Genesis Solar Wind Aluminum Abundance: Challenges with Electron Microprobe Analysis of Al in Olivine

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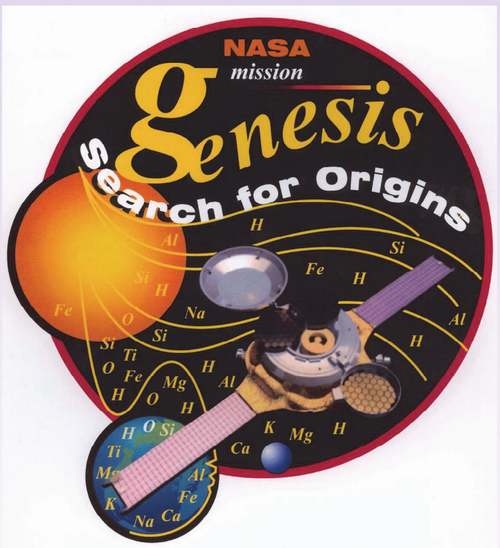


THE ALUMINUM PROBLEM

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 (Figure 1).

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 (Figure 2). The implant Al beam is rastered over 4 inches and is quite uniform, therefore the Si pieces have the same implant fluence (ions/cm^2) as San Carlos olivine.

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. 3, which shows a SIMS depth profile for Imilac pallasite 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.

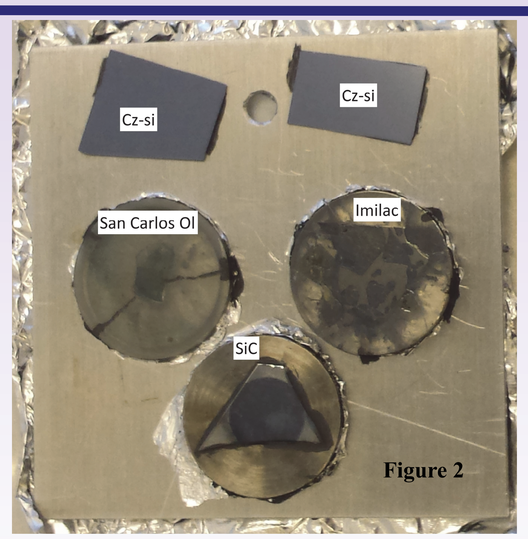


Figure 2

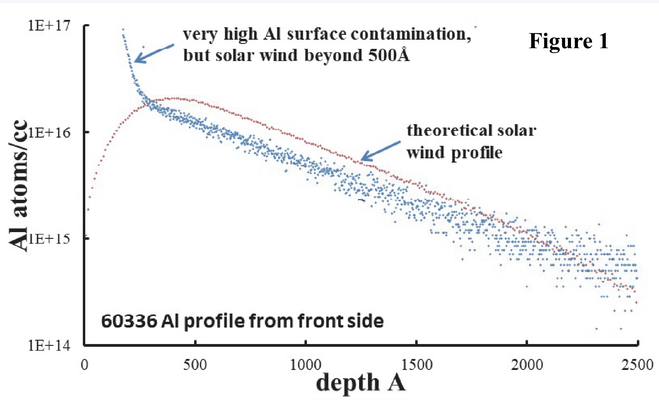


Figure 1

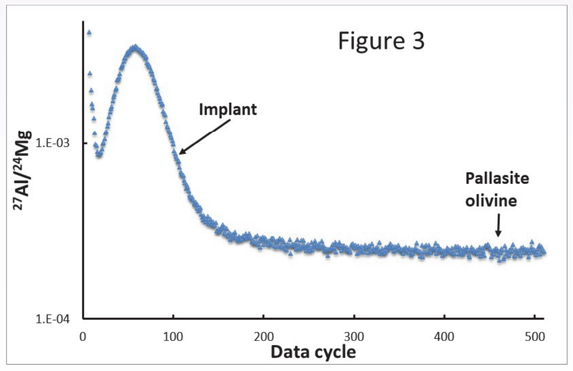


Figure 3

ANALYTICAL METHODS

Electron microprobe analyses: Systematic instrument errors

- To test for Al contamination from carbon coating a 400x400 µm area was SIMS-cleaned on Si metal and recoated with C.
- EMP analyses around the Al k-alpha peak showed a decrease in counting rate at the peak (Figure 4).
- Counts are measured on the peak first, then backgrounds, with 100 nA beam current, 10 µm spot and 10 minute count times.
- Test done with repetitive 10 minute counts on same spot (Figure 5).
- The 10 µm spot data show initial decrease in count rate (believed due to contamination from electron beam) followed by a steep increase, as the carbon coat was burned away by the electron beam. The count rate approaches that of uncoated silicon (dashed line), supporting this theory.

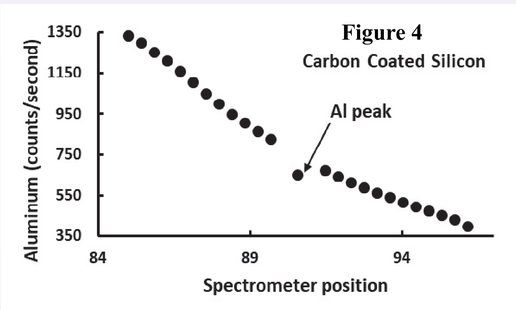
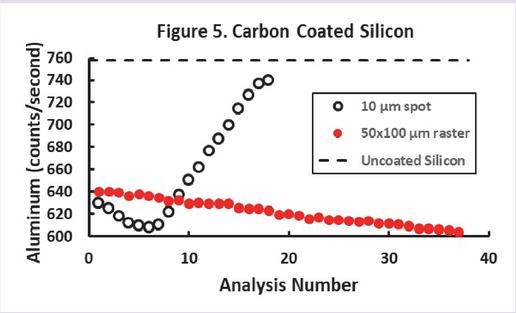


Figure 4



X-ray photoelectron (XPS) spectrometry

- Spectra collected on sapphire and San Carlos olivine
- Above-background counting rates for Al 2p electrons on sapphire were ~2x10^4 cps
- Olivine aluminum counting rates were 300-700 cps on 500x700 µm areas due to surface contamination
- Al 2p peak visibly resolvable from background at all 12 analysis locations on olivine
- >1% of Al X-rays from SC3 will be from contamination (Figure 6)
- →use the SIMS ion beam to clean the olivine surfaces of contamination and to verify the cleanliness

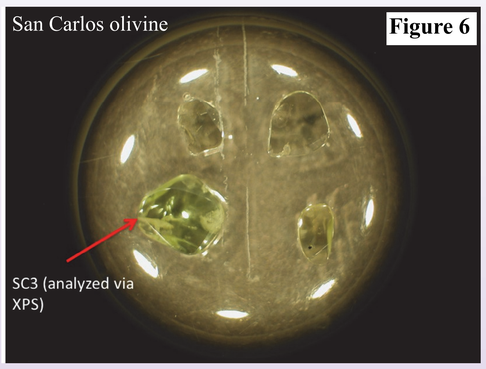


Figure 6

Mitigation

- Solid symbols on Figure 5 are from analyses using a 50x100µ spot size (still using 100 nA beam current and 10 minute count time).
- Depositional decreases in count rate over time for olivine are much smaller than for silicon; correction may not be necessary.

RESULTS

Al in San Carlos Olivine

Protocol used for analyses:
- 50x100µm raster
- 100 nA beam current
- 5 minute count time for peak and backgrounds
- 2 point linear background correction (Figure 7)

→for 100 ppm Al, this gives 4% one sigma counting statistics per point

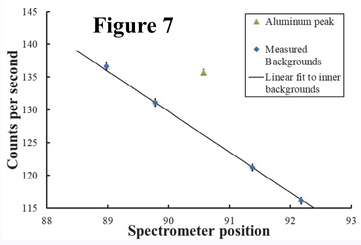


Figure 7

Three San Carlos grains have 60-70 ppm Al, and one (SC4) has ~130 ppm. With optimized analytical conditions, 13 of 14 analyses gave the same counting rate within 1σ counting statistics errors.

We have SIMS cleaned 11 areas on SC3 in preparation for additional analyses (Figure 8). The sample will be carbon coated at the same time as the standard and analyzed using the protocol listed above.

After the electron microprobe analyses are complete the same spots will be analyzed in the SIMS.

With this data, along with implant results, the solar wind aluminum fluence profiles will be recalculated.

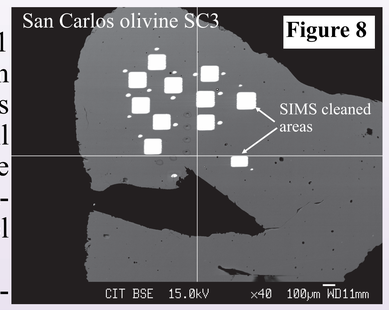


Figure 8

Al in Pallasite Olivine

We also explored the use of pallasite olivine 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 encountered 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.