

Genesis Particulate Contamination

Master Cleaning Plan II

April 21, 2011

Background 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 changed all this. Now 1 cm is a big sample, although we have significant numbers in this size range.

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 for which contamination was not an issue (noble gases) or for approaches such as SIMS or RIMS that analyze small areas and can avoid recognizable 3-5 micron or larger particulate contaminants. For SIMS or RIMS, particles as small as 100 Å in size can be recognized by distortion of the depth profiles; moreover, the loss of data from a given 100-200 micron area containing the particle, is acceptable both in terms of analysis time or in sample area loss.

Except for noble gases, particulate contamination has prevented the analysis of cm-sized samples. *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 some of the specific treatments/analyses would apply to CNO-bearing particles as well.

Because most of the collector materials are chemically resistant (Jurewicz et al., 2002), cleaning attempts to date have focused on acid treatment, following semiconductor industry recipes. Tests with reactive ion etching have not been pursued because it was difficult to avoid too much surface erosion. Effectiveness of the cleaning was originally evaluated with photoelectron spectroscopy (XPS). However, when acid-cleaned samples, measured clean by XPS, were analyzed by more sensitive techniques such as time-of-flight secondary ion mass spectrometry (TOF-SIMS), synchrotron radiation X-ray fluorescence total reflection X-ray fluorescence (SRTRXRF), or resonance ionization mass spectrometry (RIMS), unacceptable residual levels of contamination were found.

It was clear that (1) acid cleaning procedures used prior to 2009 were inadequate, and (2) XPS characterization did not have sufficient sensitivity for our purposes.

In 2009 we implemented a “Master Cleaning Plan”, built around laboratory TRXRF measurements by M. Schmeling (Loyola, Chicago). This has been quite successful, but an upgrade is required, as described here. As a major component in an upgraded (Version II) of the Master Cleaning Plan we need to add a more sensitive, but routinely available, method of surface analysis. This will be done using TOF-SIMS on a regular, routine basis. Feasibility has been demonstrated (Kuhlman et al., 2010; Lyon et al., 2011), but we need to establish it’s use on a more routine basis

Master Cleaning Plan II.

Figure 1 shows, in flow chart form, the top level design of our revised Master Cleaning Plan II, a major effort to remove inorganic contamination to sufficient levels to

permit large area analyses, e.g by ICPMS or SRTRXRF, and to establish a “verified-clean” set of cm-sized samples in the Curatorial Facility.

Sampling None of the techniques routinely employed in this study can completely map 5-10 mm-sized areas. Studies are underway to characterize as large an area as possible with lab TRXRF and TOF-SIMS; nevertheless, it will probably be necessary to rely on sampling. The requirement for larger (> 7mm) samples is to demonstrate 3 areas on a that are clean to the technique employed. When smaller 3-5 mm test samples are used, we may have to settle for fewer areas. The assumption that the areas analyzed are representative of the whole sample can be tested on those rare occasions when we have SRTRXF time, where scanning of areas of at least 5x10 mm is possible. Finally, all large area solar wind analyses must have a surface cleaning step, and this will check whether a “verified 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, although individual case assessments will be made. Most importantly, the cleaning steps developed here form the basis for the required, pre-analysis, surface cleaning step. We know that the amounts of surface contamination varies widely, thus allocation will also employ high-grading the initially-most-clean samples.

Curatorial Facility Contributions Samples for cleaning tests will be selected by the JSC Curatorial Facility. Twelve 8-10 mm sapphire and Si-on-sapphire samples have already been studied as part of the 2009 Master Cleaning Plan. These are in various stages of testing and work on these will be brought to completion. To the extent that the goal of the Plan is to determine *how* to clean samples, these materials are adequate. However, if the goal is also to produce a collection of “verified-clean” samples, then it is necessary to focus on Si collectors, as these are in the most demand.

The gross crash-derived particulate contamination will be removed by ultra-pure-water (UPW) washing which has been shown to almost quantitatively remove large (> 5 micron) particles and is expected to dissolve Utahogenic salts.

A thin flight-acquired polymerized silicone contamination film (“brown stain”) is present in widely variable amounts on all samples. In the case of all sapphire based collectors the brown stain overlies significant pre-launch particulate contamination. Removal of this brown stain by uv-ozone treatment at JSC has been demonstrated and will be done routinely on these materials to give access to pre-launch particulate contamination during the wet cleaning steps.

The situation with Si collectors is complicated. Prelaunch, CZ Si was shown to have very low levels of surface contamination, and the UV-ozone treatment is not necessary. For CZ Si, the crash-derived particulate contamination lies on the brown stain, which in could be an advantage, providing an armoring layer, enabling more aggressive acid attack. But for FZ Si, there were two flight batches. One had documented clean surfaces; the other was less clean. We can identify FZ Si among the broken pieces from the crash, but the documentation of FZ batch was lost in the crash. Thus to be safe, FZ Si cleaning test samples will be UV-ozone treated.

Particle Size Distributions The Curatorial Facility has the capability of measuring quantitative particulate size distributions for sizes greater than 0.3 microns. Previous size distribution measurements on post-UPW-cleaned samples show that essentially all particles greater than 5 microns are removed by the UPW cleaning, and that most of the mass of particles lies in the remaining larger particles. What has not yet been done is to carry out before and after measurements of the effects of cleaning on the size distributions.

Particle size distribution measurements will only be done on a subset of the Si samples involved in the overall cleaning study. The area mapped is about 250-300 microns on a side. Edge features, pits, scratches, etc will serve as fiducials to allow remeasurement of the same area after some form of cleaning. At least the larger of individual particles in the mapped area can be tracked to see whether they were removed during cleaning.

Lab TRXRF Key to this plan are surface contamination elemental analytical approaches that are 1) non-destructive, 2) much more sensitive than XPS, 3) accessible, so that trial and error, before-after, cleaning studies can be efficiently done on flight samples, 4) ideally semi-quantitative, although this is less important because the goal in most cases is to remove contaminants below detection limits; 5) clean in terms of sample handling. Items 1)- 3) are especially important, because the successful cleaning of one sample does not guarantee that all samples, even of a given material, will be adequately cleaned. *Specific allocated samples must be shown to be clean.*

Within bounds set by detection limits, laboratory TRXRF meets the above requirements. TRXRF is an essentially totally non-destructive surface analysis technique in which X-rays at, or slightly above, the critical angle for total reflection penetrate only very shallowly (order 100Å) into the substrate, but still fluoresce surface impurities. Laboratory TRXRF, with an X-ray tube, is about 2 orders of magnitude less sensitive than SRTRXRF using synchrotron radiation photons, but access to a synchrotron beam line is only possible at best once or twice a year; whereas, quick turnaround of acid cleaned samples with lab TRXRF is possible. But, in turn, the laboratory TRXRF, with sensitivities of 10^{11} - 10^{12} atoms/cm² depending on element, is 3-4 orders of magnitude more sensitive than XPS.

With TRXRF, mm-size areas are analyzed, with multiple spots possible for samples greater than 7-8 mm. Sensitivity is primarily for elements from Ca through Ge, but this region covers many of our known contaminants.

Before and after acid cleaning studies (Schmeling, 2010; King et al., 2010, Schmeling et al., 2011) have demonstrated significant reductions in surface contamination and produced a few “Martina-clean” samples, but there are also samples that are resistant. Flight spare control Si samples show no detectable elements, showing that contamination from our handling is not detectable. This work is ongoing.

It is necessary that Genesis samples be Martina-clean, but it appears that this is not sufficient:

- B/C array sapphire sample 60642 after acid cleaning appears clean to TRXRF, but SRTRXRF analyses at the Australian Synchrotron (B. King, private communication) still show measurable contamination levels of some first-row transition metals in the 10^9 – 10^{11} range.

- B/C array Si sample 60289 was clean to TRXRF after JSC UPW and hot xylene cleaning; however attempts at SIMS Ca analyses encountered large quantities of Ca surface contamination.

Acid Cleaning Acid cleaning will be done in geochemical clean laboratories with high purity reagents at Caltech (D. Burnett) and FSU (M. Humayun). Although ongoing, the acid cleaning procedures tried to date have been sufficiently successful (e.g. Schmeling et al; 2010, 2010a, 2011) that initial wet cleaning will still be acid based. Specifically, we will try to minimize use of HF to avoid insoluble fluorides (e.g. CaF₂). The use of radioactive tracers to check for redeposition from cleaning solutions will be evaluated. If variations of acid-based procedures do not give satisfactory results, we will explore the use of crown ethers used successfully by Nishiizumi in removing Utah mud from SRC lid foils.

We have done some spot checks with SIMS depth profiles on implants to show that loss of solar wind does not occur during wet cleaning. This will be done more systematically as we enter this major effort, especially if more aggressive acid cleaning is used.

The FSU approach has focused on aqua regia. This has been shown to remove large amounts of surface contamination and permitted good SIMS Fe and Cr analyses on one sample (Wang and Nittler)

SEM Some acid-cleaned samples, found not clean by lab TRXRF, will be examined by SEM to determine the mineralogy of the contaminants, which will then be used to revise the wet cleaning steps. Conductive coating is not required for Si or diamond-like-C collectors. Low vacuum (“Environmental”) SEMs have an advantage in that insulating (e.g. sapphire) or poorly conducting (e.g. Si-on-sapphire or Al-on-sapphire) collectors can be analyzed. Such instruments also minimize electron-beam-deposited C deposition, although some C deposition during SEM imaging is probably acceptable. Some tests will follow individual SEM-located particles through the wet cleaning steps to see if they are removed (return arrow to SEM box in Figure 1). This specific particle tracking will also check that C deposition has not armored particles producing resistance to acid dissolution.

TOF-SIMS analysis When we obtain samples that are clean to lab TRXRF, we will then use TOFSIMS to see what, if any, residues are left. In TOF-SIMS, a pulsed ion beam is required to obtain time of flight spectra. In this mode, sputtering is negligible compared to the implantation depths of solar wind ions, so only surface contamination is measured. All elements can be detected although there is a wide range of sensitivities among elements. Analyses can be made with either positive or negative secondary ions, but this work will involve primarily positive secondary analyses. Good time (mass) resolution helps sort out molecular interferences. TOF-SIMS has very good spatial resolution, with micron-size capabilities, but capabilities for imaging the distributions of selected elements (Kuhlman et al., 2010; Lyon et al., 2011) are more important for our purposes. Areas of up to 250x250 microns can be mapped with the Smithsonian instrument. TOF-SIMS complements TRXRF in having good sensitivities for low Z elements, such as Na, S, and K.

SRTRXRF When synchrotron time (APS or Australian or Japanese Synchrotrons) becomes available, our cleanest samples in process will be analyzed. It will be important to check a sample that is clean to TOF-SIMS.

Recycling As shown in Figure 1, when TOF-SIMS analysis shows that a sample is still contaminated after a second round of acid cleaning, the characterized, contaminated areas will be examined by SEM to see if at least the larger particles can be recognized. In turn, this can lead to a more focused round of chemical cleaning.

Finally, when samples are clean to TOF-SIMS, they will be set aside for large area analysis at JSC as a “verified clean” set of samples.

Master Plan for Sample Cleaning

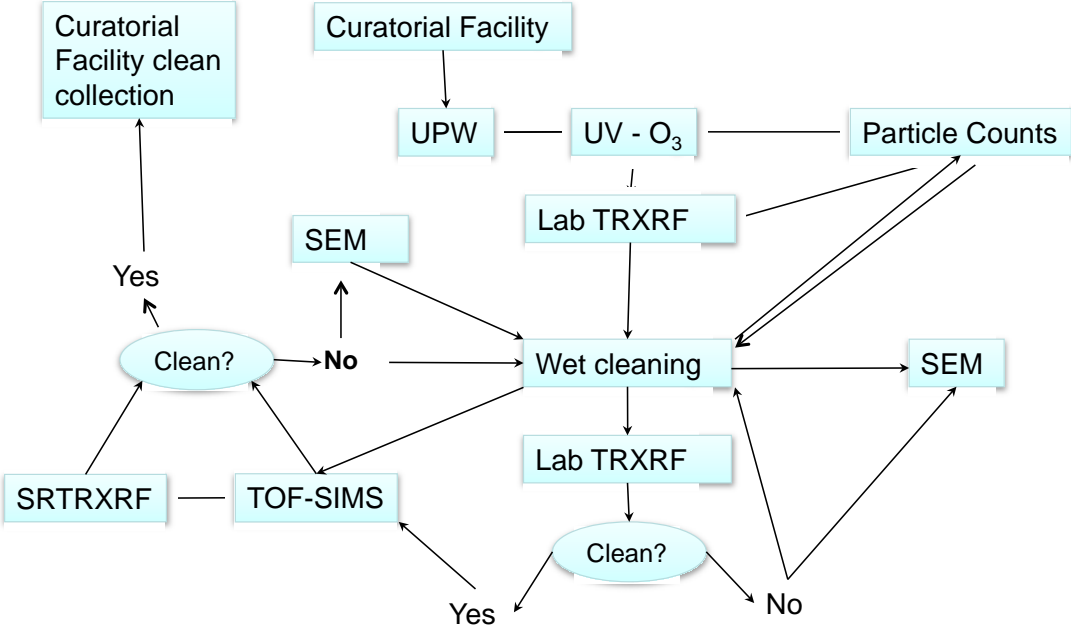


Figure 1

References

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