TOF-SIMS INVESTIGATION OF THE EFFECTIVENESS OF ACID-CLEANING PROCEDURES FOR GENESIS SOLAR WIND COLLECTORS. Y.S. Goreva[1], M. Humayun[2], D.S. Burnett[3], A.J. Jurewicz[4], C.P. Gonzalez[5]; [1]Smithsonian Institution, Washington, DC; gorevay@si.edu, [2]Florida State University, Tallahassee, FL, [3]California Institute of Technology, Pasadena,CA, [6]Arizona State University, Tempe, AZ,[5]Jacobs- JETS at NASA/Johnson Space Center, Houston, TX.

Introduction: ToF-SIMS images of Genesis sample surfaces contain an incredible amount of important information, but they also show that the crash-derived surface contamination has many components, presenting a challenge to cleaning. Within the variability, we have shown that there are some samples which appear to be clean to begin with, e.g. 60471 [1], and some are more contaminated (e.g this work and [2, 3])

Samples 60493 and 60500 are a part of a focused study of the effectiveness of aqua regia and/or sulfuric acid cleaning of small flight Si implanted with ^{6}Li using ToF-SIMS.

Case study 1: Sample 60500 is a small flight Si sample (1) cleaned of gross Utah particulate contamination in the JSC Curatorial Facility by megasonic ultrapure water (UPW) cleaning, (2) shown to have a typical (about 10-20A) amount of "brown stain" (a thin flight-acquired polymerized silicone contamination film) by photoelectron spectroscopy (XPS) [e.g. 3], (3) implanted with ^{6}Li, and (4) again cleaned with UPW to remove any handling prior to ToF-SIMS analysis. Brown stain is a flight derived silicone contamination film of highly variable thickness. Figure 1 is a JSC optical image of the sample.

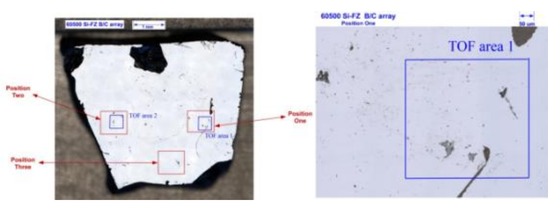

Fig. 1: JSC Curatorial optical images of 60500. Red squares are areas monitored by JSC for particle identification and size distribution (Fig. 2-4, last frame). Blue squares are areas studied by ToF-SIMS.

Figures 2-6 are ToF-SIMS ion images, each frame showing spatial distribution of a specific mass (last frame per series is an optical image for comparison). The thermal scale increases with ion intensity from blue to red. Field of view 500×500 µm. Fig. 2 shows sample surface contamination as received. There are several categories of contaminants on the surface of this sample, including inorganic (Na, K-rich) particles, an inorganic (Ca, Al, Mg, Fe-rich) "film", an elongate Ca-rich, S-rich streak (Utah gypsum?), and organic compounds. Organic contamination is ubiquitous on the surface of all flight Si wafers and is particularly abundant in sample 60500. Prominent organic species include $C_8H_5O_3^+$, $SiC_3H_9^+$, CF_3^+, and F^-. The first is a plasticizer. The second (polydimethylsiloxane, a.k.a. silicone oil) is from brown stain, as probably are the F-bearing species.

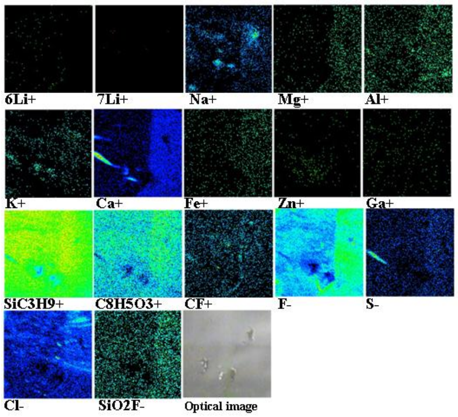

Fig. 2: ToF-SIMS ion images of 60500 before Ar sputtering.

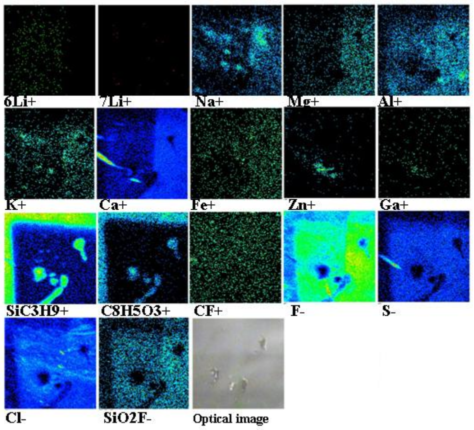

Fig. 3: Genesis sample 60500 after Ar sputtering.

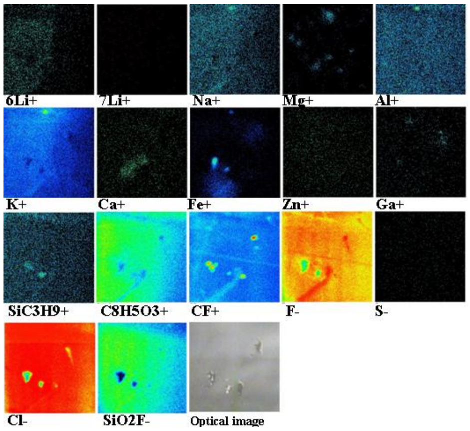

Fig. 4: Genesis sample 60500 after aqua regia treatment.

Surface adsorbed organic layers are present on all samples subjected to TOF-SIMS analysis but often can be removed by small amounts of 1keV (20nA target current) Ar sputtering [2]. Sputter depth is kept well under 10 Å (usually around 5Å) and does not affect surface particle contamination.

Figure 3 shows the effect of Ar sputtering. A small misalignment between the sputtered and TOF-SIMS analyzed area clearly shows removal of $C_8H_5O_3^+$ and $SiC_3H_9^+$. Note an overall general sharpening of the inorganic species images. The features in the optical image (last panel Fig. 3) are crash-derived pits/scratches. The post Ar $C_8H_5O_3^+$ and $SiC_3H_9^+$ ion maps show that these pits are filled with organic material which does not contain F or S.

The implant is expected to show ^{6}Li all the way to the surface, and comparison of the ^{6}Li and ^{7}Li images shows that the implant is detected. But surprisingly, the ^{6}Li is not uniform with a ^{6}Li-poor band on the right hand side of the image. Inspection of the other images shows that the ^{6}Li-poor band is brighter in Na, Mg, Al, K, Ca and Fe. The band may be the reflection of variable thickness of "brown" stain.

Fig. 4 shows the same area on 60500 after aqua regia cleaning (6 hours at 150°C in 3 steps of 2 hours each followed by rinsing with DI water). The increased darkness of the inorganic element images suggests significant contamination was removed. The gypsum particle and the ZnGa (white paint) features are gone (a weaker Ga only spot is revealed, which may represent redeposition during the cleaning). It is particularly striking that the ^{6}Li-poor, inorganic-rich bands from Fig 3 are now dark. Aqua regia appears to have removed the organic-rich fillings in the pits but, in one case, left an Fe-rich deposit.

Case Study 2: Sample 60493. Li-implant sample 60493 overall is somewhat cleaner than 60500. As with 60500, removal of hydrocarbons by Ar-sputtering revealed that surface features apparent in the optical image are pits filled with organic material (see effect of slight misalignment in ToF-SIMS image and sputtered area in SiC_3H_9 image in Figure 5).

The Ar sputter also exposed (1) multiple Fe, Cr (stainless steel) particles, (2) Na, Mg, Al, K rich particles, but with poor correlations among these elements, (3) a general aerosol film of Ca and (4) small Ga-rich ("white paint") particles associated with the stainless steel. We decided to target both stainless steel and Zn/Ga white paint particles with acid treatment using boiling sulfuric acid for 1 hour. As seen in Figure 6, sulfuric acid did a remarkable job in cleaning both types of targeted contaminants as well as the Na, Mg, Al, and K particles. However, the treatment also appears to have redeposited a Na, K – rich layer, likely accompanying oxidation of the topmost Si surface (significantly increased $Si_2O_2^+$ signal). As a non-volatile acid, sulfuric acid is not easily analyzed by ICPMS, and samples processed by this cleaning method are most effectively studied by ToF-SIMS for cleanliness prior to acid attack on the solar wind layer. The significance of the disappearance of ^{6}Li will be assessed by SIMS or ToF-SIMS depth profiling

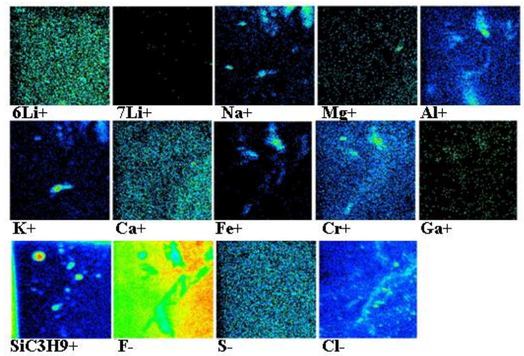

Fig. 5: Genesis sample 60493 after Ar sputtering.

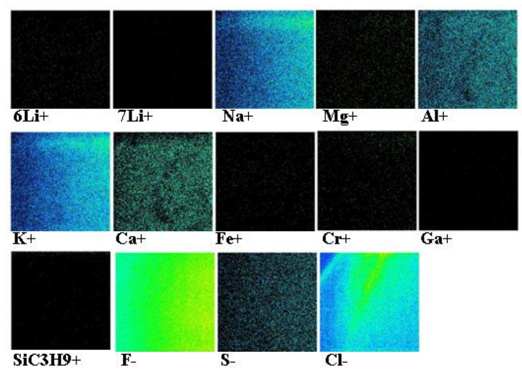

Fig. 6: Sample 60493 after sulfuric acid treatment.

Discussion: The purpose of the ^{6}Li-implanted samples is to learn how to clean samples for ICPMS measurements of Mg isotopes and a high precision solar wind Fe/Mg. Consequently, additional study of 60500 will involve SEM examination of the areas with remaining Fe and Mg particles (Fig 4; other areas have been also imaged on 60500) Depending on what the SEM images show, chemical treatment will be selected aimed at reducing ToF-SIMS Mg and Fe images to the background levels on control samples. Other elements will be followed but not considered in the design of cleaning procedures.

In general these case studies illustrate the approaches that will be followed in devising successful cleaning methods based on small sample analysis. Then the use of these on large area samples can begin.

References: [1] Goreva Y. S. and Burnett D. S. (2013) LPS 44th, #2109, [2] Lyon I. et al. (2011) LPS 42nd, #2528. [3] Gonzales et al. (2014) LPS 45th, this volume, [4] Schmeling M. (2010) LPS 41st, #1682.