Molecular Contamination on Anodized Aluminum Components of the Genesis Science Canister. D.S. Burnett;[1] K. M. McNamara[2], A. Jurewicz[1], D. Woolum[1]; [1]California Institute of Technology, Pasadena, CA 91125; [2]NASA - Johnson Space Center, Houston, TX 77058; karen.m.mcnamara@nasa.gov.

Introduction:

Evidence of Molecular Contamination**:** Inspection of the interior of the Genesis science canister after recovery in Utah, and subsequently at JSC, revealed a darkening on the aluminum canister shield and other canister components. There has been no such observation of film contamination on the collector surfaces, and preliminary spectroscopic ellipsometry measurements support the theory that the films observed on the anodized aluminum components do not appear on the collectors to any significant extent.[1] The Genesis Science Team has made an effort to characterize the thickness and composition of the "brown stain" and to determine if it is associated with molecular outgassing.

Figure 1. Examination of the 6061 aluminum canister thermal shield in the cleanroom at UTTR.

Detailed examination of the surfaces within the Genesis science canister reveals that the brown contamination is observed to varying degrees, but only on surfaces exposed in space to the Sun and solar wind hydrogen. In addition, the materials affected are primarily composed of anodized aluminum. Figure 2 shows a sharp line separating the sun and shaded portion of the thermal closeout panel. This piece was removed from a location near the gold foil collector within the canister. Future plans include a reassembly of the canister components to look for large-scale patterns of contamination within the canister to aid in revealing the root cause.

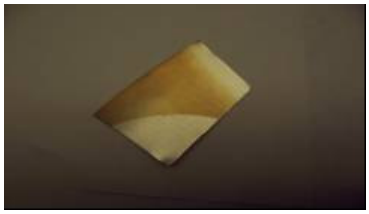

Figure 2. A section of the aluminum canister thermal shield post-flight, showing areas with and without brown discoloration.

Potential Sources of Contamination: The Genesis spacecraft and science canister were designed to minimize the potential for outgassing and subsequent surface contamination in space. The components of the canister were precision cleaned and assembled in a Class 10 cleanroom at JSC especially designed for that purpose. The canister and its contents remained under dry nitrogen purge from the time of assembly until launch.

There are a number of components or materials used in the assembly of the spacecraft and science canister that could be considered potential contamination sources. Some of these include: seals and locking elements, the electroplated gold concentrator, small amounts sealants and greases, residual films from pre-flight storage containers or processing, and residue from anodization processing. All of these could have left or deposited small amounts of molecular contaminant, which upon exposure to the Sun, solar wind hydrogen, and thermal cycling in space, could have undergone polymerization to form molecular layers with the observed optical properties.

Techniques for Characterization: Samples of the canister aluminum thermal panel were prepared and allocated for study b y the JSC curation staff. The arsenal of techniques used for characterization included: FTIR, XPS, laser Raman spectroscopy, dissolution NMR, and secondary ion mass spectroscopy. Studies were carried out at Charles Evans, MIT, JPL and Caltech.

Summary of Results: XPS studies: A monoenergentic beam of Al K X-rays was focused onto the surface of the sample shown in Figure 2. Samples analyzed included the flight coupon, an acetone-cleaned control sample, and a control sample stored in a Ziploc bag (to evaluate plasticizer outgassing. Both clear and "brown" areas were examined.

XPS is extremely depth sensitive and cannot detect electron produced at depths greater than 30-50 A. The failure to detect aluminum on the exposed surfaces, therefore demonstrates that the thickness in those regions exceeds that depth. Likewise, the ability to detect aluminum in the unexposed regions indicates a thickness below 50 A on those surfaces. XPS was performed on the exposed, unexposed and backsides of the flight samples and showed that the same composition of material existed on all of these surfaces, but to a different extent. The composition in all cases included silicon in coordination with oxygen and fluorine.

Sample	C	N	O	F	Si
Brown Stain 1	69	1.8	20	3.6	4.5
Brown Stain 2	70	3.5	17	4.3	3.8
No stain 1	35	-	38	8.8	5.9
No stain 2; diffuse edge	62	1.9	25	3.2	7.8
Underside	42	-	35	1.9	17

Table 1. XPS Results from brown and nonbrown areas of flight thermal shield.

FTIR Analysis: FTIR was performed at both Caltech and MIT on both the thermal closeout shield and actual collector materials. While the collectors showed no evidence of molecular films, the spectra obtained from the aluminum demonstrated some very weak absorptions. Though these were too weak for interpretation, multiple reflections through the surface indicated a thickness on the order of 60 A.

Laser Raman Spectroscopy: The flight sample seen in Figure 2 was examined alongside a control coupon in the spectral range from 250-2000 cm^{-1}. The control showed no features, while the most predominant signal for the flight sample was observed at 1390 cm^{-1}, which could be related to polymerized siloxanes. In addition, there was a partially resolved peak near 1600 cm^{-1}, which may be associated with sp^2-bonded carbon. The silicon flight collectors examined using laser Raman showed no signs of these signatures.

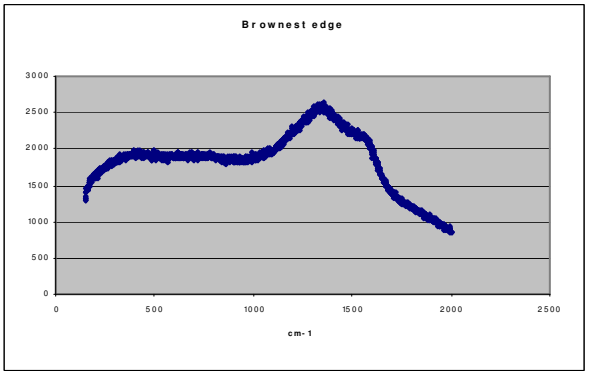

Figure 4. Laser Raman spectrum from flight aluminum thermal shield.

SIMS Analysis: Both positive and negative secondary ion mass analysis were performed on the sample shown in figure 2 at Charles Evans and Associates. The discolored regions as well as the uncolored regions were examined. Comparison of the sputtering rates of the brown or supposedly "thick" areas of the sample to those of nonvolatile organic film residues yielded a maximum thickness of 160 A. Profiles for various species, including O, C, Si, and F are different in the brown and nonbrown areas. The H profiles are similar to the C profiles. Both the brown and nonbrown data are consistent with outer layers more rich in C and H with deeper regions more rich in SiO_2 components. The F profiles are unique and not understood. The depth inhomogeneities in both films could have been derived from a homogeneous contaminant film containing both silicone and fluorocarbon components by a combination of vacuum pyrolysis and UV-induced polymerization, but this interpretation is not unambiguously established. The nonbrown films appear significantly thinner, which may reflect extensive volatilization of these before photopolymerization could take place.

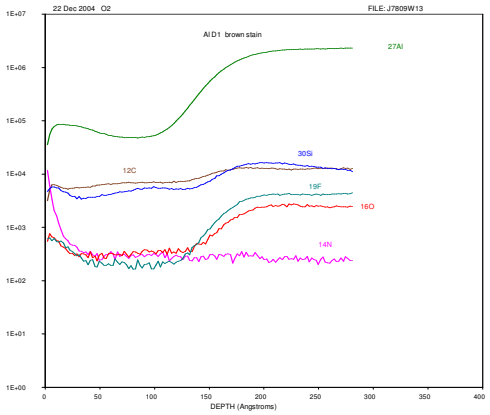

Figure 5. Positive Secondary SIMS results from brown areas of aluminum closeout shield.

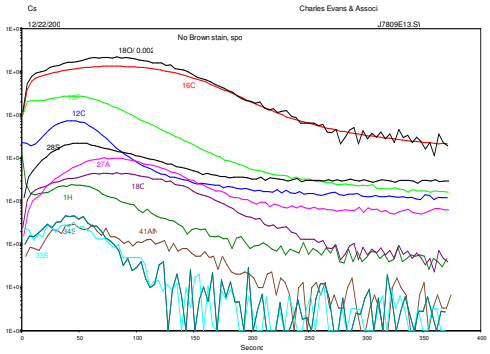

Figure 6. Negative Secondary SIMS results from nonbrown areas of aluminum closeout shield.

Conclusion: Although the brown discoloration on the anodized aluminum appears to be a UV-polymerized hydrocarbon or siloxane contaminant, its apparent thickness is such that it should not prevent detection and measurement of the solar wind in Genesis collectors. The brown discoloration and evidence of molecular contamination has not been detected on any collector materials to date.

References: [1] K.M. McNamara, LPSCXXXVI, this volume.

Acknowledgements: The author would like to acknowledge Vern Lauer of JSC for his help in sample preparation. The author would especially like to thank John Lock of the Department of Chemical Engineering at MIT for his assistance in these analyses.