GENESIS SOLAR WIND ALUMINUM ABUNDANCE: CREATING AN ALUMINUM STANDARD FOR SIMS ANALYSES.

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Introduction: The Genesis mission was designed to accurately measure the composition of the solar wind (SW). The sample return capsule crashed in the desert, fragmenting and contaminating samples. Surprisingly, one of the most difficult tasks in measuring SW from the Genesis samples is calibrating standards for SIMS (secondary ion mass spectrometry) measurements. Precise depth profiles of solar wind (SW) Al are available from backside depth profiling [1] of Genesis silicon collectors. Calculation of the solar wind Al fluence (atoms/cm^2) from these is based on a laboratory implant standard, but nominal implant fluences are only accurate to about ±20%, so independent calibration is required. This can be done as described in [2] and illustrated in Fig. 1, which shows a depth profile for San Carlos olivine (SCJ) using the Caltech Cameca 7f Geo (O$^-$ primary ion, 25 µm spot size, 200 µm field aperture, 75 µm raster and 3000 mass resolving power to resolve $^{27}Al^+$ from $^{26}MgH^+$). If the olivine Al content (deep part of profile) is known, the implant fluence can be calculated, or vice versa [2]. Control pieces of Si mounted beside the olivine during implantation receive the same fluence, becoming primary standards for analysis of Genesis Si samples.

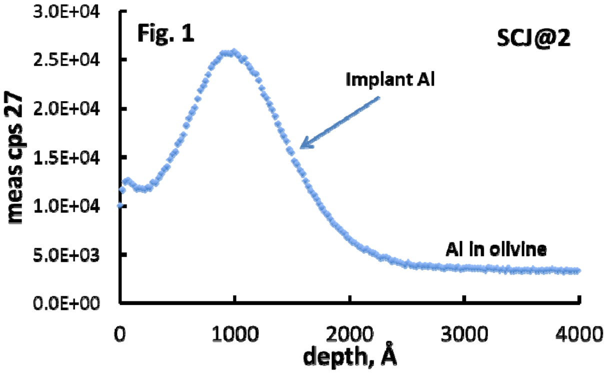


Fig. 1

San Carlos Olivine: Accurate electron microprobe (EMP) analyses of olivine Al at the ≈100 ppm level should be possible. In practice, many significant problems were encountered, whose mitigations were described in [3].

A standard with percent level Al, "enstatite 25-25," was used for our analyses. It was carefully characterized using primary standards prior to use.

For EMP analyses of San Carlos crystal SC3 we cleaned eleven 100 x 200 µm areas using the SIMS to remove Al surface contamination [3; Fig. 2]. SC3 was analyzed in two separate microprobe runs, using a 50 x 100 µm rastered beam, 100 nA current, 10 minute count time, and 4 background points plus the Al peak, measured sequentially. In the first session the enstatite standard was analyzed under the same conditions, followed by three of the San Carlos points, the standard, 2 San Carlos points and the standard. The second session followed a similar pattern, except all 11 SIMS-cleaned spots were analyzed, with the enstatite standard run every 2 or 3 points. There were 5 areas analyzed in both sessions.

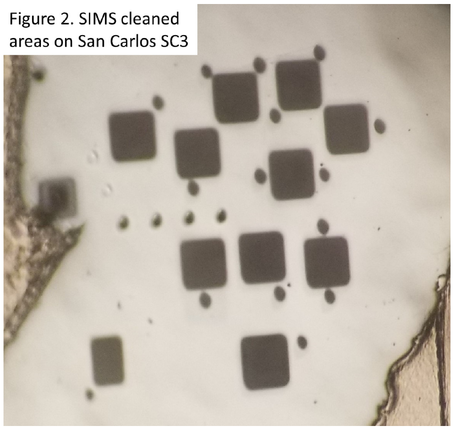


Figure 2. SIMS cleaned areas on San Carlos SC3

With our optimized analytical conditions, 13/14 analyses gave the same counting rate within 1 σ counting statistics errors with an average of 69.3 ppm Al (Fig. 3). Earlier analyses prior to optimization showed much more scatter, which, although not completely understood, may be due to surface contamination as well as to systematic errors [3]. The SC3 analyses shows no evidence for effects of Al surface contamination.

SIMS Analyses: San Carlos olivine SCJ was im-

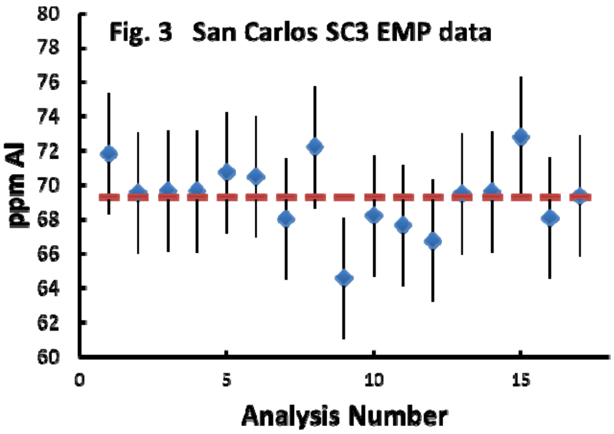
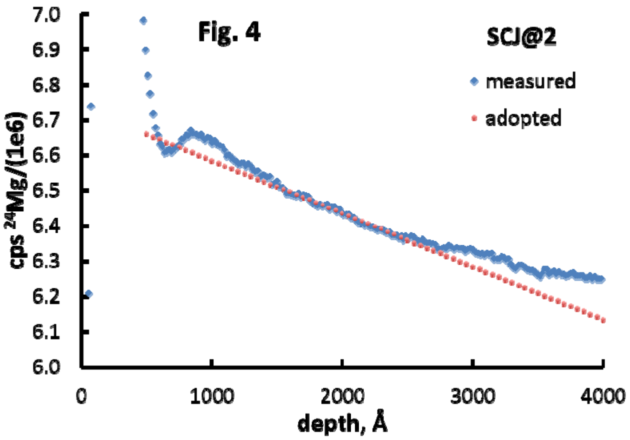


Fig. 3 San Carlos SC3 EMP data

planted with $5x10^{14}/cm^2$ Al at 80 keV (**Fig. 1**), equivalent to about 15-20 ppm in an EMP analysis, which is not negligible. Therefore, post-implant EMP analysis of SCJ cannot easily be used to calibrate the implant as an internal standard as shown in Fig. 1. Aluminum rich inclusions are also present in 2 out of 5 SCJ SIMS profiles. However, the homogeneous and well-calibrated EMP analyses enable SC3 to serve as an external standard to calibrate the SCJ Al implant fluence [1]. Two depth profiles of SC3 were bracketed between pairs of SCJ implant profiles. The SC3 Al/Mg ratios deeper than 2000Å agree to better than 0.3% and combined with the EMP Al concentration define a relative sensitivity factor (RSF) [1] with a 1 σ error of 2.2%.

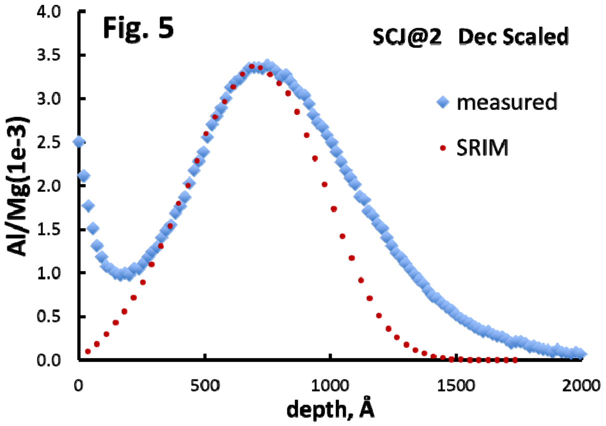
Quantitative SIMS analyses must be done under steady state conditions. Oscillatory transient structure was seen from the surface down to 1200-1500Å of all olivine ^{24}Mg, ^{30}Si, and ^{56}Fe profiles, but this depth range overlaps a significant part of the SCJ Al implant profile (Fig. 1). As shown in **Fig. 4** for SCJ Mg, at depths smaller than 600Å a large oscillatory transient is observed, but in the 600-1400Å range, the size of the Mg transient oscillations is small (<1%) and the Mg counting rate can be accurately represented by a linear extrapolation from 1400Å (red dashed line).

Deeper than 1400Å, counting rates decrease monotonically because of charging. The SCJ fluence is the product of the RSF and the (implant Al)/Mg depth integral [1]; this assumes that the charging variations in the Al/Mg counting rate ratios cancel. With one exception, constant Al/Mg ratios are observed after sputtering through the SCJ implants or beyond transients in the unimplanted SC3 profiles. The exception, profile SCJ@5 is also much broader and appears to have much larger amounts of charging.



A "surface correction" for the Al implant fluence lost in the transient region below 600Å is based on a scaled theoretical SRIM profile (**Fig. 5**). The predicted SRIM peak depth is about 33% higher, but when normalized to the measured profile, the data between 600Å and the peak are well described, although the measured peak is significantly broader overall. The contribution of the implant fluence from the surface to 600Å is calculated from the scaled SRIM profile and added to the integral of the measured (implant Al)/Mg data deeper than 600Å to give a total fluence. For the adopted SCJ profiles the surface corrections range from 21 to 29%.

Al fluence of SCJ implant. Rejecting the anomalous SCJ@5 profile, the remaining 3 SCJ profiles give fluences of (units of $10^{14}/cm^2$) 4.78, 4.36, and 4.88. The estimated precision of a single analysis is 4.8%. The measured fluence standard deviation is higher, 6.0%, which we adopt as the precision of the SCJ fluence, giving $4.67 \pm 0.30x10^{14}/cm^2$ as the calibrated fluence of the SCJ implant where the quoted error also includes a 2.2% contribution from the error in the RSF. The measured fluence is within 1 σ of the nominal $5x10^{14}$ atoms/cm^2.



Discussion: This work documents that an accurate calibration of an implant standard for the Genesis Al fluence is possible. The large surface corrections for the SCJ profiles can be greatly reduced by using a higher implant energy (factor of 2 is possible) shifting almost all of the implant from the Mg transient region. An error of 3.5% (1 σ) in the accuracy of the standard implant fluence and a total error of 5% in the solar wind Al fluence and 6% in the solar wind Al/Mg appears feasible. For comparison, the photospheric Al/Mg, among the most precise, has an error of 12%. Our work is potentially valuable for EMP trace element analyses in general.

References: [1] Heber V. S. et al. (2014) 45th LPSC, Abstract #1203. [2] Burnett, D. S. et al. (2015) *Geostandards and Geoanalytical Res. 39*, 265-276. [3] Hofmann A. E. et al. (2018) 49th LPSC, Abstract #1526.