_2^+/^{12}C^+$ (error is 4.2%). Fluences at lower $^{12}C_2^+/^{12}C^+$ tend to be ~1σ lower than the ^{24}Mg measured in Si (horizontal line). Depressed ^{24}Mg at low $^{12}C_2^+/^{12}C^+$ may be due to ^{24}Mg-H as standard was anhydrous.

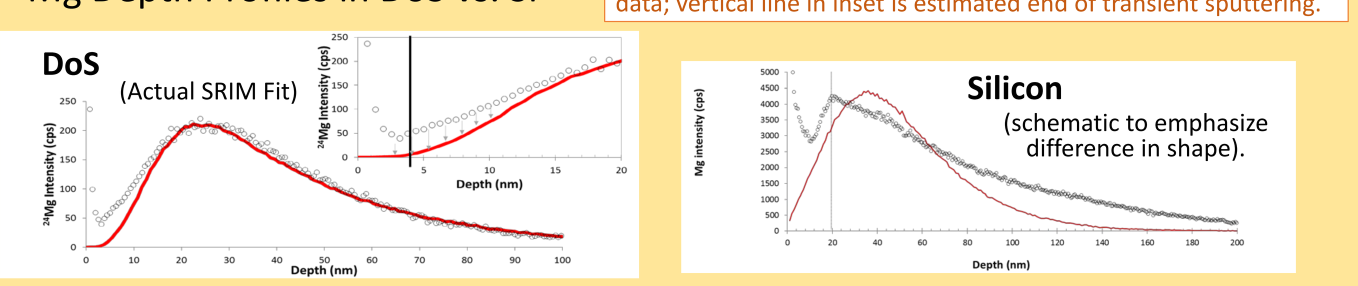
The 4.2% 1σ error on the ^{24}Mg fluence is in part due to the 1%-2% error in the background correction, which can be mitigated by significantly longer analysis times. However, some of this error may be due to the standardization. There was no H implanted into the standard, but another standard analyzed under these analytical conditions showed that ^{24}Mg-H was present at only ~3% *[3]*. However, the 3‰ was determined on a DLC matrix with a high $^{12}C_2^+/^{12}C^+$, but the $^{12}C_2^+/^{12}C^+$ values are inversely proportional to the Si-concentration [3]. Under an O_2^+ primary beam, the Si in the DLC decreases the sputtering rate and increases the ion yield by oxidizing the Si (thus adding O to the matrix) *[3]*. So, the slightly low fluences at low $^{12}C_2^+/^{12}C^+$ values (left) could be explained if ^{24}Mg-H formation increases with O in the DLC. Tracking Si- or SiC- related ions might be useful for parameterizing this effect.

The total Mg fluence from DoS (1.64±0.07E+12) is within 1σ of the Mg fluence measured in Si equal to 1.66±0.02 x10¹²/cm² *[7]*. So there is no loss or gain of Mg from either DoS or Si collectors. This result is significant because Si shows radiation-induced segregation (below).

Because radiation-induced segregation *[8]* indicates diffusion, there is potential for surface ions to diffuse into the collector or loss of SW to the surface through the zone of radiation damage. Thus, ideally, fluences from silicon need verification from another collector material *[9]*, as illustrated by a measurement of SW Na (below). In (a), SW Na data *[10]* from two different laboratories give fluences from Si at or above the predicted 1.0E+11 at/cm². In contrast, all but one SW Na measurement in DoS give significantly lower fluences. In (b), using the new correction techniques, that one fluence (and in Si) is shown to be ~2x too high.

^{24}Mg Depth Profiles in DoS vs. Si

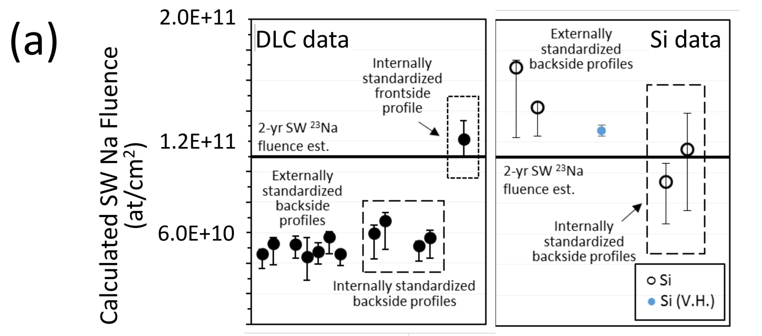
Legend (Both plots): red line = SRIM fit; markers = raw SIMS ^{24}Mg data; vertical line in inset is estimated end of transient sputtering.



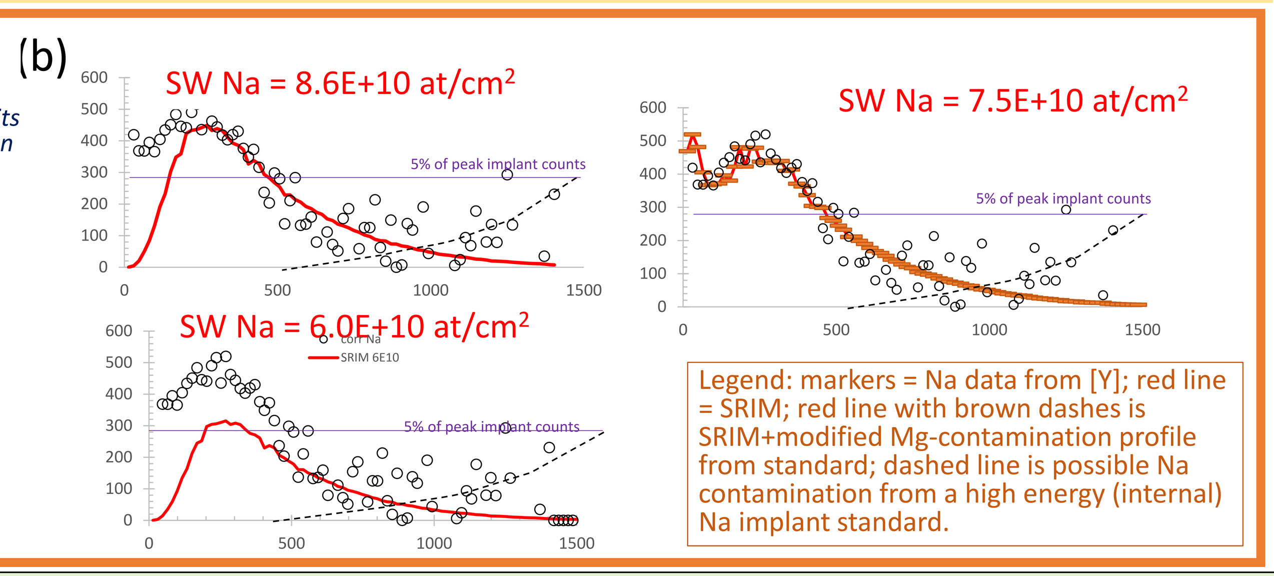
Raw data vs. SRIM model for front side depth profiles into Genesis SW collectors -- DoS (left) and Silicon (right). DoS retains the shape of the predicted SW profile to high fidelity; conversely, silicon exhibits radiation-induced segregation, a diffusive process.

Data from [10] showing discrepancy between Na Fluences from Genesis DoS and Silicon Collectors, and how this new data reduction technique may reconcile which is correct. In (a), the front-side profile is the only fluence from a DoS collector consistent with Si. (b) gives three potential fits for that data showing it is consistent with backside DLC, not Si. The two on the left are SRIM fits using a portion of the tail; the fit on the right is the sum of (stretched) Mg contamination added to a Na SRIM fit.

(a)



(b)



Legend: markers = Na data from [Y]; red line = SRIM; red line with brown dashes is SRIM+modified Mg-contamination profile from standard; dashed line is possible Na contamination from a high energy (internal) Na implant standard.

Acknowledgements and References

SIMS analysis at Arizona State University National SIMS facility, supported by EAR0622775. This work initiated using Genesis mission funds, including JPL sub-contract #1354958. Subsequent work was supported by NASA LARS Grants # NNX14AF26G, 80NSSC17K0025, NNH15AZ25I and NNH15AZ67I.

[1] Burnett et al. (2003) The Genesis Discovery mission: Return of solar matter to Earth, Spa Sci Rev 105: 509-534. [2] Siegal et al. (1996) Diamond and Diamond-like Carbon Films for Advanced Applications, SANDIA REPORT SAND96-0516 - UC-404, 42 pp. [3] Jurewicz et al. (2017) Understanding heterogeneity in Genesis diamond-like carbon film using SIMS analysis of implants. J Mater Sci DOI 10.1007/s10853-017-1267-3 (Open Access Paper).[4] Jurewicz et al. (2017) Genesis DoS Wafers: What Every SIMS Analyst Needs to Know Before Measuring Solar Wind. *48th LPSC. Abs #2120* (E-Poster); [5] Jurewicz et al. (2016) New Constraints on SW Mg Isotopes from Understanding Genesis DoS Collectors, with Implications. *47th LPSC. Abs #2350*. [6] Jurewicz et al. (2018) Raman as a Tool for Quantifying SIMS Analyses of Genesis DoS Collectors. *49th LPSC. Abs #2058.* [7] Burnett et al. Fe and Mg in the solar wind. in preparation. [8] King et al. (2008) Investigation of radiation enhanced diffusion of magnesium in substrates flown on the NASA genesis mission Applied Surf. Sci. 255 1455–1457. [9] Burnett et al. (2019, in press) The future of Genesis Science. Meteor. Planet. Sci. [10] Rieck, K.D. (2015) Solar Wind Sodium and Potassium Abundance Analysis in Genesis Diamond-on-Silicon and Silicon Bulk Solar Wind Collectors. Thesis. Arizona State University.