

INTERNALLY STANDARDIZED MEASUREMENTS OF SOLAR WIND SODIUM AND POTASSIUM IN GENESIS DIAMOND-LIKE CARBON COLLECTORS. K. D. Rieck (kriec1@asu.edu)¹, A. J. G. Jurewicz¹, D. S. Burnett², and R. L. Hervig¹; ¹School of Earth & Space Exploration, Arizona State University, Tempe, AZ, 85287-1404 USA, ²Geological & Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA.

Introduction: We present the first preliminary internally standardized measurements of bulk Solar Wind (SW) ²³Na and ³⁹K in Genesis B/C (bulk SW) array diamond-like-carbon (DIC) on Si (DoS) collectors. The internal standards were implanted from the backsides of the DIC wafers. We also present newly normalized measurements for SW ²³Na and ³⁹K in both DIC and Si collectors. All SW Na and K abundances were measured with secondary ion mass spectrometry (SIMS), and backside depth profiling (BDP) techniques.

Background: SW samples the solar photosphere, and the solar photospheric composition is a proxy for the protoplanetary disk that ultimately formed the planets. Thus, a Genesis baseline has a better founding in theory than a CI chondrite baseline, and has potential for much more accurate numbers for volatile or chemically mobile elements (e.g., Na and K [1]).

However, SW formation causes elemental fractionation relative to the solar photosphere for elements with high first ionization potentials (FIP) and long first ionization times (FIT) [2, 3]. Low FIP, short FIT elements (e.g., Na and K) likely show minimal to no fractionation relative to photospheric abundances [1], but this hypothesis needs to be tested.

SW Na and K abundances are of particular interest. Their FIP and FIT values will help to define the details of SW fractionation for correcting to photospheric composition. Na and K abundances from spacecraft data have uncertainties of up to a few tens of percent [4], but Genesis SW samples offer the opportunity to obtain accurate and precise measurements.

Backside Approach: Traditionally, SIMS and RIMS analyses involve depth profiling from the front/top/polished sample surface of a sample. However, this approach is not ideal for Genesis samples, where surface contamination and analytical transient artifacts interfere with the SW signal [5, 6]. We mitigate these interferences by using backside depth profiling techniques, which have already been successfully applied to the measurement of minor SW ions in Genesis Si [7, 8, 9] and DoS collectors [10, 11]. We note: BDP of SW through DoS is a new technique, and Genesis-specific issues preclude commercial thinning methods. Specifically, to mitigate incorporation of contaminants in the near-surface of the DIC collectors, an annealing step was skipped in the flight material. Accordingly, the DIC film is extremely fragile, making removal of the Si substrate for BDP difficult. To date, the most gentle and efficient approach for removal of

the Si has been XeF₂ etching, a technique under development at ANL [10] that removes the Si-backing while leaving the ~1 μm thick DIC mostly intact.

Backside Ion-Implantation: Once a DoS sample has been thinned until only DIC remains, the new front surface (previously the C-Si interface) can be implanted with a reference fluence without interfering with SW analysis, even for monoisotopic elements like Na. Analyzing the standard and SW fluences within a single crater is an efficient use of time and also ensures similar analytical conditions for both profiles.

Procedures: One B/C array DoS sample (60867), a well-annealed blank DoS wafer, and a DoS implant standard (Leonard Kroko, Inc.) were mounted face-down on graphite. Another B/C DoS array sample (60407) was mounted face-down on GaAs, which was in turn mounted on a graphite planchet for structural support. The purpose of these two substrates was to test which would best protect DIC film. The four wafers were etched with XeF₂ at ANL until all the backing-Si was removed. Some residual stresses in the diamond layer resulted in localized topographic highs (ridges and mounds) in both Genesis samples, regardless of substrate. Residual dust from the etching process was removed with compressed air. Acetone was an effective cleaning agent, but caused thermal stresses that eventually produced linear fractures and/or dendritic folds in the DIC. The etched samples, plus blank Si and DoS wafers, and NIST glasses were mounted together and underwent ²³Na and ⁴¹K ion implantations (Leonard Kroko, Inc.) to create new external and internal standards that we intend to absolutely calibrate.

We did not implant our existing (~1 μm) thinned Si flight wafer, or our Si implant from F. Stevie, as the implant conditions suitable for DoS implants would cause the reference ions to penetrate too deeply into Si, and interfere with the SW or standard signals. If needed, we may make internal standards in Si using thicker thinned samples.

Two SIMS instruments were used: (1) a Cameca IMS 6f at ASU, and (2) a Cameca IMS 7f-GEO at Caltech. Primary O₂⁺ helped maximize depth resolution and secondary ionization in both DIC and Si. The impact energies were 3 and 4 keV/nucleon at Caltech and ASU, respectively. We used the highest-feasible mass resolving power, for the ions of interest. Color changes in the sample during sputtering indicated break-through at the collector/epoxy interface. Sub-surface particulates and contaminants in annealing layers in the DIC

were observed as localized, intermittent peaks in Na and K signal. When these artifacts interfered significantly with implant or SW signal, that analysis was discarded, and a new analysis begun elsewhere. The Na and K ion signals were integrated and normalized to a matrix species (^{12}C for DIC, ^{28}Si or ^{30}Si for Si) to correct for variations in primary current. Relative sensitivity factors from the reference implants were used to quantify the SW measurements.

Results: The internal implant standard in DIC could be easily distinguished from SW and, in most cases, from surface contamination. All previous Na and K SW measurements were re-calibrated to the same standard implants. For the first time, we could put DIC and Si SW on a relative scale, independent of the stated nominal values of the reference implants (Table 1). Results are in Figure 1.

Discussion: Our previous data [11] showed a discrepancy in Na abundance between DIC and Si. Resolving this was the primary motivation for using internal standards. We also intercalibrated the Na in our previous (Si) standards and found significant discrepancies among reported nominal values (Table 1). Control Si and DoS were co-implanted with thinned Genesis DIC, such that the implanted Na and ^{39}K fluences would be identical between substrates. When Na or K SW fluences are calculated using this uniform $\sim 2\text{e}12$ atoms/cm 2 standard, any error in the implant fluence cancels out in the *relative* fluence of DoS and Si although not in the absolute fluences.

Despite these efforts our discrepancy in the relative SW Na abundance between DIC and Si persists. Based on solar abundance estimates [12], an average SW proton flux of $\sim 3\text{e}8$ cm $^{-2}$ s $^{-1}$, gives Na and ^{39}K fluences of $\sim 1.1\text{e}11$ and $\sim 6.6\text{e}9$ atoms/cm 2 , respectively, (assuming normal isotopic abundances) [1]. Although our Na data from Si closely approaches the predicted value, corroborating the results of [9], the Na in DIC remains low by $\sim 2\text{-}3\times$. Scatter for SW K in DIC is large in part because the variable background from the annealing steps are nontrivial relative to the SW signal. However, internal standardization suggests that there may also be a discrepancy in ^{39}K fluence between DIC and Si. Again, SW ^{39}K in Si is close to the predicted SW fluence, while SW ^{39}K in DIC appears lower.

Are these differences between DIC and Si real, or are they the result of some previously unconsidered analytical artifact? Pre-flight research indicated that Na and K were more likely to diffuse in Si than in DIC. There are no obvious discrepancies in the shapes of the measured SW profiles compared with theoretical models, and the peaks marking annealing layers are generally sharp. We find it unlikely that this large difference could be caused by processing errors: three authors did

preliminary reduction of the backside Na raw data independently and differences in results were small. Perhaps a co-implanted SW element (e.g., H?) changes the RSF? The existence of effects caused by SW exposure can be tested, in part, using H-implants.

Future work: The next step will be to precisely calibrate our standards using Na and K implants superimposed on calibrated levels in NIST glass, or by using a high dose implant calibrated with RBS. We will use this information to anchor our SW values. We will also check H-implanted standards to see if Si and DIC converge. Once defined, we will apply the Na and K results to studying the relative effects of FIT and FIP on SW generation.

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References: [1] Burnett D. S. et al. (2003) *SSR*, 105, 509-534. [2] Bochsler P. (2000) *Rev. GeoPhys.*, 38, 247-266. [3] Bochsler P. (2007) *Astron. Astrophys. Rev.*, 14, 1-40. [4] von Steiger R. et al. (2000) *JGR*, 105(A12), 27217-27238. [5] Burnett D. S. et al. (2007) *38th LPSC*, #1843. [6] Heber V. S. et al. (2010) *41st LPSC*, #2234. [7] Veryovkin I. V. et al. (2012) *43rd LPSC*, #2296. [8] Heber V. S. et al. (2012) *43rd LPSC*, #2921. [9] Heber V. S. et al. (2014) *45th LPSC*, #1203. [10] Veryovkin I. V. et al. (2013) *44th LPSC*, #2247. [11] Rieck K. D. et al. (2013) *44th LPSC*, #3030. [12] Anders E. and Grevesse N. (1989) *Geochim. et Cosmochim. Acta.*, 53, 197-214. [13] S. Smith, *oral communication*.

Table 1. Intercalibration of Na-in-Si reference "standards."

	% Deviation from Nominal Fluences*			
	Relative to Nominally Correct Si standards			
	F. S. 194	CEA 3140	V. H. 2.2 & 2.4	R. & J. 2e12
F. S. 194	0	29	41	8
CEA 3140	-23	0	9	-17
V. H. 2.2 & 2.4	-29	-8	0	-23
R. & J. 2e12	-7	20	31	0

* Nominal Na fluences (atoms/cm 2) – F. S. 194: 1e14, CEA 3140: 5e13, V. H. 2.2 & 2.4: 1e13, R. & J. 2e12: 2e12.

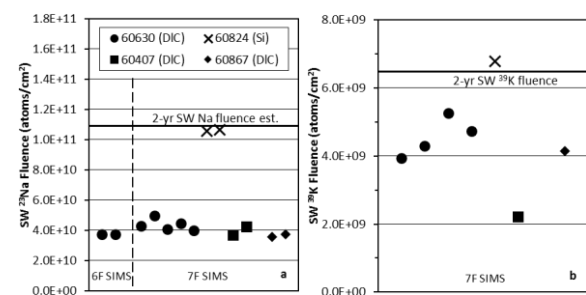


Figure 1. SW ^{23}Na and ^{39}K measured by BDP, where \blacksquare and \blacklozenge are internally standardized. Solid lines mark predicted SW fluences. a) ^{23}Na data are relative to CEA 3140, accurate to $\pm 10\%$ [13]. b) ^{39}K data are relative to a nominal $2\text{e}12$ atoms/cm 2 implant, currently undergoing recalibration.