Genesis Master Cleaning Plan III

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A pptx file: Cleaning III.pptx is available to illustrate the discussion below.

The Genesis mission (Burnett et al., 2002) was planned around 18 specific “Measurement Objectives”, sets of analyses on the returned solar wind samples designed to address specific science issues. Of these 18, only two did not anticipate the measurement of large sample areas (1-50 cm2). It was assumed that the minimum sample size allocated would be 1 cm. The re-entry crash caused major changes in the allocation plans. Now 1 cm is a big sample, although we have significant numbers in this size range for many, but not all, materials. Genesis has been very successful in working with the large number of small collector pieces recovered from the crash. But, on close inspection, the success has either been for analyses (1) for which contamination was not an issue (Ne, Ar), (2) which analyze small areas and can avoid recognizable, 3-5 micron or larger, particulate contaminants [some SIMS (secondary ion mass spectrometry aka ion probe) analyses] or (3) which use thinned samples for back side SIMS analyses (e.g. for CNO, Heber et al., 2011).

For SIMS (or resonance ionization mass spectrometry, RIMS) analyses, particles as small as 100 A in size can be recognized by distortion of the depth profiles. The loss of data from a few 100-200 micron areas containing such particles is acceptable both in terms of analysis time or in terms of sample area loss. However, elements such as Al, Ca, Cr, show ubiquitous large amounts of surface contamination in SIMS analysis due to what appears to be a crash-derived aerosol film. In these cases, the surface contamination is mixed into deeper layers by primary ion beam sputtering, producing significant interferences with solar wind analysis. This has been mitigated by sputtering toward the surface from the backside on a sample thinned to around 1 micron (Heber et al., 2011). Efforts are underway to extend this backside depth profiling technique to RIMS analyses.

Except for noble gases, particulate contamination has prevented the analysis of cm-sized samples. Many important measurements remain which require analysis of cm-sized areas. ***Particulate contamination is the major obstacle to completion of Genesis science objectives*.** This plan focuses on removing “inorganic” elements (not C, N, or O), although many of the specific treatments should apply to CNO-bearing particles as well.

A major effort, the “Genesis Cleaning Plan”, co-ordinates the efforts of several laboratories to the goal of learning how to surface clean Genesis samples without disturbing the underlying solar wind. *The ultimate goal is to accumulate a collection of “clean” cm-sized samples in the Curatorial Facility, available for allocation*. Here “clean” means to the best of our ability. From the earliest Genesis proposals on, it has been recognized that all specific solar wind analysis protocols must have a surface cleaning step, and this will be the ultimate check on whether a “clean” sample is good enough. However, this surface cleaning step should only be expected to remove/resolve an amount of contamination that is 1-10 times solar wind atoms/cm2 levels (ideally closer to 1 than 10). If the amounts present are 103-106 solar wind levels, prior cleaning like proposed here is necessary. Most importantly, the cleaning steps developed form the basis for the required, pre-analysis, surface cleaning step.

The Cleaning Plan involves testing of methods of surface **cleaning** (Table 1), and the simultaneous development of minimally-destructive surface analysis techniques (Table 2) that are the basis for **assessing** residual contamination levels after a given cleaning trial. Previous versions of the Master Cleaning Plan have used flow charts to illustrate various approaches; however, at present, both the possible means of cleaning and the assessment techniques have increased in number, and it is not possible to capture all the possible “mix and match” possibilities in a flow chart.

The basic approach is simple: assess, clean, reassess, reclean, etc. until no measurable residual contamination remains. Initial studies are on subcm test samples until reliable cleaning techniques are available. At that point, attempts to produce “clean” cm-size samples will be made. With these samples, only non-destructive assessment techniques will be used, but these are available.

**A. Cleaning Assessment Techniques.**

It is useful to discuss the assessment techniques first so that results from these can be used in subsequent cleaning discussions. Table 2 summarizes the available capabilities; all techniques will not be used on all samples. With the exception of synchrotron radiation TRXRF, none of the techniques can completely map even a multi-mm test sample. It must be assumed that sampling of a few areas, 100s of microns in size, provides a representative inventory of contaminants.

*Optical Microscope / Particle Counting* The simplest, least destructive, way to assess surface cleanliness is to look at the sample in a reflected light microscope in a clean room. In addition to bright and dark field illumination, the Curatorial Facility has an imaging system and accompanying software for obtaining particle size distributions (Rodriguez et al 2012). At the highest power, fields of view of 226 microns can be mapped with size detection limits of 1 micron. Mosaics of lower power images are possible. Only “features” are imaged, so that pits and particles are not distinguished; however, since the locations of features are known, these can be distinguished by direct microscope examination if desired.

*Scanning Electron Microscopy* This has obvious application in identifying residual particles 0.3-5 microns in size. Knowledge of particle composition allows cleaning steps to be devised which target the identified particles. It also allows “harmless” particles to be recognized; e.g. spacecraft C particles may not be a threat to inorganic element analyses. Similarly, broken collector array material fragments (Ge powder is ubiquitous) are high purity and usually not a contamination threat. The SEM has a potential downside that is currently under investigation: the possibility that the inevitable electron beam deposited C coat might armor underlying contamination making it more difficult to clean.

SEM work to date has identified several contaminants beyond broken collector materials: stainless steel, reduced C particles, Zn-Ga-spinel. The former are construction materials of the Sample Return Capsule (SRC). The latter is a component in the white thermal paint used in the SRC. In UPW-cleaned (see below) samples, large (5 micron or larger) Utah desert phases have not been identified, although the ubiquitous Ca contamination observed in SIMS and RIMS analyses may have such an origin.

*Photoelectron Spectroscopy (XPS)*. An incoming monoenergetic X-ray is stopped by photoelectric effect interactions, and if the event is within a few monolayers of the surface, the resulting photoelectron has a reasonable chance of escaping the sample without losing energy in a collision. This results in a sharp line spectrum on top of a continuum due to scattered electrons. XPS has excellent depth resolution, but it is relatively insensitive, requiring typically around 1014 atoms/cm2 using laboratory instruments based on X-ray tubes. Because it only senses the outer few monolayers, it is relatively insensitive to micron-sized particulate contamination. A major advantage is that it has useful sensitivity for light elements (CNOF). XPS is very useful in brown stain detection and removal assessment, and in checking beam deposited C layers from ion implantations, as well as handling organic contamination.

*Total Reflection X-ray Fluorescence* A monochromatic beam of high energy photons is critically reflected from a flat sample tilted at the critical angle for reflection. In the process of reflection, the photons fluoresce surface contamination. The fluorescent X-ray energies identify contaminant elements. The intensities are a measure of the total number of contaminant atoms/cm2 of surface. The photons can either come from a laboratory X-ray tube or from a high energy accelerator as synchrotron radiation (e.g. Schmeling et al., 2012). Quantification is challenging, although efforts are in progress to accomplish this. For laboratory TRXRF, sensitivities are in the range of 1011 – 1012 /cm2 for elements from Al through Rb using K lines, and roughly Hf through Pb as L lines. The synchrotron radiation sensitivities are roughly a factor of 100 better. The laboratory TRXRF has a major advantage of rapid throughput, giving short turnaround times for a given cleaning test.

Synchrotron radiation TRXRF is the ultimate tool in demonstrating clean surfaces because of very high sensitivity and of being essentially totally non-destructive; however we have only limited beam time access, so the general plan is to produce samples that appear clean to the other assessment techniques, especially lab TRXRF, then check the cleanliness when synchrotron time becomes available.

The TRXRF photon beam is basically a thin stripe, (1 mm or less) and many mm long. With synchrotron radiation, the acquisition time of a surface spectrum at the critical angle is short, and a series of step spectra can be obtained to completely check the cleanliness of a cm-sized sample.

*Time-of-flight SIMS* Here a pulsed ion beam sputters a surface and the secondary ions (either positive or negative) measured in a time of flight mass spectrometer. Heavy primary ion beams (Bi. Au) minimize ion beam mixing effects. The masses of all contaminant elements are measured, with high mass resolution possible to discriminate against molecular ion interferences. The primary ion beam can be rastered over the surface to produce element maps 10 to 1000 microns in size showing the distributions of contaminant elements (Kuhlman et al., 2010; Lyon et al 2011). Sensitivities are high, particularly for alkali and alkaline earth elements. Quantification is difficult, but as the goal is remove all elements below detection limits, accurate knowledge of the amount of dirt is not of high importance. TOF-SIMS is unique in having high sensitivity and high spatial resolution. Non-conducting samples can be analyzed with the aid of an electron flood gun. Areas analyzed by TOF SIMS are not expected to be compromised in terms of subsequent cleaning and post-cleaning re-analysis, but tests will reveal any problems.

*SIMS*  This will not be routinely used in cleanliness assessment, but once a sample appears to be clean, a test profile of Ca or Al directly demonstrates whether solar wind can be measured in the presence of whatever residual contamination remains. Contamination levels for these elements are high and ubiquitous, so this is a very good cleanliness test, possibly even using the edge or corner of a “clean” sample headed for storage at JSC.

**B. Cleaning Techniques**

This discussion is organized around Table 1, utilizing the data from the techniques discussed above.

Test samples for cleaning are selected by the JSC Curatorial Facility. Work to date has used sub-cm size samples of Si, Si-on-Sapphire (SoS), and sapphire collector array materials. Specific samples are in various stages of testing and the present focus in on bringing these samples to a state of completion. To the extent that the goal of the Plan is to determine *how* to clean samples, any of these materials is potentially adequate, but this assumes that what is required to remove a given contaminant is the same on all substrates, which may not be true. Consequently, the testing focuses on the materials that are most in demand. Moreover, the ultimate goal is to produce a collection of cm-sized “clean” samples. For these reasons, the initial focus has been on Si and SoS collectors, as these are most in demand. But since plans are being made for large area analyses of SiC and DOS (diamond-like-C) concentrator target materials, we will add these to the Cleaning Study materials.

*UPW cleaning* The samples recovered from the crash all have very high levels of particulate surface contamination. The coarsest crash-derived particulates are removed by the Curatorial Facility using ultra-pure-water (UPW) Megasonic cleaning. Particle size distributions demonstrate almost quantitatively removal of large (> 5 micron) particle. The UPW treatment is also expected to dissolve Utah-desert-derived salts.

*Brown* Stain A thin flight-acquired polymerized silicone contamination film (“brown stain”) is present in widely variable amounts on all samples. Of the collector materials flown (Jurewicz et al., 2002), only CZ Si has adequately documented prelaunch surface cleanliness. For all other materials, the brown stain must be assumed to overlay significant pre-launch particulate contamination. As verified by XPS analyses, removal of this brown stain can be achieved by UV-ozone treatment at JSC and will be done routinely for those techniques, e.g. acid cleaning, where the brown stain might block access to a contaminated surface. NanoSIMS images of a flight Si sample show residual micron-sized C-rich areas, probably incompletely removed brown stain, so the consequences of only partial removal of brown stain by uv-ozone analysis must be considered in specific cleaning tests. Only 90% brown stain removal may be acceptable in many cases, where inorganic element analysis is being tested.

Acid Cleaning. Because most of the collector materials are chemically resistant (Jurewicz et al., 2002), attempts to date have focused on acid treatment, following semiconductor industry recipes, but minimizing the use of HF to avoid insoluble fluorides (e.g. CaF2). Acid cleaning is done in geochemical clean laboratories with high purity reagents at Caltech (D. Burnett) and FSU (M. Humayun). Ongoing, laboratory TRXRF analyses show that the acid cleaning procedures tried to date have been somewhat successful (e.g. Schmeling et al; 2010, 2011); however, there are other samples where the contamination appears to be very resistant to acid attack. The case of SoS sample 60966 is discussed below. The use of radioactive isotopes or stable, minor-isotope-enriched, tracers to check for redeposition from cleaning solutions will be evaluated. If variations of acid-based procedures do not give satisfactory results, we will try the use of acetate peels, as discussed below. We can also explore crown ethers used successfully by Nishiizumi in removing Utah mud from SRC lid foils.

Spot checks with SIMS depth profiles on both implants and flight samples have been used to show that loss of solar wind does not occur during acid treatment. It is important to do this on flight samples because Humayun has shown that Si films on sapphire (SoS collectors) are unexpectedly soluble in HF (flight spare controls are not!) due to in-flight space exposure effects. We have shown that the most aggressive cleaning, with aqua regia, has not significantly disturbed solar wind Mg depth profiles in Si, but more testing is needed

*CO2 snow* The condensation and evaporation of CO2 from surfaces removes particles. An apparatus has been constructed at ANL by Veryovkin which has demonstrated partial cleaning of Genesis test SoS sample 60966 (Schmeling et al., 2012). Better results have obtained on a Si test sample (61052). Systematic tests are in progress.

*Giant Cluster Ion Beam (GCIB)*  Cameca SIMS instruments sputter using primary ion beam energies in the 5 -20 keV energy range. Ions in this energy range are not suitable for cleaning large amounts of surface contamination because the sputtering process is accompanied by ion beam mixing of surface contamination to deeper depths. Because the solar wind implants are shallow, the ion-beam-mixed contamination can cause serious interferences with solar wind analysis. However, at lower energies, sub-keV for atomic ions, the amount of ion beam mixing is much less. The Genesis RIMS instrument at ANL provides major mitigation in the effects of ion beam mixing with the use of a 250eV CW Ar ion beam for depth profiling. (Veryovkin et al., 2012a), and a similar ion gun is part of the ANL XPS instrument and, although untested at present, is available for general sample cleaning.

 The ultimate in sputter cleaning with negligible ion beam mixing is the use of singly-charged molecular clusters of 2000-3000 Ar atoms (Giant Cluster Ion Beam). At 20 keV, these ions have the same keV/amu as a 20/2000 = 1 eV atomic Ar ions. The instrument available to us, at the University of Hyago, Japan, has been able to produce controllable amounts (40-150 A) of erosion. On one test implant sample RIMS spectra show a 200-300 A particle cleanly chopped in half by the GCIB beam. A before-after GCIB sputtering measurement by lab TRXRF on a small flight Si sample (60428) showed removal of Cu and Ga contamination peaks. However synchrotron radiation TRXRF showed more contamination in a GCIB sputtered area of 60428 when compared to an unsputtered area (Veryovkin et al., 2012b), but a controlled experiment with before and after analysis of the same area is required, as well as more systematic investigation in general.

*Acetate peels* A solution of cellulose acetate in an organic solvent is allowed to dry on the surface of the sample. When the resulting cellulose acetate film (“peel”) is removed, particulate contamination is removed as well. The particles removed can be identified on the peel. This has been verified to remove particles, but systematic studies of efficiency have yet to be carried out. The acetate peels are useful on materials such as aluminum films on sapphire (AloS), and to a lesser extent, SoS which are sensitive to acid attack.

*60966: a case study* Acetate peels are currently being applied to the case of SoS sample 60966 for which HCl (twice), CO2 snow, and HNO3 cleaning have only partly removed the Ge, Fe, Ni, Pb contamination seen by laboratory TRXRF. SEM analysis of the post-peel surface may be compromised by the poor conductivity of SoS samples; this will be checked, but in any case, the particles removed with the peel can be identified and this information used to guide additional cleaning steps. In addition an “environmental” SEM can be used on the post-peel 60966; such instruments are available to us at the Smithsonian or at ASU. The peel will probably leave an organic residue but we have been quite successful removing this type of residual organic contamination with hot xylene. XPS spectra will trace the various steps (before peel, after peel, after xylene).

**Summary**

The ultimate goal of the Cleaning Study is the production of “clean” cm-sized samples, stored in the Curatorial Facility and available for allocation. At present we are in a testing phase using sub-cm samples in order to assess what cleaning techniques are effective. For a cleaning technique to be listed on Table 1, it must potentially be useful for the larger samples.

However, as shown in Table 2, not all of the assessment techniques would be applicable for testing whether a cm-sized sample is sufficiently clean. However, many of the techniques are sufficiently non-destructive that they could be used on the ultimate cm-sized “clean” samples.

Table 1. Cleaning Methods

|  |  |
| --- | --- |
|  | PIs |
| **In use** |  |
|  Ultra Pure Water | Curatorial Facility |
|  UV ozone | Curatorial Facility |
|  Wet (acids, hot xylene) | Burnett, Humayun, Jurewicz |
|  CO2 snow | Veryovkin |
|  Giant Cluster Ion Beam (GCIB) | Veryovkin |
|  Acetate peels | Kuhlman |
| **Other possibilities** |  |
|  Low energy ion beam | Veryovkin |
|  Mechanical  | Jurewicz |
|  Gas/Ion etching | Burnett, Jurewicz |
|  |  |

Table 2. Cleanliness Assessment Techniques

|  |  |
| --- | --- |
|  | PI |
| Optical microscope **\*** | Curatorial Facility |
| Optical particle counting **\*** | Curatorial Facility |
| Scanning Electron Microscope (SEM)  | Kuhlman, Goreva |
| Photoelectron Spectroscopy (XPS) **\*** | Veryovkin |
| Lab total reflection X-ray fluorescence (TRXRF) **\*** | Schmeling |
| Synchrotron Radiation TRXRF **\*** | Sutton |
| Time-of-flight SIMS (TOF-SIMS) | Goreva |
| Secondary Ion Mass Spectrometry | Jurewicz, Burnett |

**\*** Applicable for use on cm-sized “clean” samples

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