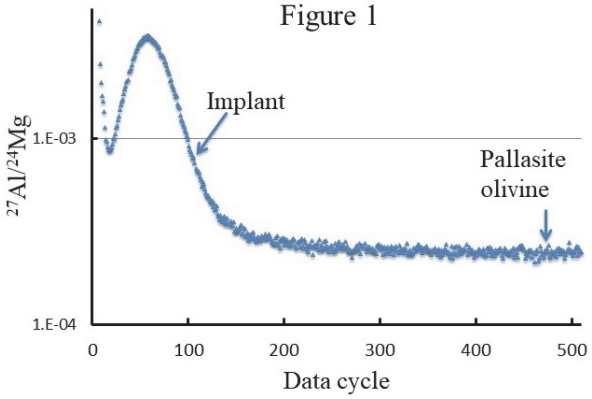
GENESIS SOLAR WIND ALUMINUM ABUNDANCE: CHALLENGES WITH ELECTRON MICROPROBE ANALYSES OF Al IN OLIVINE. A. E. Hofmann[1,2], J. M. Paque[1], D. S. Burnett[1], Y. Guan[1], A. J. G. Jurewicz[3], C. Ma[1] and G. R. Rossman[1], [1]California Institute of Technology, Div. of Geol. and Planet. Sciences, Pasadena, CA 91104. [2]Jet Propulsion Laboratory, California Institute of Technology, 488 Oak Grove Drive M/S 183-301, Pasadena, CA 91107, amy.e.hofmann@jpl.nasa.gov. [3]SESE, Arizona State University,Tempe, AZ, 85287.

Introduction: The Genesis mission was designed to accurately and precisely measure the composition of the solar wind (SW). The sample return capsule crashed in the desert, fragmenting and contaminating samples. Yet, surprisingly, one of the most difficult task in measuring SW from the Genesis samples is calibrating the SIMS (secondary ion mass spectrometry) measurements. Precise depth profiles of the solar wind aluminum 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 certified nominal implant fluences are only known to about ±20%, so independent calibration is required. This can be done as described in [2] and illustrated in Fig.1, which shows a SIMS depth profile for Imilac pallasite

Figure 1

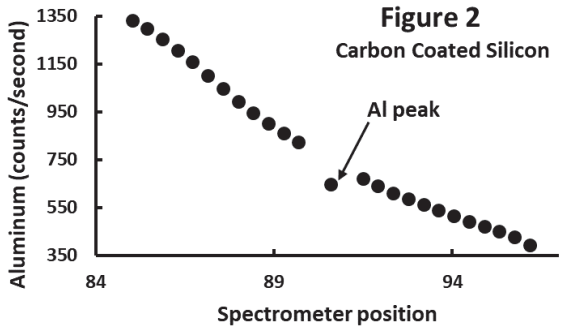


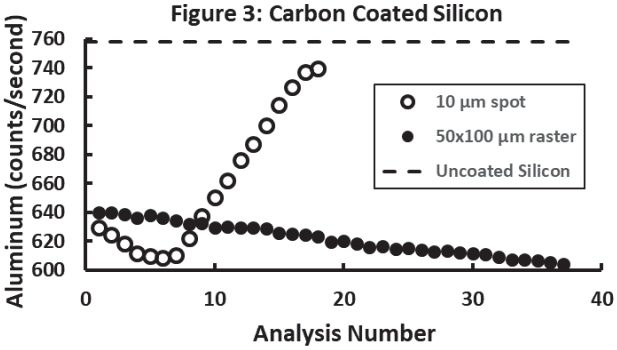
olivine using the Caltech Cameca 7f Geo with a 3000 MRP to resolve $^{27}Al^+$ from $^{26}MgH^+$. If the olivine Al content is known, the implant fluence can be calculated, or vice versa [2]. Control pieces of Si mounted beside the olivine during implanting receive the same fluence and serve as a primary standard for analysis of Genesis Si samples. 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 are described here. Our work is potentially valuable for EMP trace element analyses in general.

Surface Contamination: SIMS analysis indicates that significant Al surface contamination is ubiquitous, which is usually ignored for EMP analyses. However, a 1 µm grain of alumina contributes 10% of the atoms of Al in a 10x10x5 µm volume of olivine sampled in a typical EMP analysis (and is detected with higher efficiency); consequently *surface contamination is a serious problem for EMP analysis of Al in olivine*.

XPS analyses: Using the X-ray photoelectron (XPS) spectrometer at the Caltech Joint Center for Artificial Photosynthesis, we collected spectra from multiple locations on a cleaned piece of pure sapphire as well as on a single San Carlos olivine grain that had been polished with a 0.25 µm diamond slurry and then cleaned via ultrasonication in DI water followed by methanol. Above-background counting rates for Al 2p electrons at the cleaned sapphire surface were of order 2 x 10^4 cps. Counting rates for Al for 500 x 700 µm areas on the cleaned olivine surface were detectable—of order 300–700 cps, uncorrelated with respect to location on the sample. The Al 2p peak was visibly resolvable from the background at all 12 analysis locations, indicating the persistence of Al contamination on a nominally clean surface at levels that would be important for EMP analysis. Ion beam cleaning olivine surfaces of contamination and verifying cleanliness is possible using a SIMS instrument, and this approach has been adopted.

Systematic Instrument Errors: A SIMS-cleaned area on an olivine grain must be C-coated for EMP





analysis. To demonstrate that no new Al contamination was introduced by the C coating, we SIMS-cleaned a 400x400 μm area on Si metal and recoated with C. Surprisingly, an analysis (Fig. 2) of the bremsstrahlung background (12 points on each side of the peak) around the position of the Al K alpha peak showed a decrease in counting rate at the Al peak wavelength! The origin of this anomaly was revealed by a test in which repetitive counts at the Al peak on the same spot [Fig. 3: 10 μm spot data]. Because of software requirements, the counting rate was first measured at the Al peak, then measurements were made at the lowest spectrometer background setting, progressively stepping to higher spectrometer positions. To get a low Al detection limit, an electron beam current of 100 nA and 10 minute counting times were used. By the time on Fig. 2 when the background measurements crossed the Al peak position (the 13th analysis point), the counting rate was on the rising part of Fig. 3, giving the negative anomaly. In Fig. 3, we interpret the initial decrease as due to C deposition from the 100 nA electron beam, but as the spot heated up the C coat was burned away (literally; by residual gas oxidation) and the counting rate eventually approached that of silicon without a carbon coat (dashed line on Fig. 3). A complication is that the 16% decrease in counting rate is far larger than expected based on literature Al Kα absorption coefficients. A simple mitigation was the use of a lower current density (50x100 μm raster, Fig. 3). Analyses in the C removal region (beyond analysis 6 on Fig. 3) can be avoided, but given the low signal/noise for Al in olivine at 100 ppm (about 1/10), the small deposition decrease with the large beam spot is significant and cannot be avoided, but an accurate correction can be made.

The trends in Figs. 2 and 3 are reproducible, but there are other instrumental counting rate drifts beyond beam current variations (routinely corrected) that are important in low signal/noise measurements. On olivine, these are assessed by tracking the background counting rates on different spots, where any C deposition effects are constant. These are due to any number of instrumental or environmental conditions (e.g., room temperature). Interpolation can correct for small uniform drifts.

Results: Fig 3 shows there are limits on beam current density and counting times for EMP trace element analysis. For our olivine analyses we compromised on a protocol: a) 100 nA current; b) 5 minute counting times (peak and backgrounds); c) two point linear background correction (justified by long wavelength scans, allowing for drifts). For about 100 ppm Al, this gives 4% one sigma counting statistics errors per point with 10-15 points comfortably analyzed in a given session.

A mount of four ~5 mm-sized grains of San Carlos and similar grains from 3 pallasites have been studied. Three of the 4 San Carlos grains have 50-60 pm Al, whereas grain SC4 has around 130 ppm. With our optimized analytical conditions, 13/14 analyses gave the same counting rate within 1 sigma counting statistics errors. The anomalous analysis was 3 sigma low, which may be heterogeneity. Earlier analyses prior to optimization showed much more scatter, which, although not completely understood, may be due to surface contamination as well as to the above systematic errors. The precision of these SC4 analyses shows no evidence for effects of Al surface contamination. Analyses in progress of SIMS-cleaned areas on the San Carlos grains should result in a calibrated Al implant fluence and an accurate solar wind Al fluence.

Al in Pallasite Olivine: We also explored the use of pallasite olivines as a Genesis Al standard. Imilac was implanted (Fig 1). Preliminary estimates of ppm Al are given in Table 1 based on the nominal implant fluence. These concentrations are precise to within a few percent, thus the Imilac variations on a scale of hundreds of microns are highly significant. Systematic errors in the absolute concentrations of 15-20% are present which will eventually be eliminated. Despite the inhomogeneity, Imilac could serve as a SIMS standard for Genesis, as EMP analyses very close to an analyzed SIMS point are possible. The Eagle Station and Springwater olivine Al is inconveniently low for EMP analysis. However, the San Carlos grains appear more uniform. Once a calibrated implant is available, SIMS analyses of Al can relatively efficiently map out Al zoning. The Eagle Station and Springwater analyses took about 1 hour, including major element analyses. This could be made much more efficient. About 25% of this time was spent removing Al surface contamination.

Table 1: **Aluminum in olivine**	**ppm**
Imilac 1	50
Imilac 2	91
Imilac 3	66
Eagle Station	33
Springwater	40

Conclusions: Caution must be taken when performing trace element analyses with the electron microprobe. Unanticipated analytical artifacts, such as those we encounted during long analyses, need to be corrected.

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.