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Organic Contamination Baseline Study
in NASA Johnson Space Center Astromaterials Curation Laboratories

NASA Astromaterials Acquisition and Curation Office

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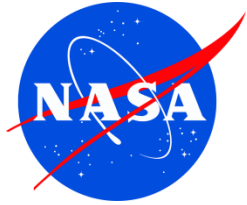
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Acknowledgments

Preface

The organic contamination baseline study has been the largest effort in understanding the role of organics in Johnson Space Center (JSC) astromaterials curation laboratories in the over 40-year history of these facilities. Scientific study of organic contamination on spacecraft and facilities will become increasingly important as NASA continues to explore the solar system well into the 21st century. The Apollo manned lunar landing program was the last NASA program that focused an enormous effort toward understanding organic contamination and mitigation. As we studied the historical data on organics from the Lunar Receiving Laboratory, it became apparent that the amount of work, volume of laboratory analyses, and scientific dedication applied by the Apollo team in such a short period of time were truly awe inspiring. Organic studies since Apollo have been limited by comparison, although they have all made significant contributions of their own to furthering the knowledge and understanding of contamination on NASA spacecraft and facilities.

In recent years, we have mainly focused our research on organic contamination by carbonaceous compounds of seven carbon atoms and greater ($> C_7$). However, much more work is required to progress our understanding of organic contamination in JSC astromaterials curation laboratories. In the coming years, we hope to extend the organic baseline study to include organics of C_1 to C_6. In addition, the role of polycyclic aromatic hydrocarbons, bacteria, and amino acids will be paramount for future exploration missions that feature an astrobiology component. This new line of research will be an important effort in JSC curation and will comprise a continuing effort.

For this NASA technical publication, we wanted to document the state of our current knowledge on organic contamination and disseminate what we know so far in order to help our colleagues planning upcoming missions for NASA. Furthermore, we hoped that this study will promote improvements to JSC curation laboratory procedures and to routine monitoring of today's astromaterial collections. We set out to compile all unpublished, historical, curation-related documents at JSC and study them in a holistic manner. In addition, we sought to conduct research where we found knowledge gaps from past studies. I hope the information found in this publication accomplished these goals and will be a resource for future scientists. We anticipate the organic contamination baseline study will be just one step toward designing better missions, improving the curation of today's astromaterial collections, and inspiring more scientists to focus on understanding terrestrial contamination and cross-contamination of pristine astromaterials. These efforts will secure the scientific integrity of each new sample.

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April 21, 2014
Houston, TX

Table of Contents

List of Figures

List of Acronyms

ACG   Advanced Curation Glovebox
ALHT   Apollo Lunar Hand Tools
ALSRC   Apollo Lunar Sample Return Container
AMC   Airborne Molecular Contamination
ANSMET   Antarctic Search for Meteorites
ARC   Ames Research Center
ARES   Astromaterial Research and Exploration Science (a NASA JSC Directorate)
B31   Building 31 (at NASA JSC)
B31N   Building 31 North (at NASA JSC)
BHT   Butylated Hydroxy Toluene
CAPTEM   Curation and Analysis Planning Team for Extraterrestrial Materials
CCO   Contamination Control Officer
CDC   Center for Disease Control
CP   Chemically Pure
CSM   Chlorosulfonated polyethylene
DBF   Dibutylformamide
DBP   Dibutyl phthalate
DEHP   Di-2-ethylhexyl phthalate
DEP   Diethyl phthalate
DI   Deionized
DIBP   Diisobutyl phthalate
DMF   N, N – Dimethylformamide
DNA   Deoxyribonucleic Acid
DNP   Dinonyl phthalate
DOP   Dioctyl phthalate
FEP   Fluorinated Ethylene Propylene
FE-SEM   Field Emission Scanning Electron Microscope
FFU   Fan Filter Unit
FT-IR   Fourier Transform Infrared Spectroscopy
FY   Fiscal Year
GAL   Gas Analysis Laboratory
GC   Gas Chromatography
GC-MS   Gas Chromatography Mass Spectroscopy
GLC-MS   Gas Liquid Chromatography – Mass Spectrometry
GN2   Gaseous Nitrogen
HEPA   High-Efficiency Particulate Air
ICBC   Interagency Committee on Back Contamination
IPA   Isopropyl alcohol
IR&D   Innovative Research and Development
ISO   International Organization for Standardization
JAXA   Japan Aerospace Exploration Agency

JSC	Johnson Space Center
LABe	Low Angled Backscatter Electron
LAPST	Lunar and Planetary Science Team
LCG	Lunar Curation Glovebox
LM	Lunar Module
LN2	Liquid Nitrogen
LRL	Lunar Receiving Laboratory
LSAPT	Lunar Sample Analysis Planning Team
LSPET	Lunar Sample Preliminary Examination Team
MCE	Mixed Cellulose Ester
MEKP	Methyl ethyl ketone peroxide
MET	Meteorite Hills (Antarctica Meteorite Recovery location)
MIBK	Methyl Isobutyl Ketone
MIL-STD	Military Standard
MPL	Meteorite Processing Laboratory (in Meteorite Laboratory in JSC B31)
MRSH	Mars Return Sample and Handling
MSC	Manned Spacecraft Center (currently JSC)
MSD	Mass Selective Detector
NASA	National Aeronautics and Space Administration
NBBS	+N-Butylbenzenesulphonamide
NMP	N-Methyl-2-Pyrrolidone
NNPL	Nonsterile Nitrogen Processing Line
NSCORT	NASA Specialized Center of Research and Training
NVR	Non Volatile Residue
NVR/FT-IR	Non Volatile Residue/ Fourier Transform Infrared Spectroscopy
OCT	Office of the Chief Technologist
OGA	Organic Gas Analysis
OM	Organic Monitor
PAH	Polycyclic Aromatic Hydrocarbon
PCA	Precision Cleaning Agent
PET	Preliminary Examination Team
PFA	Perfluoroalkoxy
PGMEA	Propylene glycol monomethyl ether acetate
PI	Principal Investigator
PLSS	Primary Life Support System
PSL	Pristine Sample Laboratory (in Lunar Laboratory JSC B31N)
PTFE	Polytetrafluoroethene
PU	Polyurethane
PVC	Poly Vinyl Chloride
RCL	Radiation Counting Lab
RNA	Ribonucleic Acid
RO	Reverse Osmosis
RSL	Return Sample Laboratory (in Lunar Laboratory JSC B31N)
SCFH	Standard Cubic Feet per Hour

SEM	Scanning Electron Microscope
SESC	Special Environmental Sample Container
SIM	Simulation
SNAP	Sterile Nitrogen Atmospheric Processing
SS	Stainless Steel
TBP	Tri-n-butyl phosphate
TCE	Trichloroethylene
TCEP	Tris(2-carboxyethyl)phosphine
TD-GC-MS	Thermal Desorption Gas Chromatography Mass Spectroscopy
TFE	Tetrafluoroethylene
THC	Total Hydrocarbon Count
TIC	Total Ion Count
TOC	Total Organic Carbon
TSP	Technical Support Procedure
TVOC	Total Volatile Organic Compounds
TXIB	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate
UCB-SSL	University of California Berkley – Space Science Laboratory
UCLA	University of California – Los Angeles
ULPA	Ultra-Low Penetration Air
UPW	Ultra-pure Water
VOC	Volatile Organic Compound
WSTF	White Sands Test Facility
XPS	X-ray Photoelectron Spectroscopy

1.0   INTRODUCTION

Future robotic and human spaceflight missions to the Moon, Mars, asteroids, and comets will require curating astromaterial samples with minimal inorganic and organic contamination to preserve the scientific integrity of each sample. The importance of proper curation has been recognized since NASA's first sample return efforts. During the Apollo program, terrestrial organic contamination was initially a great concern along with terrestrial inorganic contamination to lunar samples. Since the Apollo program ended, however, the lunar sample collection has been primarily concerned with inorganic contamination. Genesis and Stardust sample return missions have also been primarily concerned with particulate inorganic contamination, although organic reference materials and witness plates were archived. However, future missions will focus on strict protocols for reducing organic contamination that have not been seen in over 40 years. For example, OSIRIS-REx and Hayabusa-2 are two currently planned robotic sample return missions to carbon-rich asteroids. These missions will impose stringent new requirements for a reduction and characterization of organic contamination when compared to previous sample return mission practices. In addition, a future Mars Sample Return mission will have even more rigid protocols and procedural requirements on organic cleanliness as well as biological pathogen containment.

To properly curate these materials, the Astromaterials Acquisition and Curation Office under the Astromaterial Research and Exploration Science (ARES) Directorate at NASA Johnson Space Center (JSC) houses and protects all extraterrestrial materials brought back to Earth that are controlled by the United States government. As of 2014, the NASA Astromaterials Acquisition and Curation Office is responsible for the following sample collections:

- Apollo program lunar rocks and soils (est. 1969) and a subset of Soviet Union Luna program lunar material (est. 1971) – curated in an International Organization for Standardization (ISO) Class 6 cleanroom with glovebox isolation technology
- Meteorites – Antarctic Search for Meteorites (ANSMET) program (est. 1977) – ISO Class 6 cleanroom with glovebox isolation technology
- Cosmic Dust collected from high altitude aircraft (est. 1981) – ISO Class 5 cleanroom
- Space Exposed Hardware (est. 1985) – ISO Class 7 cleanroom
- Genesis Solar Wind Mission (est. 2004) – ISO Class 4 cleanroom
- Stardust Comet / Interstellar Dust Mission (est. 2006) – ISO Class 5 cleanroom
- Subset of Hayabusa Japan Aerospace Exploration Agency (JAXA) Asteroid Mission (est. 2012) – ISO Class 5 cleanroom with glovebox isolation technology

(Note: ISO 14644-1 Cleanroom Class determined by 2007 to 2012 weekly particle counts)

For over 40 years, the Astromaterials Acquisition and Curation Office has generated a legacy of preserving extraterrestrial samples in clean isolation and distributing these samples to the international scientific community. These samples are utilized for analytical investigations and for public displays throughout the world. Today, JSC curation stores and processes samples in seven major laboratory cleanrooms ranging from ISO class 7 to ISO class 4. Depending on the sample collection, samples are handled and stored in over 43 gaseous nitrogen gloveboxes, numerous gaseous nitrogen desiccators for long-term storage, class 100 flow benches, and/or cleanrooms. All curation laboratories have strict protocols for daily cleaning, daily monitoring, and material requirements for use in the laboratories to reduce cross-contamination with the samples. Materials entering the curation labs must have both low

outgassing and low particle shedding properties. In addition, sample containers, handling tools, and enclosures are routinely cleaned using well-established laboratory protocols and procedures. The result is a series of world-class scientific collections that forms an important foundation for the continuing progress of the planetary science, astrobiology, and related scientific communities.

After the Apollo program ended in 1972, the Apollo curation laboratories required little monitoring of organic contamination. This is because most laboratories that studied Apollo material were primarily concerned with inorganic contamination to their sample collections. However, organic studies have been conducted periodically in Lunar, Meteorite, and Genesis curation laboratories as directed by the Curation and Analysis Planning Team for Extraterrestrial Materials (CAPTEM), a NASA oversight committee, by the NASA JSC Contamination Control Officer (CCO), or by curators and/or individual principal investigators (PIs) upon request. The first effort to understand organic contamination was during the Apollo program. JSC's Lunar Receiving Laboratory (LRL), which was tasked with initial receipt of Apollo samples, conducted comprehensive studies on organics before and after Apollo 11 returned with samples in 1969. In addition, the program conducted many biological investigations on lunar returned materials. After the Apollo program, the next notable organic study (1986-1990) stemmed from the investigation of a lubricant compound named Xylan that was widely used in curation laboratories and was found to create a contamination risk. The largest Meteorite laboratory organic analysis was initiated in 1996 after publication of hypothesized biosignatures in the Martian meteorite ALH84001 and the subsequent findings of the Organic Contamination Working Group in 1997. This prompted additional organic testing in the Meteorite lab and reexamination of curation procedures overall, to include debate on issues such as the use of nylon bags for sample storage. Between 1998 and 2001, other organic contamination studies were developed alongside discussion of prospects for a Mars sample return mission. Genesis, the first samples returned since Apollo, was primarily concerned with organic contamination that could easily adhere to the highly pure semiconductor collectors during assembly of the spacecraft payload. Since the construction of the ISO class 4 laminar flow Genesis curation laboratory in 1999, airborne molecular contamination data have been measured in a systematic manner. Thus, airborne molecular contamination was documented during payload assembly in a newly built cleanroom, documented as the cleanroom aged and when facility changes were made, and continues today. While individual organic investigations have been carried out sporadically for over 40 years, no organic study or committee to date has taken a look at all JSC curation laboratories in a holistic study since the days of the Apollo program. The Organic Contamination Baseline Study in JSC Curation Laboratories was established to give CAPTEM, future mission planning teams, and PIs who work with astromaterial samples an understating of the current state of organic contamination in NASA JSC curation laboratories. This study was supported by the NASA Innovative Research and Development (IR&D) initiative through the Office of the Chief Technologist (OCT) at JSC, to plan for future missions that require clean handling and storage of samples with an emphasis on analyzing samples for both inorganic and organic contaminates.

During fiscal year (FY) 2012, we conducted a year-long project to compile historical documentation and laboratory tests involving organic investigations. In addition, we developed a plan to determine the current state of organic cleanliness in curation laboratories housing astromaterials. This was accomplished by focusing on current procedures and protocols for cleaning, sample handling, and storage. It should be noted that we have attempted to incorporate all relevant historical testing data for gloveboxes and cleanrooms that are found in JSC records. We augmented these studies with examination of glovebox sample processing to narrow the gap in our understanding of cleanliness during glovebox

processing. While the Genesis laboratory has performed numerous organic analyses of their ISO class 4 cleanroom environment, historically few analyses have been conducted inside gloveboxes themselves. This is important because future sample return missions concerned with organics will most likely use a form of glovebox isolation technology in addition to a cleanroom. For easier comparison of analytical results through time, we have converted all historical analytical results to the same units of measure. However, we have not included test data that have been widely published or material tests not specifically related to today's cleanrooms and gloveboxes.   While the intention of this report is to give a comprehensive overview of the current state of organic cleanliness in JSC curation laboratories, it also provides a baseline for determining whether our cleaning procedures and sample handling protocols need to be adapted and/or augmented to meet the new requirements for future human spaceflight and robotic sample return missions.

2.0 HISTORICAL ORGANIC CONTAMINATION RECORDS

2.1 *Apollo Program and the Lunar Receiving Laboratory*

NASA's first astromaterials curation collection was lunar rock and soil samples returned to Earth by the Apollo program in 1969. As early as February 1964, a Manned Spacecraft Center (MSC) internal memo written by the Assistant Chief for Space Environment to the Director of Engineering and Development identified the need for a Lunar Receiving Laboratory (LRL) and directed the concept of a 10'x10'x7' vacuum chamber operating at 10^{-5} torr with remote manipulators for handling lunar samples. A vacuum isolation chamber, rather than a positive pressure gaseous nitrogen chamber, was thought to be required to preserve the lunar volatiles for sample analysis. In addition, scientists were concerned with sample reactivity with Earth's atmosphere. By March 1965, the Center for Disease Control (CDC) published recommended procedures for Apollo sample handling and quarantine (Wood et al. 2002). In July 1965, NASA and the U.S. Public Health Service recommended construction of the LRL to have adequate biological barriers for both astronauts and returned samples. By January 1966, the Interagency Committee on Back Contamination (ICBC) was consequently established to include the CDC with Dr. David Sencer of the CDC as chairman, Department of Agriculture, Department of the Interior, Department of Health, Education, and Welfare, National Academy of Sciences, and NASA (Mangus and Larsen 2004). NASA's Planetology subcommittee of the Space Sciences Steering committee formed the LRL Working Group in May 1966 (Wood et al. 2002). The LRL Working Group and ICBC established the final design of the LRL facility (MSC building 37) in September 1967 for biological quarantine of astronauts, flown hardware, and lunar geologic material. After the establishment of the LRL, the Lunar Sample Analysis Planning Team (LSAPT) and the Lunar Sample Preliminary Examination Team (LSPET) were established to plan the handling and analysis of Apollo samples (Wood et al. 2002).

Scientists planning to work with lunar material designed a series of sample isolation chambers inside the LRL biological barrier called the "high vacuum complex" that held a 10^{-6} torr vacuum environment (White 1976) (figure 1). At the core of the high vacuum complex was the F-201 – a vacuum glove chamber designed for initial sample processing (figure 2). In the late 1960s, glovebox isolation technology was widely used by the nuclear and biological industry. The F-201 glovebox design was based on technology directly derived from handling nuclear material at Oak Ridge National Laboratory and would be used for preliminary sample examination. Materials for constructing the high vacuum complex were chosen with emphasis on reducing organic contaminates. This included stainless steel, Teflon - tetrafluoroethylene (TFE; C_2F_4), aluminum, Viton (fluorinated hydrocarbon), Pyrex glass for windows, and molydisulfide (MoS_2) lubricant. MoS_2 is usually added to synthetic ester/fatty acid amides to produce a grease applied to metal fasteners, and this compound was later determined to be a contaminant. The F-201 glove assembly arm consisted of stainless steel lined with polyurethane (White 1976). The glove assembly fingers, thumb, and part of the hand were fabricated out of nylon and the fingertips were impregnated with polyurethane. Viton A over-gloves were then used for each glove assembly arm and hand; exposing only Viton A material to the inside of the F-201 chamber. The over-gloves attached to the inner wall of the glove chamber and the glove assembly attached to a 10.5" diameter Viton A O-ring flange that created an air-tight seal (White 1976). For cabinet sterilization, both heat and peracetic acid sterilization was used in the atmospheric decontamination (R) cabinets of the complex (figure 3). The vacuum complex design also used liquid nitrogen (LN2) cold traps that were installed to reduce vacuum oil and other organic contamination. Further information on the design of the F-201 and the high vacuum complex was written by David White in NASA technical Note D-8298

(August 1976) entitled, "Apollo Experience Report – Lunar Sample Processing in the Lunar Receiving Laboratory High Vacuum Complex" (White 1976).
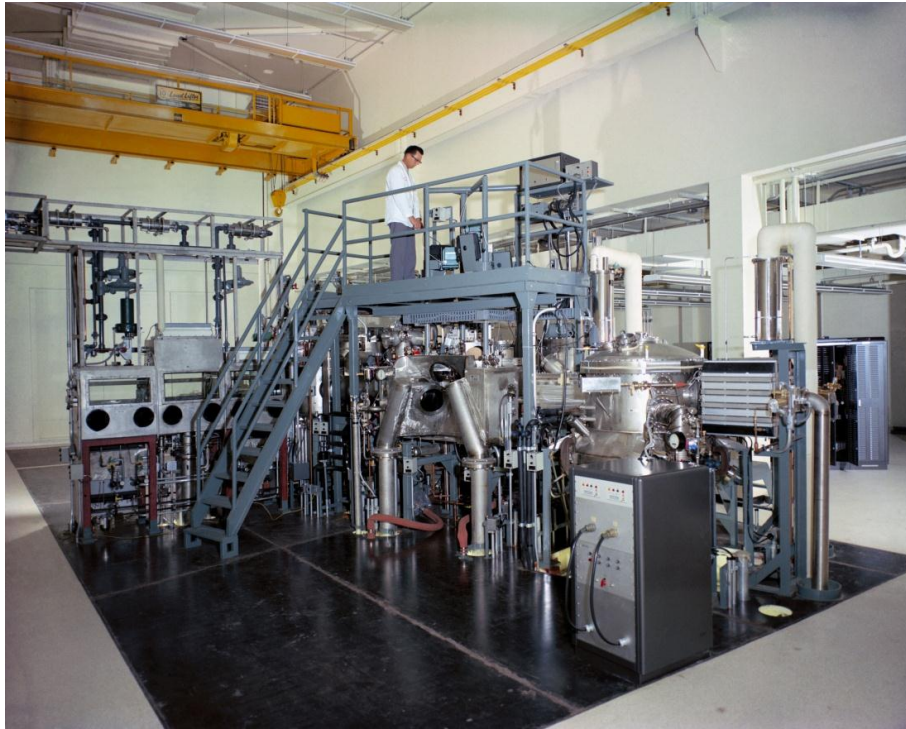
Figure 1: High Vacuum Complex during construction of the Lunar Receiving Laboratory in 1968 (NASA Photo # S68-25212).
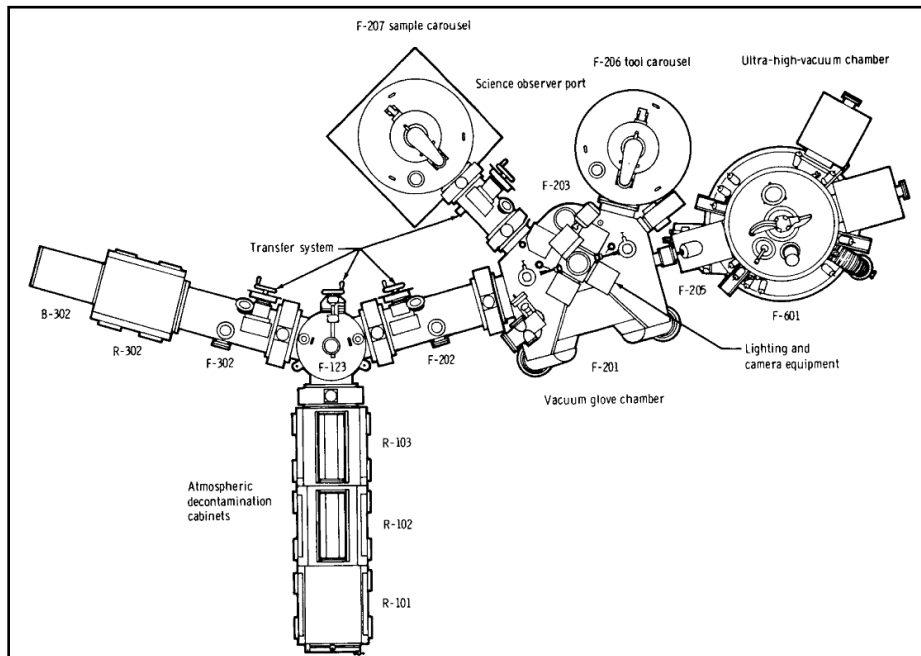
Figure 2: Components of the High Vacuum Complex in the Lunar Receiving Laboratory (White 1976:3).
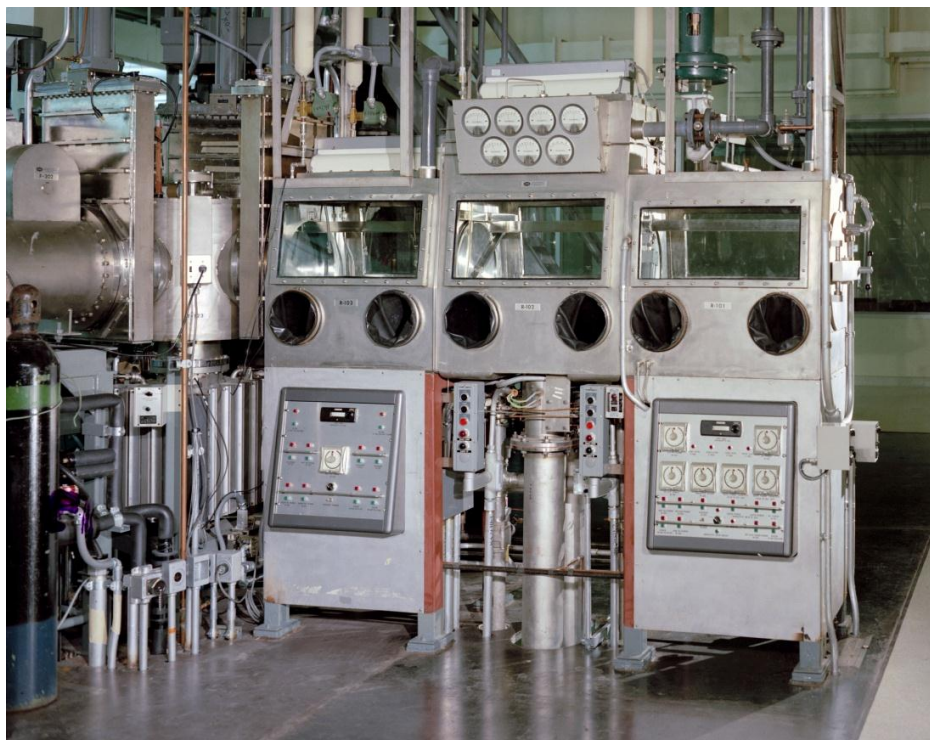
Figure 3: R-cabinets (Atmospheric Decontamination Cabinets) during construction of the High Vacuum Complex in 1968 (NASA Photo # S68-25204).

The first analyses of organics in Apollo materials were completed by the Organic Gas Analysis Group and the Action Committee on Organic Contamination. After the Apollo 11 mission, D.A. Flory of NASA Manned Spacecraft Center, and B.R. Simoneit and D.H. Smith of Space Sciences Laboratory, University of California, Berkeley submitted an unpublished report entitled the "Apollo 11 Organic Contamination History" (Flory et al. 1969) to the Organic Gas Analysis Group and the Action Committee on Organic Contamination. In May 1971, Simoneit and Flory wrote a full comprehensive report on organic contamination in a Lunar and Earth Science Division Internal Note MSC-04350 entitled "Apollo 11, 12, and 13 Organic Contamination Monitoring History" (Simoneit and Flory 1971). This document included results and discussions about potential surface contamination of Apollo materials from a wide variety of possible mechanisms. These include contaminants arising from the Apollo Lunar Sample Return Container (ALSRC) and contents, Apollo Lunar Hand Tools (ALHT), exhaust products from the Lunar Module (LM) (LM outgassing, venting of tanks, and Primary Life Support System (PLSS)), astronauts suit leakage, astronaut suit abrasion, all miscellaneous samples, cleaning at the White Sands Test Facility (WSTF), and contamination monitoring at the LRL. Flory and Simoneit (1972) also published their findings from this report in *Space Life Sciences* on "Terrestrial Organic Contamination in Apollo Lunar Samples" that has served the scientific community for years in understanding terrestrial organic contamination on Apollo Lunar Samples. The JSC organic baseline contamination study will focus on these historical reports concerning curation contamination analysis. We will highlight the Apollo 11 and 12 organic studies that involved the LRL and high vacuum complex contamination monitoring (Flory et al. 1969; Simoneit and Flory 1971; Flory and Simoneit 1972; Simoneit et al. 1973). This will include information from the March and June 1969 simulations, F-201 high-resolution mass spectral analyses, J-Traps, LRL Ottawa sand organic monitors, and LRL and WSTF tool cleaning.

2.1.1   Lunar Receiving Laboratory Simulations and Cold Trap Analyses

Apollo sample curation procedures were quickly developed, practiced, and refined prior to Apollo 11 sample return on July 24, 1969. JSC curation performed a rigorous cleaning procedure before simulating the receipt of Apollo 11 samples and conducting organic contamination monitoring in the LRL high vacuum complex.   "Procedure for Cleaning the Sample Processing Complex (F-201)", which was designated CP-3, was used to reduce organic contamination from June 19, 1969 (Simoneit and Flory 1971). This procedure was also applied to the cleaning of the F-201, F-123, F-207, F-202, F-206, F-302, and F-203 components of the high vacuum complex (figure 2). The following is a condensed version of this procedure:

- Vacuum interior with stainless steel or Teflon attachments
- Wipe down with lint-free KimWipes and ethyl alcohol (190 proof)
- Prepare complex for bakeout: open and close several series of valves, install cold panels, and fill LN2 cold traps
- Bakeout heat sterilization at 130°C ± 5°C for 48 hours
- Cool complex to 50°C and backfill with nitrogen
- Secure LN2 flow to cold traps; clean cold traps and seals with benzene/methanol solution

The CP-3 procedure relied heavily on the vacuum complex cold trap design to reduce organic contamination. A residual gas analyzer was used to check cleanliness during the cleaning and visual inspection. Due to higher-than-desired contamination levels found during Apollo 11 F-201 organic monitoring, a CP-3 revision A was implemented in preparation for Apollo 12 (Simoneit and Flory 1971). A written version of CP-3 revision A is dated to March 26, 1970, directly before Apollo 13 (Simoneit and Flory 1971). The procedural revision of CP-3 replaced the use of ethyl alcohol with redistilled precision cleaning agent (PCA) grade Freon 113 and added the use of dry, sterile nitrogen for drying the cabinets before conducting the 130°C bakeout:

- Vacuum interior with stainless steel or Teflon attachments
- Wipe down with lint-free KimWipes and PCA Freon 113
- Dry with sterile gaseous nitrogen (GN2)
- Prepare complex for bakeout: open and close several series of valves, install cold panels, and fill LN2 cold traps.
- Bakeout heat sterilization at 130°C ± 5°C for 48 hours
- Cool complex to 50°C and backfill with nitrogen
- Secure LN2 flow to cold traps; clean with benzene/methanol solution

Two simulations were conducted in the high vacuum complex before Apollo 11 samples returned to Earth. A series of test samples were analyzed to monitor organic cleanliness during the sample handling process utilized in F-201. The samples were tested at both the University of California Berkley – Space Science Laboratory (UCB-SSL) and the Gas Analysis Laboratory (GAL) at the MSC LRL. The March 1969 simulation reported the first contamination results from a sample for the Burlingame-Biemann experiment. A fired "Chromosorb-X" sample in a stainless steel container was introduced into F-201 under vacuum. The Chromosorb-X sample was transferred to aluminum foil inside the F-201 using the glovebox gloves. The sample was then placed into a nickel container through a Teflon funnel and the container was then analyzed in the GAL. According to the laboratory notes, the container and funnel

were exposed to contamination on the glovebox floor surface of the F-201. The experimental results report a relatively large amount of organic contaminants with silicone oil being the largest component. Silicone grease was predominately used for sealing flanges in the high vacuum complex including the O-ring flanges on the F-201 glovebox gloves. The March 1969 simulation was the first indication that the cold traps were not effectively removing all the silicone oil and other organic contaminants from the high vacuum complex. The Simoneit and Flory (1971) report also mentions that the silicone oil would prove to be very difficult to remove once it was introduced into the vacuum system.

Sample handling simulations continued in order to further reduce contamination. In the June 1969 simulation, five samples were run on the Organic Gas Analysis (OGA) Experiment, namely simulation (SIM) samples 2, 3, 4, 5, and 6. SIM sample 2 was a chromosorb sample supplied by F. Woller at NASA Ames Research Center (ARC) that was exposed to F-201 and a rock box. The analysis spectra indicated unsaturated hydrocarbons, with the highest observed peaks at a mass to charge ratio for the ion, m/e = 103 – 105 with 7.34×10^4 ion current/mg. SIM sample 5 was the control blank for SIM 2 run through the GAL. A major peak was found at m/e = 18, 47% of the total ion current. The total yield was found to be 1.59×10^4 ion current/mg, a factor of 4.6 below the F-201 sample. SIM sample 3 was a quartz sample tube that had a relatively high ion current of 7.02×10^5 ion current/mg. However, it was noted that there was a manufacturing defect with the sample tube. SIM sample 4 was a quartz sample tube that was placed in an indium sealed container. The container was transferred to the F-201 through a glove port and exposed for 4 days before the simulation. SIM 4 produced a mixture of unsaturated hydrocarbons, as noted in the chromosorb spectra with peaks to about m/e = 300. The second highest peaks were at m/e = 55 and lesser peaks up to m/e = 130. The third highest peaks range from m/e = 50 – 57. The team interpreted some of the spectra as benzene from the cleaning procedure. The total yield resulted in 1.38×10^5 ion current/mg. SIM sample 6 was a quartz blank from the Physical Chemistry test area. The total yield was 4.1×10^3 ion current/mg, a factor of 34 below the F-201 exposed sample. The report notes that another experiment was run by summarizing the quartz sample data with all masses above m/e = 50. This resulted with the blank at 3.7×10^2 ion current/mg and the F-201 at 5.56×10^4 ion current/mg. This was a factor of 165 more total ionization above m/e = 50 for the F-201 exposed sample.

Prior to the return of Apollo 11, high-resolution mass spectral analyses were also conducted on the F-201 vacuum system Granville-Phillips cold trap to identify organic contamination. Rinse residue from the CP-3 (1969 version) F-201 cleaning procedure was analyzed by gas liquid chromatography and high-resolution mass spectrometry (GLC-MS). The GLC-MS analyses were run on a Varian-Aerograph Model 204 gas chromatograph or a Perkin-Elmer Model 900 gas chromatograph with packed columns and GEC-AEI MS-902 mass spectrometer online to an XDS Sigma-7 computer. The mass spectra showed large amounts of octoil (dioctyl phthalate (DOP) plasticizer) and hydrocarbons through C_{30}, predominantly through C_{24}. Several molecular compounds containing one oxygen atom were found, mostly $C_{19}H_{32}O$ (androstanol) and $C_{19}H_{28}O$ (androstenone, predominantly found in sweat and urine). The interpretation at the time was that these compounds were possibly steroidal in nature due to the degree of unsaturation.

The F-201 LN2 cryogenic cold trap was tested for organic contamination after subsequent 120°C sterilization of the vacuum system. Rinse residue from the washings was again analyzed by GLC-MS. This residue was much more complex in nature compared to the Granville-Phillips cold trap with many different classes of compounds represented. The major compounds included octoil (dioctyl phthalate (DOP)), tri-n-butyl phosphate (TBP) – organophosphorus compound, a plasticizer, and hydrocarbons through C_{33}, predominantly unsaturated. An unknown silicone oil/grease used for the vacuum glove seals

was also found in large quantities in the F-201. Several unidentified organic chemicals related to silicone oils/grease were found on a fired Chromosorb X after the March 1969 simulation and is explained in more detail in the "Supplementary Report to G. Eglinton's Report to LSAPT on Organic Contamination Problems," April 17, 1969, by A.L. Burlingame and D.H. Smith, Space Sciences Laboratory, University of California, Berkeley. The minor components were $C_{16} - C_{18}$ free acids and di-n-butyl decanedioate, $C_4H_9OGO(CH_2)_8COOC_4H_9$ (dibutyl ester). The sebacic acids (naturally occurring dicarboxylic acid) are used in formulation of alkyd resins, and their esters are typically used as plasticizers, paint, hydraulic fluids, and synthetic lubricants. The silicone oils and plasticizers were found to be present even after multiple cleanings of the F-201. Today, it is hypothesized that the molydisulfide lubricant used throughout the high vacuum complex contributed to this silicone oil contamination (Charles Meyer, pers. comm. 2012). The results from the cold panel cryotrap were also noted to have major components of dibutyl phthalate, dioctyl phthalate, and decanedioate esters and minor components of cyclohexanone and other oxygenated fragments, unsaturated hydrocarbons $< C_{20}$, and carboxylic acids.

The cold finger J-Traps (J-101, J-124, and J-125) during bakeout for Apollo 11 were also analyzed by GLC-MS.   J-101 resulted in the identification of dioctyl phthalate, hydrocarbons $< C_{18}$ (possible hydrocarbon oils) and carboxylic acids $< C_7$. J-124 resulted in major components of $C_4H_8O_2$, m/e = 88, $C_2H_4O_2$ m/e = 60, M-CH$_3$, m/e = 73; and M-OH m/e = 71 mixture with butyric acid. In addition, dibutyl phthalate, as was reported for F-201, and dioctyl phthalate were also found. The J-125 had similar result to J-124 with a higher dioctyl phthalate peak.

2.1.2   Lunar Receiving Laboratory Ottawa Sand Organic Monitors

Ottawa sand organic monitors (OMs) were developed to monitor background contamination levels in the LRL processing cabinets. Two batches of standard Ottawa sand was sieved to 20-30 mesh for the F-201 vacuum system and for "bioprep" nitrogen processing cabinets. The F-201 system sand was washed with water and baked at 1000°C overnight. The bioprep batch was prepared with an acid washing reagent and baked at 1000°C for 30 hours at ARC. Control analyses of the batches used a benzene/methanol extraction and high-resolution mass spectrometry at UCB-SSL and the pyrolysis-mass spectrometer at the LRL. The F-201 OM control resulted in 3.08 µg/g of adsorbed organics with a calculated 136 ng/cm². The bioprep OM sand control generated 2.32 µg/g of adsorbed organics with a calculated 103 ng/cm². The spectral data shows mainly hydrocarbons from C_4 to C_{25} and dioctyl phthalate. Minor amounts of oxygenated species (such as cyclic ketones and carboxylic acids), and unknown $C_{23}H_{32}O_2$ and $C_{13}H_{12}O_2$ species were also found. Two Ottawa sand monitor backgrounds were established for the curator sample packaging clean cabinet that had adsorbed organics of 3.75 µg/g with a calculated 170 ng/cm² and 6.3 µg/g with a calculated 280 ng/cm². The GLC spectra also showed traces of dioctyl phthalate and some other lower weight organics.

Background monitoring for Apollo 11 was done with Ottawa sand in the LRL GAL and corrected with the OM controls. Samples were labeled as "BL" (Blank) with a corresponding sample number in some cases. Figure 4 shows the complied results from Simoneit and Flory (1971) report.

LRL Apollo 11 Organic Monitors					
Sample	Sample Type	LRL Location	Exposure Time	ion current/mg	Estimated Organic Contamination Level (ng/cm^2)
BL01 (#1007)	Ottawa Sand Blank in an outgassed Ni capsule	BioPrep Cabinetry	2.1 hours	6.35×10^5	240
BL02 (#1008)	Ottawa Sand Blank in an outgassed Ni capsule	BioPrep Cabinetry	2.1 hours	7.0×10^5	230
BL03 (#1010)	Ottawa Sand Blank transferred from glass ampoule to an outgassed Ni capsule	BioPrep Cabinetry	30 min.	6.3×10^6	17.2
BL04 (#1011)	Ottawa Sand Blank transferred from glass ampoule to an outgassed Ni capsule	BioPrep Cabinetry	3.5 hours	9.3×10^6	13.7
BL05 (#1014)	Empty Ni Capsule cleaned at WSTF, baked in F-201 at 120°C for 12 hours	F-207	Sample processing	4.1×10^6	7.8
BL06 (#1015)	Ottawa Sand Blank in an outgassed Ni capsule	F-201	20 days	1.3×10^8	490

Figure 4: LRL Apollo 11 Ottawa sand organic monitoring results (Simoneit and Flory 1971).

In the Simoneit and Flory (1971) report, BL 03 was considered a "good blank" for the bioprep cabinetry atmosphere with an estimated organic contamination level of 17.2 ng/cm^2 (<1 ppm) along with 13.7 ng/cm^2 (<0.5 ppm) for BL 04. The BL 03 sample consisted mainly of volatile hydrocarbons and some formaldehyde residue. The sample also had traces of silicone oil, Teflon, indium, and lead. The F-207/F-201 sample was also low with 7.8 ng/cm^2 estimated organic contamination for BL 05. The F-201 BL 06 sample was heavily contaminated with hydrocarbons from turbo pump oil and an unknown source of chlorinated diphenyls.

The Apollo 11 organic monitoring also sampled a WSTF cleaning blank (sample number 1006) and Ni capsule blanks. The WSTF OM resulted in 30 ng/cm^2 surface contamination. The major product of the contamination was from solvents such as Freon and benzene. A Ni capsule blank (sample number 1009) resulted in 6×10^5 ion current/mg with a calculated organic contamination level of 1.2 ng/cm^2. The GAL Ni capsule blank (sample number 1016) resulted in no significant organic material evolved from the capsule. The total ionization was 7.6×10^5 ion current/mg with an estimated organic contamination level of 1.5 ng/cm^2. The peracetic acid used at the LRL for sterilization was also analyzed for residual films by Dr. Rainer Berger (UCLA). After procedural deionized water washing, the organic residue extractable with 3:1 benzene/methanol was found to range from 1 to 10 μg/cm^2. It was also reported that the first benzene/methanol extract after the water washing reduces the organic contamination level by a factor of 5 to 7.

Apollo 12 background organic monitoring was also conducted in the GAL in the LRL. Based on the results from the organic monitoring during Apollo 11, the F cabinet cleaning procedure CP-3 was improved with revision A and resulted in reducing the overall organic load with the introduction of Freon 113. The figure below shows the complied Apollo 12 OM results from the Simoneit and Flory (1971) report.

LRL Apollo 12 Organic Monitors					
Sample	Sample Type	LRL Location	Exposure Time	ion current/mg	Estimated Organic Contamination Level (ng/cm^2)
BL07	Ames Ottawa Sand	BioPrep Cabinetry	BioPrep Control	3.3×10^5	0.7
BL08	Ames Ottawa Sand	BioPrep Cabinetry	5 hours	5.2×10^5	0.6
BL15	Ames Ottawa Sand	BioPrep Cabinetry	48 days	6.9×10^6	40
BL10	LRL Ottawa Sand	F-201	F-201 Control	1.5×10^6	1.5
BL11	LRL Ottawa Sand	F-201	11 days	2.3×10^6	1.7

Figure 5: LRL Apollo 12 Ottawa sand organic monitoring results (Simoneit and Flory 1971).

BL 08 sample was exposed to the bioprep cabinet for 5 hours with an observed 5.2×10^5 ion current/mg and a calculated organic content of 0.6 ng/cm^2 (<0.1 ppm). The BL 07 Ames Ottawa Sand monitor was the control monitor for BL 08 and had an observed 3.3×10^5 ion current/mg with a calculated organic content of 0.7 ng/cm^2 (<0.1 ppm). BL 15 was an Ottawa Sand organic monitor with exposure to the bioprep cabinetry for 48 hours. The result was 6.9×10^6 ion current/mg with a calculated organic load of 40 ng/cm^2. This analysis also highlighted the detection of decomposition products of some Teflon contamination, as well as volatile hydrocarbon contamination. BL 16 was the bioprep Ottawa Sand OM control that resulted in 1.9×10^6 current/mg with an estimated organic load of 12 ng/cm^2. BL 17 was an empty sample capsule from the previous analyses that was reinserted after sand removal. The results reported 5.0×10^5 current/mg with an estimated organic load of 2 ng/cm^2.

BL 11 F-201 Ottawa Sand was exposed to the F-201 vacuum chamber for 11 days with nitrogen backfilled three times for a total of 60 hours under nitrogen. This resulted in 2.3×10^6 ion current/mg with a calculated organic content of 1.7 ng/cm^2 (<0.1 ppm). The F-201 control was BL 10 Ottawa Sand. The sample had an observed 1.5×10^6 ion current/mg with an estimated organic content of 1.5 ng/cm^2 (<0.1 ppm). BL 12 was a solvent background for BL 07 resulting in 0.1×10^6 ion current/mg with an estimated 0.04 ppm organic content. BL 13 and 14 were run as calibration tests. BL 13 experienced some sample insertion problems and BL 14 was the rerun background monitor. BL 14 resulted in 2.38×10^6 ion current/mg.

For Apollo 13, the cabinets were cleaned again with CP-3 revision A and the formal procedure was written on March 26, 1970. The CP-12 procedure, dated March 26, 1970, was established for sampling and counting air particles in the LRL clean rooms, clean workstations, or controlled work areas. The procedure was the first detailed process for microscopic particle counting on work surfaces and gloveboxes and is the progenitor for similar, modern-day cleanroom processes. Unfortunately, no simulations or organic monitors were conducted for Apollo 13. The Simoneit and Flory (1971) report suggest that this was due to changes in personnel in the LRL and waiting on the success of Apollo 13.

2.1.3 Lunar Receiving Laboratory and White Sands Test Facility Tool Cleaning

The LRL cabinet tools were originally cleaned with a special LRL "flush and wipe" procedure. The procedure used lint-free KimWipes and Freon 113 to wipe or flush the tools along with a final rinse with Freon 113. Tool cleanliness was verified by a series of Total Organic Carbon (TOC) analyses that were run by GLC in the GAL. The first TOC analyses from a Freon blank, Gas Reaction Cell, and Gas Sampling Probe resulted in 200 ppm (mg/L) of organic contamination. The 200 ppm TOC levels were found to be too high for curation use, possibly due to the Freon distillation equipment installed at NASA MSC. Therefore, modified cleaning procedures sent all sample containers except the radiation counting lab (RCL) containers to WSTF for cleaning. For emergency situations, any tools that were not cleaned at WSTF could be cleaned at the LRL by a procedure outlined by the Organic Contamination Control Officer, entitled "Contingency Cleaning Procedure for LRL Apollo 11 Lunar Processing Tools." The following is a condensed version of this procedure for cleaning stainless steel, aluminum, and Teflon:

Preclean:
- 5 min. immersion in PCA Freon 113
- 5 min. ultrasonication in 1% Alconox detergent solution
- Rinse with tap water
- Rinse with deionized (DI) water
- Rinse with isopropyl alcohol (IPA)
- Dry with filtered dry sterile nitrogen

Final Clean in Class 100 Cleanroom:
- 5 min. ultrasonication in PCA Freon 113 with Bendix ultrasonic degreaser
- Spray rinse in PCA Freon 113
- Collect spray rinse sample for particle counts, Non Volatile Residue (NVR), and TOC analysis in LRL GAL

The condensed procedure for Viton cleaning was the following:

Preclean:
- Flush with cold tap water
- 10 min. immersion in 150°F Oakite Liqui-Det #2 (1 oz. to 1 gal. water) detergent solution assisted with nylon brushes
- Rinse with hot tap water (max. 140°F)
- Rinse with DI water
- Dry with filtered dry sterile nitrogen

Final Clean in Class 100 Cleanroom:
- 1 min. spray rinse with PCA Freon 113
- Collect spray rinse sample for particle counts only

The revised *Contingency Cleaning Procedure for LRL Apollo 11 Lunar Processing Tools* resulted in TOC Freon blanks of 0.08 ppm (mg/L), much lower than with the special LRL "flush and wipe" procedure. TOC analyses with this new contingency cleaning procedure for LRL tools and parts ranged from 0.02 to

5.24 ppm (mg/L) (Simoneit and Flory 1971). At WSTF, the majority of LRL tools were cleaned by CP-7 (Revision A) "Procedure for Cleaning Tools and Equipment used in the Vacuum Laboratory Processing Complex", dated September 24, 1969, and March 26, 1970. The following is a condensed version of this procedure:

Preclean:
- 10 min. immersion in PCA Freon 113
- 5 min. ultrasonicate in 1% Alconox detergent solution
- Rinse with tap water
- Rinse with DI water
- Rinse with chemically pure (CP) IPA
- Dry with filtered dry sterile nitrogen (GN2)

Final Clean:
- 10 min. immersion in 3:1 benzene/methanol solution, reagent grade
- 30 sec. immersion in PCA Freon 113
- 15 sec. spray rinse with PCA Freon 113
- Air dry

Class 100 Cleanroom Clean:
- 5 min. ultrasonicate in PCA Freon 113
- Spray rinse with PCA Freon 113
- Placed parts in clean Teflon bags purged with GN2

Samples were also collected during the final Freon ultrasonication bath and spray rinse for particle counts, Non Volatile Residue (NVR), and TOC analysis. "Procedure for Cleaning Plastic and /or Rubber Tools or Equipment for Use in LRL", designated CP-5, dated August 1, 1969, was also used at WSTF. The following is a condensed version of this procedure:

- 5 min. ultrasonication with 1% Alconox cleaning solution
- Rinse with tap water
- Rinse with DI water
- At a Class 100 workstation, Rinse with 190 proof ethyl alcohol
- Run TOC analysis

CP-5 revision A, March 26, 1970

- 5 min. ultrasonication with 1% Alconox cleaning solution
- Rinse with DI water at 140° F
- Rinse with filtered DI water
- Take particle counts
- Air dry for 1 hour and package in Teflon
- For Viton over gloves, wipe down with KimWipes and 190-proof ethyl alcohol

The WSTF LRL tool organic analyses from CP-7 and CP-5 cleaning procedures showed the level of organic cleanliness to be between 0.5 to 1.0 ng/cm^2 and were thought at the time to be well within specifications for most tools. However, the WSTF high-resolution mass spectral analyses showed evidence of dioctyl phthalate, phthalate esters, carboxylic acids, and traces of hydrocarbons.

ALSRCs were designed to preserve samples in a lunar-like vacuum. A York mesh lining, knitted from 2024 aluminum alloy, inside the ALSRC was used to protect the samples from vibration and shock during return flight. Analyses of aluminum foil and York mesh samples from the Apollo 11 mission indicated organic contamination levels of about 1 $\mu g/cm^2$. Paradoxically, Apollo 11 bakeout of the ALSRCs in the LRL actually resulted in adding organic contamination. These organic monitoring results led to improvement in flight hardware for Apollo 12 and future missions and resulted in about 10-100 ng/cm^2 of organic contamination. For the York mesh material, a 100 ng/cm^2 cleanliness level was the lowest achieved. This was possibly due to aluminum oxide residues and high adsorption characteristics of the material.

Outgassing of Apollo spacecraft, spacesuit, equipment, et cetera introduced no detectable contamination to the lunar samples from Apollo 11 and 12. However, LM engine exhaust products were seen in the samples. The exhaust products were minor in concentration, but can be seen over large areas. Organic compounds consisted of acetylene, hydrogen cyanide, ethylene, formaldehyde, propadiene, ketene, cyanous acid, hydrazoic acid, various methyl amines, acetaldehyde, methyl nitrite, formic acid, nitrous acid, butadiyne, various hydrazines, nitromethane and some nitrosohydrazines with traces of other oxidation derivatives of UDMH and hydrazine. For the bulk sample box, organic contamination levels were calculated to be 2.5 x 10^{-10} g/g for LM contamination.

2.1.4 Lunar Receiving Laboratory Organic Results Summary

Lunar samples placed into the F-201 glovebox were mostly contaminated by large amounts of octoil (i.e., DOP) and hydrocarbons predominantly through C_{24} (Flory et al. 1969; Simoneit and Flory 1971). Tri-n-butyl phosphate and di-n-butyl decanedioate were also found in significant quantities. The unknown silicone oils (mostly likely from the use of molydisulfide lubricant) were also present, but in much lower concentrations. The June 1969 simulation analyses found large amounts of contamination due to unsaturated hydrocarbons. However, hydrocarbon contamination was largely absent from the R cabinetry blanks even though these samples documented a peracetic acid leak. R cabinetry (R-101, R-102, R-103) were the atmospheric decontamination "airlocks" attached to the vacuum system (figures 2 and 3). Particulate contamination was also observed during both Apollo 11 and 12 during LRL preliminary examination by the Preliminary Examination Team (PET). It was noted that, in one case, small fragments of gold-coated Mylar insulation was found from the LM. Teflon particles from the sample bags were also found on the samples. Figure 6 is the compiled summary list of LRL organic contaminates (Flory and Simoneit 1972; Simoneit and Flory 1971; Simoneit et al. 1973).

Organic Compounds	LRL Location
Hydrocarbons	Ubiquitous
Fatty Acids	F-201 (LRL High Vacuum Complex Processing)
Palmitic Add	F-201 (LRL High Vacuum Complex Processing)
Stearic Acid	F-201 (LRL High Vacuum Complex Processing)
Dibutyl Phthalate	F-201
Dioctyl Phthalate	Ubiquitous
Didecyl Phthalate	Apollo Lunar Sample return Container (ALSRC)
Dinonyl Phthalate	Apollo Lunar Sample return Container (ALSRC)
Dioctadecyl Phthalate	Apollo Lunar Sample return Container (ALSRC)
Silicones	F-201, Astronaut suit
Trimethylene oxide	Nitrogen Sample Processing cabinet
P-Dioxane	Nitrogen Sample Processing cabinet
1,3,5,-Trimethyl-2,4,6 -Trioxane	Nitrogen Sample Processing cabinet
Orcinol	Nitrogen Sample Processing cabinet
Freons	NASA WSTF Cleaning
Tributyl Phosphate	F-201
Trihexyl Phosphate	ALSRC
Oleamide	ALSRC
Cholesterol	ALSRC
Dibutylsebacate	F-201
Dioctyladipate	SESC Lid (Apollo 12)
Chlorodiphenyls	ALSRC
Diisopropyldisulfide	ALSRC
Pyrene	F-201
Tetrahydronaphthol	ALSRC
Ionol	polypropylene bottles
Teflon	Nitrogen Sample Processing cabinet

Figure 6: Compilation of known LRL organic contaminants (Flory and Simoneit 1972; Simoneit et al. 1973; Simoneit and Flory 1971).

The Apollo program organic contamination summary described the desire to reduce potential contamination to below 1 ng/g (Flory et al. 1969; Simoneit and Flory 1971; Simoneit et al. 1973). It also desired the development of cleaning protocols capable of reducing organic contamination below 1 ng/cm^2 on surfaces (Simoneit and Flory 1971; Flory and Simoneit 1972). In most cases, cleaning for bright, polished, planar surfaces resulted in cleanliness levels in the range of 1 to 10 ng/cm^2. From the point of sample collection with the ALSRC to scientific distribution of sample from the LRL, the report highlights several potential significant sources of organic contamination. For the LRL, prior to Apollo 11, organic contamination levels were observed as high as 1000 ppm, and could potentially be introduced to lunar samples. Revamping laboratory sample handling and cleaning procedures reduced this level of organic contamination to < 1 ppm for the Apollo 11 samples (Flory and Simoneit 1972; Simoneit et al. 1973). Further procedural revisions based on organic monitors and careful analysis of contamination sources, reduced organic contamination levels even further to below 0.1 ppm during Apollo 12 and later missions. In many cases, this was below the level of contamination in organic geochemistry research laboratories at the time.

The LRL facility organic monitoring results are the most comparable data with today's curation cleanrooms and gloveboxes (figures 4 and 5). In the late 1960s, gas chromatographic and mass spectrometry techniques used in organic geochemical and bioscience investigations were capable of detecting organic compounds in quantities < 1 ng/g (ppb) (Simoneit and Flory 1971 and Flory and Simoneit 1972). As a comparison, today's gas chromatography mass spectroscopy instruments are capable of detecting organic compounds in quantities < 0.1 ng/g (ppb), an order of magnitude lower, with limits of detection of mass per volume approaching < 20 fg/ml (ppq) (Fialkov et al. 2007).

2.1.5 Lunar Receiving Laboratory Biological Containment

In addition to geologic preliminary examination in the high vacuum complex, a subset of lunar samples were required to be examined by biologists in separate laboratories inside the biological barrier in the LRL building 37. Lunar samples were placed inside a series of class III biological containment gloveboxes to evaluate the risk of biological pathogens and other signs of back contamination. The class III biological glovebox technology was based on biosafety level 4 isolation technology derived from handling the most extreme pathogens at Fort Detrick. However, little is known about the manufacturer of these Class III gloveboxes and any organic contamination testing that may have been done prior to the arrival of samples. Lunar samples were initially processed in the F-201 glovebox simultaneously with the quarantine period. The biological safety tests were derived from the Comprehensive Biological Protocol for the Lunar Receiving Laboratory (Baylor University College of Medicine 1967). The Baylor University College of Medicine developed the "Baylor Protocol," which was a series of biological tests of lunar material. The Baylor Protocol included tests of bacteriology, mycology, virology mycoplasma, mammalian animals, botanical systems, and invertebrate/lower vertebrate systems. However, the full procedure was never fully implemented. The biological quarantine of the Apollo program in the LRL is well documented. Suggested further reading includes: Mangus and Larsen 2004; McLane et al. 1967; Allton et al. 1998; Benschoter et al. 1970; Eglinton et al. 1974; Fox et al. 1981; Gehrke et al. 1971, 1972, 1975; Harada et al. 1971; Holland et al. 1973; Johnson et al. 1972; Kemmerer et al. 1969; Long et al. 1972; Sagan 1972; Taylor et al. 1970, 1971, 1973; Walkinshaw et al. 1970, 1973; Weete and Walkinshaw 1972. The final conclusion of these studies stated that all soluble organic compounds and amino acids found in the samples were indigenous to Earth. The lunar sample quarantine testing concluded that there was no evidence of life or any biological hazard to impede the release and distribution of samples for scientific research outside the LRL biological barrier. After the Apollo 14 mission, all quarantine protocols were abandoned and only a few fundamental carbon studies were done on later missions (Mangus and Larsen 2004). In addition to the biological studies, several published studies on carbon, C isotopes, carbon monoxide, methane, carbon dioxide, and hydrocarbons found in lunar material are available and suggested readings include: Abell et al. 1971; Burlingame et al. 1970; Cadogan et al. 1971, 1972; Chang et al. 1971; Epstein and Taylor 1970, 1973; Friedman et al. 1970; Holland et al. 1972; Kaplan and Smith 1970; Kaplan et al. 1970; Kvenvolden 1972; Moore et al. 1970; Nagy et al. 1970, 1971; Oró et al. 1970, 1971.

High vacuum is intrinsically difficult to work with, especially when manipulating large numbers of samples. As a result, the F-201 and other components in the high vacuum complex were prone to leaks and glove failure. After Apollo 12, high vacuum was replaced with gaseous nitrogen gloveboxes based on biological isolation cabinet designs. In November 1970, just before Apollo 14 return samples, the LSAPT deactivated F-201 and replaced it with a series of gloveboxes called the Sterile Nitrogen Atmospheric Processing (SNAP) Line (figure 7) and Nonsterile Nitrogen Processing Line (NNPL) (Wood

et al. 2002). During Apollo 14, the SNAP line gloveboxes were used as the primary quarantine and were set at 1.0 inH$_2$O negative pressure with oxygen at 25 to 50 ppm and moisture restricted to 85 to 125 ppm (Reynolds et al. 1973). The NNPL was used to process lunar material more quickly after the quarantine period in the SNAP line. The NNPL was set at a slight positive pressure nitrogen environment with oxygen at 10 to 30 ppm and moisture at 15 to 25 ppm (Reynolds et al. 1973). Flory and Simoneit (1972) suggest that as much as 10 ppm of organic contamination was added by the introduction of the SNAP line over the use of the high vacuum complex (Simoneit et al. 1973). The main source of organic contamination was the sterilization process, which used ethylene oxide and created polymerization products as well as introduced dioctyl phthalate.

After Apollo 14, the Apollo program quarantine requirements were abandoned. The LRL continued to operate more as a curation laboratory than a quarantine facility for Apollo 15 through 17. In 1973, all Class III biological gloveboxes and the high vacuum complex were abandoned and disassembled in favor of the continued use of positive pressure GN2 environment gloveboxes. We have little documentation of what happened to these LRL gloveboxes. However, Everett Gibson (pers. comm. 2012) suggest that the F-201 glovebox and high vacuum complex was disassembled and relocated to Los Alamos National Laboratory to be used for other government projects.

Figure 7: SNAP line in LRL during Apollo 14 in 1971 (NASA Photo # S-71-19264).

2.2   Establishing the Lunar Curation Laboratory 1973 to 1979

After Apollo, the LRL was replaced with a dedicated curation facility. From 1973 to 1979, an interim lunar curation laboratory was established on the second floor of JSC building 31 (B31). Today, this area houses the Antarctic Meteorite, Stardust, and Cosmic Dust laboratories. During this time, a plan was initiated to expand B31 and construct a new facility called building 31 North (B31N). From 1970 to 1972, new GN2 gloveboxes were manufactured by Stainless Equipment Company in Englewood, Colorado, and placed in the interim lunar laboratory in B31. In addition to planning B31N, NASA built a remote storage facility for lunar samples at Brooks Air Force Base in San Antonio, Texas, in 1975. This remote storage facility was designed to continuously house a subset of the lunar sample collection in case of a catastrophic event in Houston. In 1979, B31N was established as the new lunar curation laboratory. About 80%, by weight, of lunar samples still reside in this facility with a subset stored at a remote location as well as samples allocated for scientific research and educational outreach. The B31N gloveboxes were manufactured from 1977 to 1978 by the Stainless Equipment Company and were designed with 316L stainless steel (11 and 14 gauge with continuous welds), 304 stainless steel pipe fittings, Viton gaskets, safety glass windows, and neoprene gloves. It should be noted that the glove material was not mentioned in Stainless Equipment Company primary documents, but these gloves are used today and are thought to be the original choice in 1978. Most of the original glass windows cracked early on and were replaced with Lexan (polycarbonate) material (Jack Warren and Charles Meyer pers. comm. 2012). After an extensive data mining effort in the JSC curation data center, no primary documentation or reports were found that detailed organic testing for the gloveboxes purchased from the Stainless Equipment Company from 1970 to 1978. However, there are LSAPT facility subcommittee minutes from May 1975 to March 1979 that document the construction of the B31N Lunar Laboratory as well as Brooks Air Force Base remote storage. After Apollo 12, the Apollo program in 1970 began to relax organic requirements for Apollo 13 and subsequent missions. This relaxation of requirements seems to coincide with the LSAPT discussions that the scientific community no longer required organically clean samples. However, facility construction memos and LSAPT meeting minutes do suggest that material testing did occur after Apollo 12, but the role of organics was not thoroughly explored. Some LSAPT memos suggest that these organic investigations may have been related to future human spaceflight Mars mission planning in the early 1970s at the end of the Apollo program.

2.3   Xylan Contamination and Lessons Learned 1972 to 1990

Xylan is a lubricating polytetrafluoroethene (PTFE) Teflon paint coating manufactured by Whitford Corporation in West Chester, Pennsylvania. In 1972, Xylan was proposed as a replacement for the molydisulfide lubricant universally used on fasteners in the LRL. For about 18 years (1972 to 1990), Xylan was primarily used in the Lunar and Meteorite laboratories for stainless steel fastener (screw and bolt) threads. Xylan was used to prevent galling in lab jacks, bolt top sample containers, inside and outside glovebox door handles, camera mounts, band saw stage, band saw blades, band saw screws, and various core drive tube dissection hardware. The introduction of Xylan into the Lunar curation laboratory was documented in a series of internal JSC memos in the early 1970s. A.H. Beatty, Jr. of Brown & Root – Northrop first proposed on January 12, 1972 an evaluation and use of Xylan 1010 coating on bolts to prevent stainless steel galling in the Lunar curation facility. The next day (January 13) Kenneth Suit in the Laboratory Operations Branch requested that the Contamination Control Committee approve Xylan 1010 as an accepted material for use in the curation labs based on Beatty's proposal. On January 25, 1972, the use of Xylan 1010 was conditionally approved by Michael Duke, chairman of the Contamination Control Committee, with three constraints: 1) no pigment used in manufacturing; 2) 20

test coupons were requested for stainless steel and aluminum; and 3) the Whitiford Corporation must submit all operating procedures related to manufacturing of Xylan. The Duke memo further stated that if all three criteria were met, the contamination control committee would formally consider the material for acceptance. The next day (January 26) Kenneth Suit wrote a memo delaying the proposed investigation of Xylan due to the Apollo 16 schedule. On February 2, 1973, the Contamination Control Committee chair, now Michael Reynolds, approved Xylan after receiving documentation from JSC and the Xylan manufacturer. The memo also notes that JSC personnel visited the Whitford manufacturing plant in Pennsylvania and provided the requested chemical information to the committee. However, it is unclear from the available documentation whether all the constraints on Duke's memo were met and completed.

The first written indication of possible Xylan contamination was documented in an internal routine memo on October 22, 1986, by Charles Meyer, JSC Contamination Control Officer. Meyer mentions that JSC scientist Dave McKay observed flakes of the Xylan material on the lunar core extrusion table during sample processing. Meyer states that this warrants further investigation of Xylan contamination. On December 1, 1986, Meyer wrote a memo to JSC Deputy Chief Biomedical Branch on the Xylan offgassing analysis. The report discusses the real possibility that Xylan is contaminating the astromaterial collections and should be removed from all curation labs (Lunar, Meteorite, and Cosmic Dust labs at the time). This memo did not prompt the immediate removal of Xylan, to a certain extent, because no adequate substitute was proposed to prevent thread galling and subsequent particle contamination.

Ian Wright et al. (1989) of The Open University in the United Kingdom (UK) published an article in the July 20, 1989 issue of *Nature* entitled "Organic Materials in a Martian Meteorite." This scientific team claimed to have found the first chemical signatures of organic compounds from Mars. After internal discussions of this publication and the possibility of JSC contamination affecting the results, Charles Meyer wrote another memo about the contamination report on Xylan to the Lunar Sample Curator on October 16, 1989 – almost 3 years later. The memo again discusses the possibility that Xylan was contaminating astromaterial collections and should be removed from all curation labs. After little response from the Lunar Sample Curator, on April 20, 1990, Meyer wrote a memo to the general curation staff on the Xylan problem and potential for contamination. In addition, on May 21, 1990, Charles Meyer, now Associate Curator, wrote another memo to the Lunar Sample Curator about the Xylan problem. Meyer further reported and officially briefed curation on the February 1990 Lunar and Planetary Science Team (LAPST) meeting discussion on Xylan contamination and the possibility of causing a false positive chemical signature of organic compounds from the Martian meteorite.

On May 25, 1990, NASA LAPST chairmen Michael Drake and Lunar and Planetary Institute director David Black wrote an official letter to NASA JSC Solar System Exploration Division Chief Michael Duke. Duke was the chairman of the Contamination Control Committee who had requested additional testing of Xylan before material approval in 1972. In the LAPST memo, Drake wrote that JSC curation must cease all operational use of Xylan and eliminate Xylan contamination effective immediately. The memo also stated that JSC curation must document all present and past usage of the material. From February to June 1990, several curatorial orders were written by Meyer to investigate the extent of Xylan use and to remove it from curation labs.

Based on this letter, Ruska Laboratories were contracted by JSC curation to conduct a complete analysis of Xylan in May 1990. After testing, Xylan was found not to be a pure fluoropolymer but a combination

of multiple chemicals when applied as a liquid resin. The results showed that the chemical composition of Xylan 1010 included the following:

- Polytetrafluoroethylene (PTFE)
- Fluorinated ethylene propylene (FEP)
- Polyamide
- Ethyl Acetate
- N, N – Dimethylformamide (DMF)
- Xylene
- N-Methyl-2-pyrrolidone (NMP)

While the major components of Xylan were found to be a mixed fluoropolymer, PFTE and FEP, plasticizers were also found to be present. The report also tested a newer Xylan that contained even more compounds including butylated hydroxy toluene (BHT), a series of methylphenyl siloxanes (a type of silicone rubber), and a series of n-alkanes with carbon numbers from 21 to 31. Minor compounds were also found in the new Xylan that included ethyl acetate, benzene, acetic acid, p or m-xylene, o-xylene, several phthalates, hexadecanoic and octadecanoic acids, and an alkyl amide. These minor chemical compounds were used as binding agents and additives during the manufacturing process to create a complex chemical structure. As a result, the potential for particle and outgassing contamination to astromaterials increased the complexity of understanding point sources of contamination during organic monitoring. In addition, the Xylan study recognized that polyamides in the gloveboxes could potentially give a false biochemical signal, particularly for research involving amino acids and proteins. However, only JSC curation internal memos documented this hypothesis and this interpretation of the data set was not noted in the final Xylan reports.

In August 1990, JSC implemented a plan for removal of Xylan from all curation laboratories. In most cases, Teflon replaced Xylan for lab jacks and glovebox doors. However, most stainless steel bolts and screws remained with no alternative for the anti-galling coating. This made it difficult to work with glovebox windows, bolt-top sample containers, and fasteners in curation labs. As a result, since 1990 many bolt-top sample containers in long-term storage have required the bolts be cut or drilled to open the containers.

The Ruska Laboratory findings on Xylan prompted a series of inquiries into potential contamination by that material. After Ian Wright's team studied the Ruska laboratory findings, they believed that compounds described by Wright et al. (1989) Nature publication bore a resemblance to constituents of Xylan. Wright et al. (1992) published an article in Proceedings of Lunar and Planetary Science entitled "Xylan: A Potential Contaminant for Lunar Samples and Antarctic Meteorites." This article retracts some of the claims from their 1989 publication about finding organic compounds from Mars and concludes that Xylan contamination may have the potential to hinder past and future scientific investigations of organics. The article highlights the Xylan contamination found in JSC curation laboratories and includes some of the results from the Ruska Laboratory report on Xylan.

The timeline for the 1972 introduction of Xylan into curation laboratories to the 1990 removal is well documented through many internal NASA memos and reports. To date, the Xylan contamination story is the best example of JSC organic contamination found that has adversely affected the scientific analyses of

astromaterials. The study of these memos and timeline of events could potentially be used as lessons learned for the development of future curation practices.

2.4   Organic Contamination Review Group 1997

The discovery of possible polycyclic aromatic hydrocarbons (PAHs) and other biomarkers identified in the ALH84001 Martian meteorite in 1996 motivated the next organic study in JSC curation (McKay et al. 1996; Bada et al. 1998; Golden et al. 2001 and 2004). In 1997, NASA commissioned the Organic Contamination Review Group to review potential organic contamination in the Antarctic Meteorite laboratory. Jeffrey Bada, Director of the NASA Specialized Center of Research and Training (NSCORT) in Exobiology at the Scripps Institution of Oceanography, University of California at San Diego was the chair of the committee that reviewed the handling and cleaning procedures in the laboratory. The committee was charged with evaluating four types of contamination: 1) contamination of organic compounds that have a major role in biochemistry, such as amino acids; 2) contamination of organic compounds that are common in the environment, such as PAHs; 3) contamination of viable microorganisms, such as bacteria; and 4) contamination with macromolecular biomolecules, such as deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). However, the final Bada report (Bada et al. 1997) does not directly address the four types of contamination with new data.

The highlighted findings from the Bada report do include several interesting observations and recommendations. The report first draws attention to a 1992 NASA memo written by John James who was the JSC Chief Scientist for Toxicology at the time. The memo states that the potential for contamination of samples can be linked to the use of nylon sample bags. This internal memo perhaps is a continuation of further examining the polyamides contamination from Xylan, knowing that nylon bags also contain polyamides. Heat sealing nylon and polyethylene bags generate many compounds. Caprolactam, found on many Balazs test reports, is usually generated from pyrolysis of nylon-6 and can hydrolyze to the non-protein amino acid 6-amino-n-hexanoic acid. In addition, heating polyethylene can also liberate phthalates that are used as plasticizers.

The common use of nylon and polyethylene bags in JSC curation was first initiated in 1979 by LAPST in view of the relatively high permeability of Teflon to water during cleaning at WSTF and JSC.   Before 1979, the lunar and meteorite collection only used Teflon bags for samples. Budget cuts also prompted JSC curation to find costs savings plans through reviews of curation procedures. An April 1, 1980, memo written by James Townsend entitled "Cost Reduction in Cleaning" initiated several major changes to curation: 1) the use of Teflon was changed to the use of nylon and polyethylene bags that was noted to save $7972.00 (in 1980 dollars); 2) the use of pressurized IPA (85 psig) replaced the Toluene/Methanol washing in many cleaning procedures (it should be noted that while this memo is written with "Toluene/Methanol" washing; JSC-03243 cleaning procedures from this era only mentions a "3:1 Benzene/Methanol" washing and this may have been a clerical error); 3) the use of a black light inspection, quality assurance procedures and the use of class 100 flow bench during final flush rinsing was eliminated to save procedural time and personnel costs.

Below are condensed steps of the glovebox/cabinet nominal cleaning procedure entitled "Lunar Sample Curatorial Facility Cleaning Procedures for Contamination Control" – JSC document #03243, June 1, 1981, which superseded the October 1, 1971, procedure version (appendix II has CP-1 pages 4 – 7):

- Acid Wash 2% nitric acid solution with distilled water (when required)
- 1% Oakite Liqui-Det detergent solution with distilled water
- Mechanical scrubbing with nylon brushes, scouring pads, Scotch Brite pads and stainless steel toothbrushes
- Rinse with distilled water
- Isopropyl alcohol (IPA) rinse and gaseous nitrogen (GN2) dry
- Black light inspection
- 1% Oakite Liqui-Det solution with distilled water (Millipore can at 85 psig)
- Isopropyl alcohol (IPA) rinse (Millipore can at 85 psig)
- Vacuum flask for liquid pickup and squeegee with GN2 dry
- Acid Wash 2% nitric acid solution with distilled water (when required)
- Freon 113 (Millipore can at 85 psig)
- Perform particle counts, total hydrocarbon counts (THCs), and non-volatile residue (NVR) analysis.

A separate degreasing procedure for cabinets in the 1981 procedure uses high-pressurized Freon 113 and 2% nitric acid wash along with mechanical scrubbing. The major difference between the 1971 JSC 03243 cleaning procedure is the replacement of the 3:1 Benzene/Methanol washing with IPA. Historically, the 3:1 benzene/methanol solution was used in the 1969 LRL high vacuum complex cleaning procedure for degreasing. The addition of nitric acid in the procedure was initiated for concerns of lead contamination and was not meant to be used for passivation of the stainless steel in the gloveboxes. After these cleaning procedures were adopted on October 1, 1971 (JSC 03243), JSC curation entered a period that included adapted cleaning procedures due to cost saving plans, chemical phase-outs, and safety issues without officially investigating how this change will affect the laboratory cleanliness standards. Even though there is little documentation for the reasons of these changes, the JSC 03243 cleaning procedure document can be used as a primary source for lessons learned on cleaning protocols for over 40 years.

In the Bada final report, the committee also mentioned the lack of documentation when changes were made in the JSC curation cleaning procedures. Specifically, the committee noted that curation tool cleaning procedures were significantly changed by switching from Freon 113 to Ultra-pure Water (UPW) in 1994. The committee states that the new cleaning procedure using UPW needs to be further investigated to confirm that these changes do not hinder cleanliness standards. This change in the cleaning procedures meant that tools and gloveboxes were no longer being adequately degreased by a solvent and reducing organic contamination. The Organic Contamination Review Group also stated that the cleaning procedures do not include organic contamination specifications and no data currently existed in 1997 on organic contamination. In addition, the Bada report mentions that Isopods, containers used to transport meteorites from Antarctica, could possibly be a "huge potential source of bioorganic concentration" as well as flow benches used in the Meteorite laboratory that are continuously exposed to humans and other biocontaminants. The Bada report provides two final recommendations: (1) JSC curation must establish routine organic testing of the Meteorite lab and UPW with TOC analysis; and (2) JSC curation must have more control of samples and segregation of unique meteorite samples. While the Meteorite lab today does not routinely measure for organics, the UPW is monitored by TOC and unique samples are segregated in the Meteorite laboratory.

JSC curation began other studies in organic contamination from 1998 to 2001 in addition to those surrounding ALH84001. Both the Genesis solar wind mission and a potential, future Mars Sample Return mission prompted several small studies on organics contamination in curation. JSC Center Director Discretionary Funding was used to conduct several organic baseline tests in Lunar and Meteorite laboratories. These studies were conducted serendipitously at the same time that the Tagish Lake meteorite was examined at JSC in 2000. However, no results were published related to Tagish Lake or ALH84001 involving these organic tests. In addition to organic testing, several biological investigations on extremophiles were conducted in the JSC Genesis laboratory and compared with other NASA cleanroom environments (Venkateswaran et al. 2004; La Duc et al. 2007; Moissl et al. 2007, 2008; Moissl-Eichinger 2011).

2.5   *Glovebox Organic Contamination Results 1998 to Present*

For Lunar and Meteorite curation laboratory gloveboxes, no documents are known to exist before 1998 concerning organic analyses. This report has compiled all existing documents from organic tests that have been completed by JSC curation since 1998. The following analyses are for all glovebox testing prior to the 2012 organic baseline study. In addition, some of the glovebox testing was in conjunction with cleanroom testing. In all of these cases, we have provided all organic testing data that include both gloveboxes and cleanrooms for comparison.

2.5.1   1998 Meteorite Laboratory Organic Analyses

The first in-air organics sampling was taken in 1998 in the Meteorite laboratory. The testing included the laboratory cleanroom and inside the Mars meteorite glovebox. Organics were collected with an adsorbent inside a stainless steel tube connected to a pump. The procedure is explained in more detail in the 2012 organic in air analysis in the next section. The adsorbent tube was analyzed at Balazs Analytics, Inc. by thermal desorption gas chromatography mass spectroscopy (TD-GC-MS) and the results were given in nanograms per liter (ng/L). The asterisks in all of the Balazs reports indicate that while a compound may have been detected, it was below the reporting limit of the instrumentation. For example, in the 1998 Study of Organics in Air, Trichloroethylene (TCE) has an asterisk. This means that the instrument identified a peak for TCE, however, the concentration of TCE was below 1.0 ng/L.

1998 Study of Organics in Air			
Hydrocarbons	Control Blank (ng/L)	Meteorite Cleanroom TD-GC-MS Results (ng/L)	Mars Glovebox TD-GC-MS Results (ng/L)
Low boilers C6-C10	10	63	16
Medium boilers >C10-C20	2	93	11
High boilers >C20	*	1	*
Sum >= C6	12	157	27
Identified Organic Compounds			
Benezene	*	1	*
Trichloroethylene	*	*	*
Toluene	2	4	3
Tetrachlorethylene	*	*	*
Ethylbenzene	*	1	*
m, p-Xylenes	*	1	*
Styrene	*	*	*
o-Xylene	*	1	*
NMP	<0.5	<0.5	<0.5
Hexamethyldisiloxane	<0.1	<0.1	<0.1
Cyclo(Me2SiO)3	<0.1	2.9	5.8
Cyclo(Me2SiO)4	<0.1	2.6	3
Cyclo(Me2SiO)5	<0.1	26	1
TXIB	<0.1	0.8	<0.1
Fluorocarbons	*	6	*
Isopropanol	*	1	2
C6-C10 Hydrocarbons	8	32	10
Butanol + benzene	*	1	*
Propoxypropanol	*	3	*
2-Butoxypropanol		2	*
Butoxypropanol	*	6	*
C11-C18 Hydrocarbons	1	43	3
C3-benzene+dipropylene glycol	*	6	*
Methoxypropoxypropanol	*	1	*
2-Ethylhexanol	*	3	0.3
Nonanal	*	2	*
Caprolactam	*	*	0.2
Cyclo(Me2SiO)6	*	2	0.3
Cyclo(Me2SiO)7	*	*	0.5
diethyl phthalate	*	0.9	*
dibutyl phthalate	*	0.4	*
dioctyl phthalate (DOP)	*	0.1	*
* Reporting Limit = < 1 ng/L			

Figure 8: 1998 Balazs Report.

The 1998 Meteorite laboratory results show that the cleanroom has almost six times the amount of hydrocarbons present in the glovebox. While it is typical that more hydrocarbons are present inside the cleanroom than in a GN2 glovebox environment, these numbers are relatively high. The hydrocarbons probably arise from offgassing plastics and heat sealing. The 1998 Balazs report suggests that aromatic compounds such as toluene, ethylbenzene, xylenes and alkybenzenes and aliphatic compounds such as low- to medium-boil hydrocarbons are common urban air pollutants from gasoline and diesel and may also be used as solvents. Fluorocarbons and certain plasticizers are also present in these samples and many of these organic compounds are most likely from sample bags and handling supplies. The report suggests that the fluorocarbons detected in the Meteorite laboratory, room center, may be from refrigerants. Caprolactam was detected at very low levels only in the Mars cabinet outlet. Caprolactam is used in the manufacturing of nylon-6 and as a solvent for high molecular weight polymers. Therefore, the practice of heat sealing nylon bags will outgas caprolactam. Isopropanol, butanol, propoxypropanol, 2-butoxyethanol, butoxypropanol, dipropyleneglycol, and methoxyproxypropanol may be solvents. High

levels of silicones (cyclic siloxanes) were also detected in both samples. Silicone contaminants often originate from silicone sealants used in adhesives, flooring, the seals on High-Efficiency Particulate Air (HEPA) and Ultra-low Penetration Air (ULPA) filters, and cleanroom wall joints. Siloxanes are also used as lubricants in motors, and elastomers in gaskets. JSC curation labs frequently use silicone tapes and the meteorite processing lab contains two freezers with motors. The common plasticizers 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB), diethyl phthalate, dibutyl phthalate, and DOP were detected in the Meteorite lab room center. 2-Ethylhexanol was detected in both samples and is a common impurity in plasticizers and may form as a hydrolysis or decomposition product of dioctyl phthalate. The report suggests that most of the compounds detected are commonly found in industrial indoor air.

Schilling and Schneider (1998) further interpreted the Balazs 1998 report for JSC curation. They suggest that hydrocarbons, benzene, toluene and xylenes are common contaminates from outside Houston air entering the laboratory through the air handling system. The report cites that Houston air routinely contains levels of these chemicals on the order of 5 to 10 ng/L. The report further suggests that butanol is from human metabolic by-products and fluorocarbons are most likely the result of residual Freon 113 that was once used for cleaning and/or the use of freezers inside the lab. The isopropanol, butanol, propoxypropanol, 2-butoxyethanol, butoxypropanol, dipropyleneglycol, and methoxyproxypropanol found are thought to be from outgassing of flooring, paints, markers and wet wipes in the lab. Sample bags, vinyl gloves, gasket materials and other room plastics were linked with TXIB, diethyl phthalate, dibutyl phthalate, and DOP. Schilling and Schneider (1999) also reported finding bacteria colonies in the meteorite processing laboratory on the order of 7.9 to 11.8 colony forming units per cubic meter (CFU/m^3) dependent on the growth media.

The overall 1998 organic levels from the Mars cabinet outlet were lower than in the Meteorite lab, room center, which is to be expected. However, these results seem relatively high compared with all other Balazs data in JSC curation. In general, organics in air testing will produce higher precision results for understanding the volatile organic compounds compared to organic wafer testing. However, it should be noted that no other data exist for direct comparison from 1998. The Balazs report does state that JSC curation should conduct more tests with heat sealing nylon bags. Since the meteorite lab is the only lab that has multiple freezers inside a cleanroom at JSC, further investigation may also be warranted with respect to refrigerant offgassing and cleanliness of the cleanroom laboratory.

2.5.2 Dixon Report: Evaluation of Organic Contamination in Curation

In 2000, Eleanor Dixon wrote an internal unpublished report entitled "Storage and Processing of Extraterrestrial Samples from the Standpoint of Nitrogen Gas Purity: a Progress Report" (Dixon 2000). While the report focused on gaseous nitrogen (GN2) purity and contamination, the report provides a detailed analysis of the Balazs wafer organic tests conducted in 2000. The Dixon study also provides the first organic test conducted on the JSC curation 45 psi house GN2 main supply pipe located in mechanical room 1108 of B31N. A May 18, 2000 Balazs test report provides the organic results from a TD-GC-MS analysis of organics in air by proprietary adsorbent inside a stainless steel tube exposed to the GN2 for 24 hours with a 100 mL/min flow. The hydrocarbon boilers showed a value of 2.0 ng/L of $C_7 - C_{10}$ versus a "shipping control" blank designed to monitor contaminants accrued during shipping which showed 0.9 ng/L with all others below the reporting limit of 0.2 ng/L. In addition, toluene was reported at 1.1 ng/L (shipping control = 0.5 ng/L) and 4.3 ng/L of C_7 hydrocarbon (shipping control = 1.1 ng/L). All other detected compounds were below the 0.2 ng/L reporting limit. Since the control also contained C_7

hydrocarbons and toluene above reporting limits, Dixon's report suggests that the special grade C LN2 boil-off between the tank and main mechanical room in 2000 was relatively free of organics. Air Product, Inc., the LN2 supplier in 2000, certifies that the special grade C LN2 delivered to JSC will contain < 0.1 ppm of hydrocarbons and states this will be mostly methane. As a comparison, subsequent GN2 testing in B31 and B31N in 2004 and 2012, reported later in this report, detected no organics $>C_7$ with a reporting limit of < 0.1 ng/L.

In January 2000, silicon wafer organic tests were conducted in the Genesis, Meteorite and Lunar laboratories simultaneously. These tests were conducted in the following locations: (1) Genesis ISO class 4 cleanroom where wafers were exposed in room center of room 1107 and 1112; (2) Lunar laboratory glovebox, Apollo 16 cabinet 307-38 (PSL-38), where the pristine processing glovebox was cleaned and not used before testing; (3) Lunar laboratory glovebox, returned sample cabinet 309-49 (RSL-49), where the wafer samples were exposed to heat sealing sample bags. Ten heat-seals each of Teflon, nylon and polyethylene bags were performed in RSL-49; and (4) Meteorite laboratory Mars meteorite glovebox (MPL-Met Mars). All silicon wafers were exposed for 42 – 47 hours in each location and analyzed by TD-GC-MS. The Balazs and Dixon reports do not mention that the RSL-49 or MPL-Met Mars gloveboxes were cleaned before testing. Therefore, we assume that the PSL-38 lunar glovebox was the only glovebox cleaned before the experiment. Figures 9 – 11 show images of the gloveboxes and figure 12 reports the results from testing.

Figure 9: Lunar Lab Glovebox Apollo 16 – Cabinet 307-38 (PSL-38).

Figure 10: Lunar Lab Glovebox – Cabinet 309-49 (RSL-49).

Figure 11: Mars Meteorite cabinet in the Meteorite Curation Laboratory.

January 2000 Organic Wafer Testing						
Hydrocarbons	**Control Blank (ng/cm^2)**	**Genesis 1112 Cleanroom TD-GC-MS Results (ng/cm^2)**	**Genesis 1107 Cleanroom TD-GC-MS Results (ng/cm^2)**	**Lunar Glovebox PSL-38 TD-GC-MS Results (ng/cm^2)**	**Lunar Glovebox RSL-49** TD-GC-MS Results (ng/cm^2)**	**Meteoroite Glovebox MPL-MET MARS TD-GC-MS Results (ng/cm^2)**
Low boilers C7-C10	0.3	0.97	0.57	0.53	0.64	0.74
Medium boilers >C10-C20	0.61	20.89	16.86	4.93	10.15	5.55
High boilers >C20	0.17	4.44	3.25	0.81	1.72	1.3
Sum >= C7	1.07	26.3	20.67	6.28	12.51	7.59
Identified Organic Compounds						
NMP	*	*	*	*	*	*
Hexamethyldisiloxane	*	*	*	*	*	*
Cyclo(Me2SiO)3	*	0.08	*	*	*	*
Cyclo(Me2SiO)4	*	*	*	*	*	*
Cyclo(Me2SiO)5	*	*	*	0.09	*	0.09
TXIB	*	3.5	3.08	0.13	0.18	0.24
Dibutylamine	*	*	*	0.09	0.7	*
Caprolactam	*	0.11	*	0.11	3.63	0.17
N, N-dibutylformamide	*	*	*	1.59	1.13	0.57
Dimethylcyclohexanol	*	0.17	0.2	*	*	*
Isopropenylbenzene	*	0.29	0.39	*	*	*
N-N-dibutylacetamide	*	*	*	0.22	0.35	0.08
Isopropenylacetophenone	*	1.02	1.09	*	*	*
Alkyl ester	*	0.42	0.2	*	*	*
Diacetylbenzene	*	1.36	0.57	*	*	*
Unkown (me/: 43, 163)	*	0.83	0.28	*	*	*
Cyclo(Me2SiO)7	*	0.11	0.08	0.07	*	*
Diethyl phthalate (DEP)	*	*	*	*	*	0.26
Cyclo(Me2SiO)8	*	0.89	0.73	0.29	0.67	*
Dodecanamide	*	0.15	*	*	*	*
Other siloxanes	*	0.41	0.4	*	*	*
Didecyl ester of decanedioic acid	*	0.08	0.12	*	*	*
Isopropyl myristate	*	0.12	0.14	*	*	0.08
Diisobutyl phthalate	*	0.33	0.48	*	*	*
Cyclo(Me2SiO)9	*	1.17	1.3	0.08	0.25	*
Dibutyl phthalate (DBP)	*	0.34	0.33	0.15	1.02	*
Cyclo(Me2SiO)10	*	0.28	0.26	*	0.08	*

* Reporting Limit = < 0.08 ng/cm^2
** Note heat sealing in RSL-49 during testing

Figure 12: January 2000 Balazs Report.

The results show that the RSL-49 has the most contaminants compared to the other two gloveboxes. A comparison between all three gloveboxes provides an insight into the distribution of different contaminants and sources as well as the impact from heat sealing Teflon, nylon, and polyethylene bags. The PSL-38 organic concentrations could potentially show the lowest possible organic loads using the 2000 glovebox cabinet cleaning procedures. The results in both the PSL-38 and MPL-Met Mars gloveboxes are slightly lower, but not much lower than RSL-49. Dixon interprets these results to mean

that the higher organic concentrations in RSL-49 are directly related to the release of organics due to heat sealing of sample bags. In addition to organic additives from heat sealing, these results may also show the difference between a clean and unclean glovebox since the cleaning dates are not documented. A comparison of the results between RSL-49 and PSL-38 show that the RSL-49 glovebox environment has higher concentrations of dibutyl phthalate (DBP), cyclo(Me_2SiO)$_x$, TXIB, N-N dibutylacetamide, and caprolactam. The relatively high concentrations of these organics in glovebox RSL-49 suggests that increase volatilization may have occurred during heat-sealing of sample bags. The concentrations of medium and high boiling point hydrocarbons are much higher for all of the gloveboxes than for the control wafer. Since high concentrations of organics are present in PSL-38, relative to the control wafer, suggests that other sources of organic contamination exist in addition to the organics released from heat sealing in RSL-49. The role of organic contaminant accumulation during different GN2 flow rates inside gloveboxes is also not known. For example, in the Lunar laboratory, sample processors routinely adjust the gloveboxes from a low flow rate of 10 standard cubic feet per hour (scfh) during static non-working hours compared to 100 scfh during the time when they are working inside the glovebox. This was adopted in the early 1980s to save on GN2 delivery costs. Dixon also mentions that oil in the mechanical room can commonly contribute to organic contamination by permeating through the GN2 line connections. However, Dixon states that it is very unlikely that the B31N GN2 supply to the curation gloveboxes experienced significant contamination from the mechanical room.

The results also show that all of the gloveboxes are less contaminated by organics compared to the Genesis cleanrooms 1107 and 1112. Higher levels of hydrocarbons are noticeable in the 2000 results. There are elevated levels of TXIB, isopropenyl acetophenone, diacetylbenzene, and silicone complexes (cyclo(Me_2SiO)$_x$). The gloveboxes and Genesis cleanroom both have relatively high amounts of amides (for example caprolactam), as well as DBP and TXIB. Dixon also mentions that caprolactam contamination is possible due to nylon bag usage, as well as contamination by TXIB and DBP plasticizer additives. The silicones detected are possibly due to adhesives in the ULPA fan filter units and the newly constructed cleanroom walls and flooring. Concentrations of organic compounds found in the Genesis cleanroom and PSL-38 glovebox show that Genesis has much higher levels. The gloveboxes seem to have additional compounds that are not found in the Genesis cleanroom, such as N-N dibutylformamide, N-N dibutylacetamide, dibutylamine and cyclo(Me_2SiO)$_5$. Similarly, siloxanes are found much more in the Genesis cleanroom compared to the gloveboxes. Dixon also mentioned that it is difficult to determine whether the organic compounds only found in the gloveboxes (and not from heat sealing) are from organic materials used in the gloveboxes or from the introduction of GN2 organic contamination. However, it is noteworthy that the highest amount of N-N dibutylformamide is found in PSL-38, which has six neoprene gloves as opposed to four neoprene gloves in both the RSL-49 and MPL-Met Mars gloveboxes.

The April 2000, Balazs organic testing was conducted for the meteorite carbonaceous chondrite glovebox and the Genesis Terra Universal nitrogen storage cabinet. The Genesis cabinet was connected to a Terra Universal Nitroplex nitrogen purge system that contained many unknown rubber gaskets and plastics that were purported to have offgassed into the stainless steel cabinet. Due to results of this test, the Nitroplex system was removed. As a result, the meteorite glovebox was found to be much more organically clean compared to similar testing performed in January 2000. The carbonaceous chondrite glovebox does show detectable hydrocarbons, TXIB, DMF, and diethyl phthalate (DEP). TXIB is mainly a plasticizer and can be found in the manufacturing of vinyl flooring, walls covering, automotive plastics, nail care, and in many poly vinyl chloride (PVC) and rubber manufacturing. DEP is a plasticizer largely used in the fragrance industry as well as the processing of cellulose acetates. DMF is a solvent used in production of

acrylic fibers and plastics. In addition, DMF can be found in the manufacturing of pesticides, adhesives, films, and surface coatings. The Genesis cabinet had high levels of hydrocarbons, TXIB, and cyclic tetramethylene adipate. These are common plasticizers added to floor tiles, plastic curtains, and coatings. However, these elevated plasticizers could possibly be due to the Nitroplex system.

April 2000 Organic Wafer Testing				
Hydrocarbons	**Genesis Cabinet Control Blank (ng/cm^2)**	**Genesis Cabinet TD-GC-MS Results (ng/cm^2)**	**Meteorite Glovebox Control Blank (ng/cm^2)**	**Meteorite Glovebox TD-GC-MS Results (ng/cm^2)**
Low boilers C7-C10	0.3	0.7	0.1	0.1
Medium boilers >C10-C20	1.6	16.2	0.2	0.2
High boilers >C20	0.1	0.9	0.1	0.5
Sum >= C7	2	17.8	0.4	0.8
Identified Organic Compounds				
NMP	*	*	*	*
Hexamethyldisiloxane	*	*	*	*
Cyclo(Me2SiO)3	*	*	*	*
Cyclo(Me2SiO)4	*	*	*	*
Cyclo(Me2SiO)5	*	*	*	*
TXIB	0.1	1	*	0.2
Diacetoxy butane	*	0.2	*	*
Butoxyethoxy ethanol	*	0.2	*	*
Caprolactam	*	0.1	*	*
N, N-dimethyl formamide	*	*	*	0.1
Unknown (m/z: 55, 84, 112, 142)	*	0.3	*	*
Isopropenyl acetophenone	0.2	0.2	*	*
Unknown (m/z: 43, 56, 71, 173)	*	0.4	*	*
Diacetyl benzene	0.2	0.4	*	*
Cyclic tetramethylene adipate	*	5.4	*	*
Adipic acid derivative	*	0.2	*	*
Diethyl phthalate (DEP)	*	*	*	0.2
Unknown (m/z: 43, 57, 101, 127)	*	1.9	*	*
Unknown (m/z: 43, 55, 115, 127)	*	0.9	*	*
Unknown (m/z: 43, 55, 127, 155, 183)	*	0.6	*	*
Dibutyl phthalate (DBP)	*	0.1	*	*
Unknown (m/z: 43, 55, 127, 155, 183)	*	0.3	*	*
Unknown (m/z: 57, 165, 267, 282)	*	*	*	0.1
* Reporting Limit = < 0.1 ng/cm^2				

Figure 13: April 2000 Balazs Report.

2.5.3 White Sands Test Facility Glovebox Glove Analyses

In 2001, samples of potential glovebox glove materials were sent to the NASA WSTF for organic offgas testing by NASA-STD-6001c; Test 7: Determination of Offgassed Products. The intent of this test was to determine the glove material that generated the least organic contamination. The glove offgassing results show many different hydrocarbons, plasticizers, and rubber chemicals. Butyl rubber has the lowest amount of organic species overall with carbon monoxide as the most voluminous constituent. For Viton B, $C_{10} - C_{13}$ hydrocarbons, CO, and methylisobutylketone contribute the predominant offgassing chemicals. Neoprene shows a strong offgassing of carbonyl sulfide, CO, acetone, and $C_{10} - C_{12}$ hydrocarbons. Hypalon gloves generate carbonyl sulfide, sulfur dioxide, $C_{10} - C_{12}$ hydrocarbons, and xylenes. IPA is found to be a relatively common contaminant for all glove materials, especially in the Viton B and Hypalon results. However, IPA is commonly used during glove cleaning, which is the most likely source for the IPA.

Glovebox Gloves WSTF Outgassing Test 2001				
Identified Compounds	Neoprene GW (ppm)	Viton B (ppm)	Chlorobutyl Exxon 268 (ppm)	Hypalon (ppm)
2·Nitropropane	40	*	*	*
Acetaldehyde	140	30	*	10
Acetone	270	100	5	10
Acrolein	*	*	*	5
Acetonitrile	7	*	*	*
Butene	200	*	20	*
Butyraldehyde	170	*	*	*
C7 Ketone	*	*	*	6
C7 Saturated aliphatic hydrocarbons	*	*	5	*
C8 – C9 Saturated aliphatic hydrocarbons	*	40	*	*
C8 – C9 Saturated and unsaturated aliphatic hydrocarbons	*	*	*	20
C9 Aromatic hydrocarbon	*	*	*	5
C10 – C11 Saturated aliphatic hydrocarbons	*	*	40	*
C10 – C12 Saturated aliphatic hydrocarbons	230	*	*	280
C10 – C13 Saturated aliphatic hydrocarbons	*	410	*	*
C14 Saturated aliphatic hydrocarbons	50	*	*	*
Carbon disulfide	30	*	*	*
Carbon monoxide	670	280	300	100
Carbonyl sulfide	4400	*	30	500
Decamethylcyclopentasiloxane	*	*	*	6
Difluorodimethyl silane	*	*	30	*
Ethyl benzene	5	5	10	20
Hexamethylcyclotrisiloxane	5	20	*	*
Isobutyraldehyde	*	50	*	*
Isopropyl alcohol	200	15000	5	1200
Methylethylketone	9	*	*	*
Methylisobutylketone	*	200	*	7
Methyl isopropyl ether	*	*	6	*
Octamethylcyclotetrasiloxane	*	*	*	30
Sulfur dioxide	*	*	*	490
Toluene	7	5	5	7
Xylenes	30	5	50	180
Unidentified component	*	*	5	*
* Below reporting limit				

Figure 14: 2001 WSTF outgassing test results from glovebox gloves.

The glove material results are reported in a 2001 unpublished Worcester Polytechnic Institute BA theses by Eric Kenney and Michael Young entitled "Glove Material Selection for Cleanroom Gloveboxes" (Kenney and Young 2001). This glovebox glove report suggested that Hypalon and Viton shed many fewer particles than butyl rubber and neoprene. Butyl rubber is the least permeable material followed by Hypalon, Viton, and neoprene. Butyl rubber was the least clean material and generated the most particles during cleaning. Viton was the cleanest material and had the lowest TOC counts. However, Viton was observed to be tacky after cleaning.

This study recommended the replacement of neoprene with chlorosulfonated polyethylene (Hypalon) gloves manufactured by North Safety based on criteria for offgassing, permeability, particle shedding, and cleanability. Since this study, North Safety now manufactures a Hypalon/neoprene glove that combines the dexterity and flexibility of neoprene and the chemical resistance of Hypalon. Honeywell also manufactures a polyurethane/chlorosulfonated polyethylene glove, which is Hypalon on the outside and polyurethane on the inside that lowers the permeability and allows easy removal of the hand/arm. Species of offgassing or shed particles may be an important criterion depending on analytical goals; e.g. sulfur or chlorine isotopes. It is also important to mention that many of the common plasticizers, solvents, and silicone complexes can also be found in beauty products such as perfumes, hand creams, and nail polish. Therefore, the possibility exists that contamination by these species is from human use of gloveboxes where organics migrate through the neoprene gloves, the same glove material that is predominately used in the Meteorite and Lunar laboratories.

2.5.4 Contamination by Glovebox Materials: A Case Study

In 2007, an MBraun, Inc. glovebox was purchased for conducting preliminary cold curation experiments (figure 15). The glovebox was constructed from 304 stainless steel brushed finished, expandable PTFE Gore-Tex seals, Hypalon gloves, and polycarbonate window. The glovebox was also fitted with a -35°C cold plate and freezer for sample storage. In 2012, the MBraun glovebox was modified for storage of asteroidal samples collected by the Hayabusa JAXA mission, and placed inside an ISO class 5 cleanroom in B31N, room 1106. The MBraun glovebox's polycarbonate window was replaced with safety glass and PTFE gaskets were replaced with Viton. The freezer and cold plate were also removed along with the unknown plastic materials used in the antechamber door. The following Balazs organic results were taken when the glovebox was used as a cold curation glovebox in 2008 and recent organic tests in 2012 for the modified Hayabusa glovebox. Since this is the same glovebox using different materials, this is an excellent record of material changes for a modified glovebox. In addition, the MBraun glovebox used for cold curation is the only data point for the use of an integrated cold trap for collecting organics. These results can be viewed for the silicon wafer testing of the cold plate in 2008 (figure 16).

Figure 15: 2008 MBraun glovebox in B31N, Room 1106.

Figure 16: 2008 Balazs organic wafer testing on cold plate and weighing balance.

Cold Curation	2008 Testing		
Hydrocarbons	**Control Blank (ng/cm²)**	**Mbraun Glovebox Cold Plate TD-GC-MS Results (ng/cm²)**	**Mbraun Glovebox TD-GC-MS Results (ng/cm²)**
Low boilers C7-C10	*	0.2	0.1
Medium boilers >C10-C20	*	8.2	1.2
High boilers >C20	*	2.7	0.9
Sum >= C7	*	11.1	2.2
Identified Organic Compounds			
Butanol	*	*	*
Dimethyl benzyl amine	*	1.7	*
Triethyl phosphate	*	0.2	*
Caprolactam	*	0.3	*
2,6-di-tert	*	*	*
butylbenzoquinone	*	*	*
Butyl hydroxy toluene (BHT)	*	*	*
Unknown(m/z: 41, 55, 84,100, 129)	*	*	*
TXIB + Diethyl phthalate	*	0.2	*
Cyclododecane	*	0.2	0.1
Unknown (m/z: 70, 77, 105,112, 123)	*	0.3	*
Isoprpoyl myristate	*	*	*
Diisobutyl phthalate	*	0.2	*
Dibutyl phthalate	*	0.2	*
Octasulfur	*	0.2	*
C6-C9 Hydrocarbons	*	*	*
C16-C20 Hydrocarbon	*	3.4	0.5
Possible fluorochlorocarbons (m/z: 85, 101, 135,151)	*	0.8	0.4
* Reporting Limit = < 0.1 ng/cm2			

Figure 17: 2008 Balazs results for the MBraun glovebox organic testing.

The 2008 glovebox configuration consisted of PTFE Gore-Tex seals, Hypalon gloves, and Lexan (polycarbonate) window. The results in figure 17 show three organics in both wafers: hydrocarbons, cyclododecane, and possible fluorochlorocarbons. Cyclododecane is used as an intermediate in the production of flame retardants, detergents and other chemicals. Fluorochlorocarbons are generally associated with Freon type products. Given the amount of unknown material in the MBraun glovebox, it is difficult to pinpoint the nature of this contamination. However, we can speculate that the cold plate, freezer, antechamber door handles, and viewing window are the most obvious source. As expected, the organic contamination load is much higher on the cold plate, acting as a contamination cold trap. This is noticeable from the hydrocarbons concentrations. In addition, dimethyl benzylamine and $C_{16} - C_{20}$ hydrocarbons are relatively high. Dimethyl benzylamine is found in polyurethane products and epoxy resins.

Hayabusa Laboratory	July 2012 Organic Wafer Testing		
Hydrocarbons	Control Blank (ng/cm^2)	Hayabusa MBraun Glovebox TD-GC-MS Results (ng/cm^2)	Hayabusa Cleanroom TD-GC-MS Results (ng/cm^2)
Low boilers C7-C10	*	0.2	0.6
Medium boilers >C10-C20	*	0.8	8.9
High boilers >C20	*	0.1	0.2
Sum >= C7	*	1.1	9.7
Identified Organic Compounds			
MIBK	*	*	*
Butoxy ethanol	*	*	*
Benzaldehyde	*	*	*
Dipropylene glycol methyl ether	*	*	*
2-Propanol, 1-(2-methoxypropoxy)-	*	*	*
Ethyl hexanol	*	*	*
Acetophenone	*	*	*
Ethanol, 2-(2-butoxyethoxy)- + Cyclo(Me2SiO)5	*	*	0.2
Caprolactam	*	0.1	0.7
Alkyl ester	*	*	0.5
Texanol	*	*	0.8
p-Diacetylbenzene	*	*	0.1
Diisopropyl adipate	*	*	*
Diisopropyl phenol	*	*	0.1
2,6-di-tert-Butylquinone	*	*	*
2,6-di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one	*	*	*
BHT-quinone-methide + Ethanone, 1-[4-(1-hydroxy-1-methylethyl)phenyl]-	*	*	*
Cyclic tetramehtylene adipate	*	*	*
Diethyl phthalate	*	*	0.4
TXIB	*	*	0.8
Hexadecamethylheptasiloxane	*	*	*
Cyclooctasiloxane, hexadecamethyl-	*	*	0.3
BHT-aldehyde	*	*	0.2
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	*	*	*
Isopropyl Myristate	*	*	*
Diisobutyl phthalate	*	*	0.2
Cyclo(Me2SiO)9	*	*	0.2
Dibutyl phthalate	*	*	0.1
Cyclo(Me2SiO)10	*	*	*
Cyclo(Me2SiO)11	*	*	*
Hexanedioic acid, bis(2-ethylhexyl) ester	*	*	*
Di-n-octyl phthalate	*	*	*
Siloxane	*	*	0.1
* Reporting Limit = < 0.1 ng/cm2			

Figure 18: 2012 Balazs report for the MBraun glovebox organic testing for the Hayabusa Laboratory.

The 2012 Hayabusa MBraun glovebox configuration consisted of Viton seals, Hypalon gloves, and glass window. The results in figure 18 show a very low level of organics, mostly below the reporting limit of < 0.1 ng/cm^2. The only organic compounds detected are a small amount of hydrocarbons and caprolactam. This contamination may have been a result of testing while simultaneously inserting a polypropylene box holding a sampling wafer for inorganic particulate contamination testing. The box was previously stored in a nylon bag and may have absorbed caprolactam during transport. It should also be noted that we do not find certain organics in the MBraun glovebox compared with the Lunar and Meteorite laboratory gloveboxes. With the clear absence of detectable organics such as TXIB, DMF, and DEP, N-N dibutylformamide, N-N dibutylacetamide, and dibutylamine, we can speculate that this may have been caused by changing the gloves from neoprene to Hypalon and/or changing the polycarbonate window to glass. Polycarbonate windows have a large surface area and may potentially offgas more than gloves interacting with the GN2 environment. The Hayabusa room 1106 cleanroom results show a similar pattern with the Genesis cleanroom with the presence of plasticizers and silicone adhesives. However, Texanol was detected and is one of the main chemicals in latex paint as well as some adhesives. In addition, detectable levels of TXIB, a plasticizer, can also be found in paints and adhesives. The cleanroom results also show that caprolactam was detected and possibly due to the extensive use of nylon bags in the laboratory.

2.6   Cleanroom Organic Contamination Results 2000 to Present

The use of reduced particulate cleanrooms for handling astromaterials can be traced to the Apollo program. The LRL in JSC B37 was the first curation facility to be concerned about monitoring and lowering air particulate contamination. In addition, LRL tool cleaning procedures required the use of ISO class 5 (former class 100) laminar air flow during final cleaning steps. The LRL also began conducting particulate testing and monitoring inside the SNAP and NNPL lines during Apollo 14 and later missions (Reynolds et al. 1972). However, gloveboxes inside the LRL were not required to utilize a certified particulate reduced air flow. Instead, the B37 facility used a traditional filtered air handling systems to clean laboratory air. The later-established lunar and meteorite curation laboratories also used gloveboxes using air filtered through the building air handling system. In 1981, the cosmic dust laboratory established a trend toward the use of more modern airflow filtration. Instead of using gloveboxes for sample containment, sample processing of cosmic dust was conducted using ISO Class 5 laminar flow workstations. The processing of samples under laminar flow proved to be cleaner with respect to particulates than sample processing within a glovebox environment.

In 1998, the Genesis laboratory was established with two ISO class 4 cleanrooms and was considered to be the first cleanroom in JSC curation to be modeled after semiconductor industry cleanrooms. The Genesis lab was constructed on the first floor of B31N in the old lunar public viewing area. The construction was state-of-the-art at the time with ULPA filtration fan filter units (FFUs) in the ceiling and a raised floor to create a total laminar flow cleanroom environment. This room was sufficiently clean to accommodate both preflight assembly of the science canister and post-flight sample processing. This design allows the laminar air to flow directly from the FFU in the ceiling through the perforated floor and back up the outside of the inner wall panel for recirculation to the FFU. The Stardust curation facility was constructed in 2006 and Hayabusa in 2012. Both are ISO class 5 cleanrooms and also have laminar air flow with ULPA FFU in the ceiling, but do not have a raised floor. This creates some turbulent air flow at the bottom of the floor with the air exiting through the bottom wall panels. While Stardust and

Hayabusa laboratories do not have a raised floor, organic testing conducted in these cleanrooms should give similar results to Genesis due to the similarities in cleanroom construction materials.

2.6.1 Genesis Laboratory Organic Analyses

The Genesis laboratory is the only curation laboratory that regularly tests for organic contamination. These routine organic tests from 2000 to 2011 in both ISO 4 class cleanrooms 1112 and 1107 provide an excellent baseline for organics in the JSC curation cleanrooms that are modeled after the semiconductor industry. In 2000, Balazs Analytical Inc. was contracted to provide all molecular organic testing by exposure of 6- or 8-inch silicon wafer for 24 hours and measurement by TD-GC-MS. Early testing was documented in a 2001 Worcester Polytechnic Institute BA thesis by Dan Erickson and Kathy Pacheco entitled "Organic Outgassing in NASA's JSC Genesis Cleanrooms" (Erickson and Pacheco 2001). In addition, adsorbent tube organic testing measured by TD-GC-MS analysis was conducted in 2001 and 2002 in the Genesis cleanroom and on the Genesis GN2 in 2004. All Balazs reports were reviewed by the Genesis curator and subsequently provided to the CAPTEM Genesis oversight subcommittee for review. The following are all the organic results from the Genesis cleanroom from 2000 to 2011 (figures 19 to 23).

Genesis Cleanroom	June 2000		August 2000		Feburary 2001	
Hydrocarbons	Genesis Cleanroom 1107 Control Blank (ng/cm^2)	Genesis Cleanroom 1107 TD-GC-MS Results (ng/cm^2)	Genesis Cleanroom 1107 Control Blank (ng/cm^2)	Genesis Cleanroom 1107 TD-GC-MS Results (ng/cm^2)	Genesis Cleanroom 1112 Control Blank (ng/cm^2)	Genesis Cleanroom 1112 TD-GC-MS Results (ng/cm^2)
Low boilers C7-C10	0.2	0.6	0.88	0.94	0.2	0.5
Medium boilers >C10-C20	0.3	17.9	0.37	15.35	0.3	6.4
High boilers >C20	*	2	0.43	3.57	*	3
Sum >= C7	0.5	20.5	1.68	19.86	0.5	9.9
Identified Organic Compounds						
2-(2-Butoxyethoxy) ethanol						0.2
2-Octyl-3-isothiazolinone	*	0.3	*	0.2	*	*
4'-(hydroxymethlethyl)-acetophenone	*	*	*	*	*	0.5
Acetophenone derivative	*	1.8	*	*	*	*
Alkyl ester	*	*	*	*	*	0.1
Alkylphenol	*	*	*	1.5	*	*
Butoxyethoxy ethanol	*	0.6	*	0.4	*	*
C20 Hydrocarbon	*	*	*	*	*	*
Caprolactam	*	*	*	0.1	*	*
Cyclo(Me2SiO)10	*	*	*	0.2	*	*
Cyclo(Me2SiO)11	*	*	*	*	*	*
Cyclo(Me2SiO)3	*	*	*	*	*	*
Cyclo(Me2SiO)4	*	*	*	*	*	*
Cyclo(Me2SiO)5	*	*	*	*	0.2	*
Cyclo(Me2SiO)8	*	0.2	*	0.2	*	0.1
Cyclo(Me2SiO)9	*	*	*	*	*	0.1
Dibutyl phthalate (DBP)	*	0.4	*	0.3	*	0.1
Diethyl phthalate (DEP)	*	0.3	*	0.8	*	0.1
Di-isobutyl phthalate	*	0.8	*	0.7	*	*
Di-isopropenylbenzene	*	*	*	*	*	0.2
Dioctyl phthalate (DOP)	*	*	*	0.2	*	*
Dodecanamide	*	0.1	*	0.1	*	*
Hexamethyldisiloxane	*	*	*	*	*	*
Isopropyl myristate	*	0.1	*	0.2	*	0.1
Naphthalene + Butoxethoxy ethanol + Cyclo (Me2SiO)5	*	*	*	*	*	*
NMP	*	*	*	*	*	*
p-Acetyl acetophenone	*	1.3	*	*	*	0.3
p-Acetyl-isopropenylbenzene	*	*	*	*	*	0.5
Siloxane	*	*	*	0.5	*	*
Texanol	*	0.4	*	*	*	*
TXIB	*	1.6	*	2.79	*	1
Unknown (m/z: 111, 125, 140)	*	*	*	*	*	*
Unknown (m/z: 115, 145, 160)	*	1.1	*	0.7	*	*
Unknown (m/z: 115, 158)	*	*	*	*	*	*
Unknown (m/z: 138, 208)	*	*	*	*	*	*
Unknown (m/z: 153, 183, 198)	*	*	*	*	*	*
Unknown (m/z: 43, 161, 176)	*	*	*	*	*	*
Unknown (m/z: 43, 163)	*	*	*	*	*	*

* Reporting Limit = < 0.1 ng/cm^2

Figure 19: Balazs wafer exposure TD-GC-MS results for Genesis Laboratory from 2000 to 2001.

Genesis Cleanroom	November 2001 Testing		September 2002 Testing	
Hydrocarbons	**Control Blank (ng/L)**	**Genesis 1112 Cleanroom TD-GC-MS Results (ng/L)**	**Control Blank (ng/L)**	**Genesis 1112 Cleanroom TD-GC-MS Results (ng/L)**
Low boilers C7-C10	1.0	6.0	**	12.0
Medium boilers >C10-C20	*	3.0	**	8.0
High boilers >C20	*	*	**	**
Sum >= C7	1.0	9.0	**	20.0
Identified Organic Compounds				
Benzaldehyde	*	*	**	**
Cyclo(Me2SiO)3	*	*	**	**
Cyclo(Me2SiO)4	*	*	**	**
Cyclo(Me2SiO)5	*	*	**	**
Ethyl hexanol	*	*	**	**
Ethylbenzene	*	*	**	**
Hexamethyldisiloxane	*	*	**	**
m,p-Xylenes	*	*	**	**
Methyl naphthalene isomers	*	*	**	**
Naphthalene	*	*	**	**
NMP	*	*	**	**
o-Xylene	*	*	**	**
Styrene	*	*	**	**
Tetrachloroethylene	*	*	**	**
Toluene	*	2.0	**	**
TXIB	*	*	**	**
* Reporting Limit = < 1.0 ng/L				
** Reporting Limit = < 2.0 ng/L				

Figure 20: Balazs adsorbent tube TD-GC-MS results for Genesis Laboratory from 2001 and 2002.

Genesis Cleanroom	September 2002 Testing			July 2003 Testing		September 2003 Testing		March 2004 Testing		June 2004 Testing	
Hydrocarbons	Control Blank (ng/cm²)	Genesis 1107 Cleanroom TD-GC-MS Results (ng/cm²)	Genesis 1112 Cleanroom TD-GC-MS Results (ng/cm²)	Control Blank (ng/cm²)	Genesis 1112 Cleanroom TD-GC-MS Results (ng/cm²)	Control Blank (ng/cm²)	Genesis 1107 Cleanroom TD-GC-MS Results (ng/cm²)	Control Blank (ng/cm²)	Genesis 1107 Cleanroom TD-GC-MS Results (ng/cm²)	Control Blank (ng/cm²)	Genesis 1112 Cleanroom TD-GC-MS Results (ng/cm²)
Low boilers C7-C10	0.1	1.1	0.9	*	0.7	0.1	0.7	0.1	1.1	0.2	0.7
Medium boilers >C10-C20	*	8.6	6.4	*	3.9	0.2	5.1	0.1	5.1	0.3	6.6
High boilers >C20	*	3.5	3	*	2.1	*	2.5	*	1.8	0.1	2
Sum >= C7	0.1	13.2	10.3	*	6.7	0.3	8.3	0.2	8.0	0.6	9.3
Identified Organic Compounds											
2-(2-butoxy ethoxy) ethanol	*	0.2	0.9	*	*	*	0.5	*	*	*	0.3
2-(2-Butoxyethoxy) ethanol + Cyclo (Me2SiO)7	*	*	*	*	0.1	*	*	*	*	*	*
2-n-Octyl-3 (2H)-Isothiazolone	*	*	0.1	*	*	*	*	*	*	*	*
Acetyl phenyl propanol	*	*	*	*	*	*	0.2	*	*	*	*
Alkyl acrylate	*	*	*	*	*	*	*	*	*	*	*
Alkyl esters	*	0.1	0.4	*	0.2	*	0.2	*	0.1	*	0.1
Alkyl nitrile	*	*	*	*	*	*	0.1	*	*	*	*
Benzoic acid + 2-(2-butoxy ethoxy) ethanol	*	*	*	*	*	*	*	*	0.4	*	*
Benzoic acid + Decanal	*	*	*	*	*	*	*	*	*	*	0.1
Butoxy ethanol	*	0.1	*	*	*	*	*	*	*	*	*
C10 - C25 hydrocarbons	*	*	*	*	1.8	*	*	*	*	*	*
C21-C25 Hydrocarbons	*	*	*	*	*	*	*	*	*	*	0.2
C21-C26 hydrocarbons	*	*	*	*	*	*	2.2	*	0.2	*	*
C8 hydrocarbons	*	*	*	*	*	*	0.3	*	0.4	*	0.1
C8-C23 hydrocarbons	*	0.2	0.4	*	*	*	*	*	*	*	*
Caprolactam	*	0.2	0.2	*	0.1	*	0.2	*	0.1	*	0.1
Cyclo (Me2SiO)10	*	0.1	*	*	*	*	*	*	*	*	*
Cyclo (Me2SiO)7	*	*	*	*	*	*	*	*	*	*	*
Cyclo (Me2SiO)8	*	0.1	0.1	*	*	*	*	*	*	*	0.1
Cyclo (Me2SiO)9	*	0.1	0.1	*	*	*	*	*	*	*	*
Cyclo(Me2SiO)6	*	*	*	*	*	*	*	*	*	*	0.1
Cyclo(Me2SiO)7 + 2,6-di-tert-butyl benzoquinone	*	*	*	*	*	*	*	*	*	*	0.1
Diacetyl acetophenone	*	0.5	0.5	*	*	*	*	*	*	*	*
Diacetyl benzene	*	*	*	*	*	*	0.3	*	0.3	*	0.4
Dibutyl phthalate	*	0.1	0.2	*	*	*	0.1	*	0.1	*	0.1
Diethyl phthalate	*	0.2	0.2	*	0.3	*	0.2	*	0.2	*	0.3
Diisobutyl phthalate	*	0.1	0.6	*	*	*	0.4	*	0.2	*	0.1
Diisopropenyl benzene	*	0.1	0.1	*	0.1	*	*	*	0.1	*	0.1
Diisopropyl phenol	*	0.1	0.4	*	0.1	*	*	*	0.1	*	0.1
Dimethyl phthalate	*	*	*	*	*	*	*	*	*	*	0.1
Ethyl hexanal	*	*	0.1	*	*	*	0.1	*	*	*	*
Hydroxymethylethyl-acetophenone	*	*	*	*	0.2	*	*	*	*	*	*
Isopropenyl acetophenone	*	0.6	0.5	*	0.2	*	0.3	*	0.4	*	0.6
Isopropyl myristate	*	*	*	*	*	*	*	*	*	*	*
NMP	*	*	*	*	*	*	*	*	*	*	0.1
PGMEA	*	*	*	*	*	*	*	*	*	*	*
Phenols	*	*	*	*	*	*	*	*	*	*	*
Propylene glycol glyme isomers	*	*	*	*	*	*	*	*	*	*	0.1
Styrene	*	*	*	*	*	*	*	*	*	*	*
TXIB	*	0.4	0.4	*	0.3	*	0.4	*	0.3	*	0.4
Undecanonitrile	*	0.1	0.1	*	*	*	*	*	*	*	*
Unknown (m/z: 43, 55, 71, 95)	*	*	*	*	*	*	*	*	*	*	*
Unknown (m/z: 55, 97, 150)	*	*	*	*	0.1	*	*	*	*	*	*
Unknown (m/z: 55, 99, 173)	*	0.1	0.1	*	*	*	0.1	*	*	*	*
Unknown(m/z: 55, 84, 99, 173)	*	*	*	*	*	*	*	*	*	*	0.1
Unknown(m/z: 76,104,149,193)	*	*	*	*	*	*	*	*	*	*	0.1

* Reporting Limit = < 0.1 ng/cm²

Figure 21: Balazs wafer exposure TD-GC-MS results for Genesis Laboratory from 2002 to 2004.

Genesis Cleanroom	May 2005 Testing		May 2006 Testing		October 2008 Testing		April 2010 Testing		July 2011 Testing		
Hydrocarbons	Control Blank (ng/cm²)	Genesis 1107 Cleanroom TD-GC-MS Results (ng/cm²)	Control Blank (ng/cm²)	Genesis 1107 Cleanroom TD-GC-MS Results (ng/cm²)	Control Blank (ng/cm²)	Genesis 1107 Cleanroom TD-GC-MS Results (ng/cm²)	Control Blank (ng/cm²)	Genesis 1107 Cleanroom TD-GC-MS Results (ng/cm²)	Control Blank (ng/cm²)	Genesis 1107 Cleanroom TD-GC-MS Results (ng/cm²)	Genesis 1112 Cleanroom TD-GC-MS Results (ng/cm²)
Low boilers C7-C10	*	0.5	*	0.5	*	1.3	*	0.9	*	0.7	0.6
Medium boilers >C10-C20	*	8.2	*	7.3	*	6.1	*	11.8	*	9.2	10.4
High boilers >C20	*	2.7	*		*	1.9	*	2.8	*	4.4	2.8
Sum >= C7	*	11.4	*	7.8	*	9.3	*	15.5	*	14.3	13.8
Identified Organic Compounds											
1-(2-Butoxyethoxy) ethanol	*	*	*	*	*	*	*	*	*	*	*
2(2-Butoxyethoxy)ethanol + Cyclo(Me2SiO)5	*	0.2	*	*	*	0.2	*	*	*	0.2	0.2
2,6-di-butyl-2,5-cyclohexadiene-1,4-dione	*	*	*	*	*	*	*	*	*	*	*
Acetyl acetophenone	*	0.4	*	0.4	*	*	*	*	*	*	
Alkyl ester	*	0.3	*	*	*	0.3	*	3.2	*	0.4	0.6
Alkyl ester + Cyclo(Me2SiO)6	*	*	*	*	*	0.1	*	*	*	*	
Alkyl nitrile	*	*	*	*	*	*	*	*	*	*	*
Alkyl phthalate	*	*	*	*	*	*	*	*	*	*	*
Butoxyethanol	*	*	*	*	*	*	*	*	*	*	
Butyl benzyl phthalate	*	*	*	*	*	*	*	*	*	0.1	*
C12 hydrocarbon + Unknown(m/z:97,110)	*	*	*	*	*	*	*	*	*	0.1	0.1
C18-C27 hydrocarbons	*	*	*	*	*	*	*	*	*	0.2	0.2
C20-C24 hydrocarbons	*	*	*	*	*	*	*	2.0	*	*	
C5-C9 hydrocarbons	*	*	*	*	*	*	*	0.6	*	*	
C6-C7 hydrocarbons	*	*	*	*	*	*	*	*	*	0.2	*
C6-C9 hydrocarbons	*	*	*	*	*	0.4	*	*	*	*	
C8 hydrocarbon	*	*	*	0.4	*	*	*	*	*	*	
C8-C25 Hydrocarbons	*	0.6	*	*	*	*	*	*	*	*	
Caprolactam	*	0.1	*	0.3	*	0.3	*	*	*	0.1	0.1
Cyclo (Me2SiO)10	*	*	*	*	*	*	*	*	*	*	
Cyclo (Me2SiO)4	*	*	*	*	*	*	*	*	*	*	
Cyclo (Me2SiO)7	*	0.2	*	*	*	*	*	0.8	*	*	0.1
Cyclo (Me2SiO)8	*	0.2	*	*	*	0.2	*	0.9	*	*	0.4
Cyclo (Me2SiO)9	*	0.2	*	*	*	*	*	*	*	0.2	0.1
Cyclododecane	*	*	*	*	*	*	*	*	*	*	*
Di(2-ethylhexyl)adipate	*	*	*	*	*	*	*	*	*	*	*
Diacetyl benzene	*	*	*	*	*	0.2	*	*	*	*	
Dibutyl phthalate	*	0.2	*	0.4	*	0.3	*	0.4	*	0.3	0.3
Didecyl sebacate	*	*	*	*	*	*	*	*	*	*	
Diethyl phthalate	*	0.8	*	0.5	*	0.4	*	1.0	*	0.6	0.5
Diisobutyl phthalate	*	0.4	*	0.5	*	0.3	*	0.6	*	0.5	0.3
Diisopropenylbenzene	*	*	*	*	*	*	*	*	*	*	
Diisopropyl adipate	*	*	*	*	*	*	*	*	*	*	
Diisopropyl phenol	*	0.1	*	*	*	*	*	*	*	*	
Dioctyl adipate	*	*	*	*	*	*	*	0.2	*	0.1	*
Dioctyl phthalate	*	*	*	*	*	*	*	*	*	1.0	0.2
Dipropyl phthalate	*	*	*	*	*	*	*	*	*	*	
Dipropyleneglycol	*	*	*	*	*	0.1	*	*	*	*	
Dodecanamide	*	*	*	*	*	*	*	*	*	0.1	0.1
Dodecanenitrile	*	*	*	*	*	*	*	*	*	*	
Ethyl hexanol	*	0.1	*	*	*	0.1	*	0.1	*	*	
Hexadecamethylheptasiloxane	*	*	*	*	*	*	*	*	*	*	
Isopropenyl acetophenone + Cyclo(Me2SiO)6	*	0.2	*	*	*	*	*	*	*	*	
Isopropyl myristate	*	*	*	*	*	*	*	*	*	*	
Methyl palmitate	*	*	*	*	*	*	*	*	*	*	
MIBK	*	*	*	*	*	*	*	*	*	*	
NMP	*	*	*	*	*	*	*	*	*	*	
Phenol	*	*	*	*	*	*	*	*	*	*	
Siloxane	*	*	*	*	*	*	*	0.5	*	*	0.1
Surfynol	*	*	*	*	*	*	*	*	*	*	
Texanol	*	*	*	*	*	*	*	*	*	1.0	1.4
Triphenyl phosphate	*	*	*	*	*	*	*	*	*	*	
Tripropylene glycol	*	*	*	*	*	*	*	*	*	0.5	0.6
TXIB	*	0.8	*	0.9	*	0.3	*	0.9	*	0.5	0.5
Undecanenitrile	*	0.1	*	*	*	0.1	*	*	*	*	
Unknown (43, 71, 115, 145, 160)	*	*	*	*	*	*	*	*	*	*	
Unknown (m/z: 43, 163)	*	*	*	*	*	*	*	*	*	*	
Unknown (m/z: 55, 99, 173, 221)	*	0.2	*	*	*	*	*	*	*	*	
Unknown(m/z:71 , 83, 101 , 113, 119)	*	*	*	*	*	0.1	*	*	*	*	
Unknown(m/z:43, 55, 71, 97, 110)	*	*	*	*	*	*	*	0.2	*	*	
Unknown(m/z:43,57,71,83,101,113,119,132, 147)	*	*	*	*	*	*	*	0.2	*	0.5	0.2
Unknown(m/z:43,71,91,115,145,160) + Cyclo(Me2Sio)6	*	*	*	*	*	*	*	*	*	*	

* Reporting Limit = < 0.1 ng/cm²

Figure 22: Balazs wafer exposure TD-GC-MS results for Genesis Laboratory from 2005 to 2011.

The Genesis ISO 4 class cleanroom test results generally illustrate that hydrocarbons, plasticizers, and silicone compounds are the primary organic contaminants in this environment. The Genesis 2000 and 2001 results show elevated levels of TXIB, p-Acetyl acetophenone, acetophenone derivatives, DEP, DBP, diisobutyl phthalate (DIBP), and alkylphenol. The acetophenones are found mainly in fragrances and

perfumes as well as resins used in inks and coatings. Alkylphenol is used in detergents and additives in fuels, lubricants, polymers, high performance rubbers, phenolic resins, fragrances, thermoplastic elastomers, fire retardants, oil field chemicals, and antioxidants. The TXIB, DEP, DBP, and DIBP are all plasticizers. TXIB is widely used in the manufacturing of PVC, coatings for automotive plastics, lithographic and letterpress oil-based inks, nail care products, phthalate-free diluents for methyl ethyl ketone peroxide (MEKP) formulations, plastisols, sheet vinyl flooring, toys/sporting goods plastic products, traffic cones, vinyl compounding and gloves, and common wall coverings. DEP is largely used in the perfume and fragrance industry as well as the processing of cellulose acetates. The DBP plasticizer is found in adhesives, solvents, and inks. DIBP is used in nitro cellulose plastic, nail polish, explosive material, and lacquer manufacturing. These early Genesis results also show an increased use of isopropyl compared with later years. This is most likely related to the use of IPA wipes and ultra-pure cleaning solvents in the laboratory.

As a comparison with early years, the Genesis 2010-2011 results still show the increased levels of TXIB, DEP, and DIBP plasticizers as well as DOP, used as a plasticizer in resins and elastomers. The test results also show an increase in texanol and alkyl ester compared with earlier years. Texanol is most commonly found in latex paint and ink coatings. The texanol and alkyl ester could also be derivatives in plasticizers. All of these increased levels may be from renovations adjacent to the cleanrooms because in 2009 a new air handling system was installed in B31N, room 1108 adjacent to the Genesis laboratory. In addition, the Genesis lab experienced a minor flood and underwent some renovations inside the laboratory in 2010 before this testing. The texanol found in 2011 could also be from fresh wall painting that was done outside room 1105 a few weeks before testing. The presence of silicone and plasticizers is noticeably higher in the early years compared to the laboratory today. Silicone and plasticizers are common in ULPA fan filter units, cleanroom paneling sealants, and flooring sealants. This is most likely due to the change in offgassing of the new lab construction compared to the current lab that has had time to offgas some products. It is also important to note that many of the common plasticizers, solvents, and silicone complexes can also be found in beauty products such as perfumes, hand creams, and nail polish. The Genesis laboratory has added cleanliness restrictions for personnel and the use of personnel hygiene products has been very restrictive. However, we cannot rule out human contamination of the laboratory. In addition, the air handling system brings in about 10% fresh outside air. Molecular organic contamination < 0.1 to 0.2 µm from the local environment cannot be removed by filtration through ULPA fan filter units (IEST-RP-CC001.5).

Figure 23 below is a summary plot for $>C_7$ hydrocarbons in Genesis over time. The summary plot also illustrates that the materials of the newly constructed cleanroom probably outgassed more in 2000 compared to other years. The other possible contributing factor for the increase in hydrocarbons could be the assembly of the Genesis science canister with increased activity and personnel entering the lab. Figure 23 also shows increased hydrocarbons between 2008 and 2010 – 2011. This could also be due to the renovations in adjacent rooms around the time of the testing, such as the new air handler or flood renovations. As a comparison to figure 23 wafer exposure results, figure 20 above shows the adsorbent tube results in 2001 and 2002. The amount of $>C_7$ hydrocarbons are almost doubled in 2002, but this may be because adsorbent tubes usually provide a better indicator of volatile organic compounds (VOCs) than exposed Si wafers. If adsorbents were used for testing in every year, we would probably see an increase in $>C_7$ hydrocarbons values.
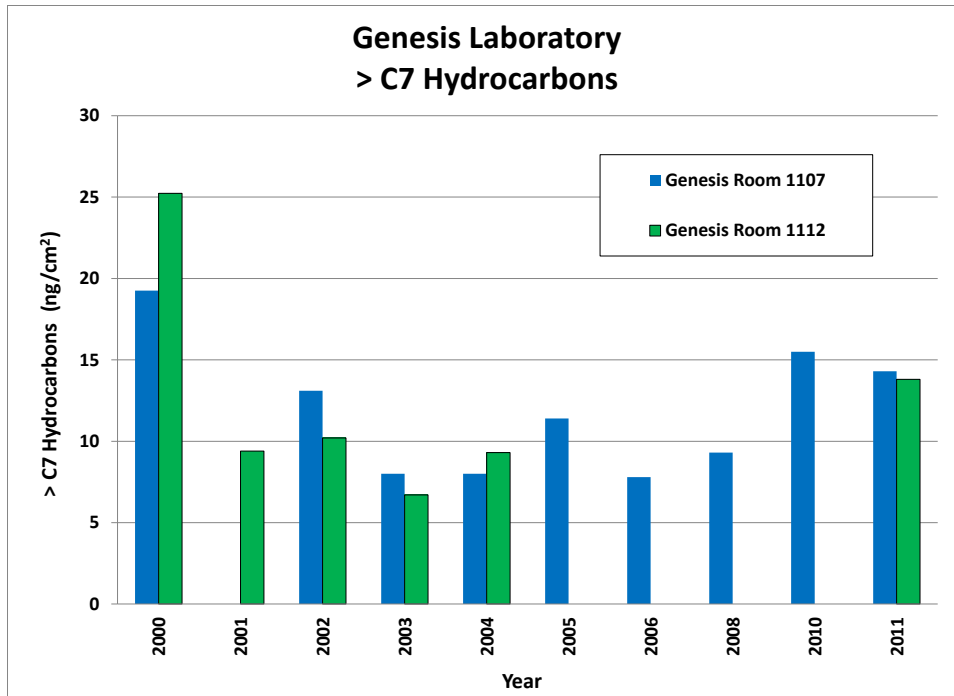
Figure 23: Genesis Laboratory measured > C₇ hydrocarbons from 2000 to 2011.

In 2004, the Genesis B31N house GN2 source was tested for organic contamination. The test consisted of exposing a Balazs proprietary adsorbent tube to the GN2 supply in the Genesis mechanical room 1108 and Genesis cleanroom 1107. In addition, the GN2 supply was tested after passing through a Pall purifier and particle filter in 1107 as well as the GN2 environment inside an array sample storage cabinet. The adsorbent tubes were then analyzed by TD-GC-MS and the results are presented below in figure 24.

Genesis Cleanroom	April 2004 Testing				
Hydrocarbons	Control Blank (ng/L)	Genesis 1107 Array Cabinet TD-GC-MS Results (ng/L)	Genesis 1107 GN2 After Filter TD-GC-MS Results (ng/L)	Genesis 1107 GN2 Supply TD-GC-MS Results (ng/L)	Mech Room 1108 GN2 Supply TD-GC-MS Results (ng/L)
Low boilers C7-C10	*	0.4	0.4	*	*
Medium boilers >C10-C20	*	*	*	*	*
High boilers >C20	*	*	*	*	*
Sum >= C7	*	0.4	0.4	*	*
Identified Organic Compounds					
Benzene	*	*	0.2	*	*
C6 Hydrocarbons	*	*	3.8	*	*
Ethyl benzene	*	*	*	*	*
m,p-Xylene	*	*	0.1	*	*
Trichloroethylene	*	0.3	*	*	*
* Reporting Limit = < 0.1 ng/L					

Figure 24: 2004 Balazs adsorbent tube TD-GC-MS results for GN2 in the Genesis Laboratory.

The 2004 GN2 organic tests shows that the GN2 house supply is free of organic contamination for >C₇ hydrocarbons at < 0.1 ng/L. This also matches the results in 2013, shown later in this report. The GN2 supply after the Pall purifier/filter and inside the storage cabinet show increased low boiler hydrocarbons at 0.4 ng/L. The TCE found in the cabinet could be from initial cleaning before installation inside the

laboratory. The increased hydrocarbons $>C_7$, benzene, C_6 hydrocarbons, and m,p-Xylene found are most likely the result of Pall's proprietary filter/purifier media.

2.6.2 Camenzind Report: Evaluation of Cleanroom Contamination

In 2000, Mark Camenzind, Senior Research Chemist of Balazs Analytical Laboratory was contracted by NASA JSC curation to assess organic airborne contamination sources in all JSC curation cleanrooms and evaluate alternative state-of-the-art concepts for the proposed future Mars Sample Handling Facility (Camenzind 2000). Camenzind toured the JSC facility on August 31, 2000, to September 1, 2000. In general, the report outlines laboratory processes for each lab and suggests alternative methods based on the experience of the semiconductor industry. While the report discusses new methods for sampling handling, including robotics for Mars sample handling, only the relevant findings will be highlighted from Camenzind's tour of the Lunar, Meteorite, and Genesis laboratories.

In the Lunar laboratory, Camenzind mentions that the heat sealing process causes outgassing of bag materials similar to the Bada final report. The heat sealer works by heating a Nichrome wire with a silicone strip backing surface, and welding the plastic by pressing it against this assembly. Unlike silicone products that are made for high-temperature environments, the silicone heat sealer strip is manufactured to slowly ablate over time and will readily outgas. Clean tools and samples that are heat sealed in bags may have organic contamination by this process. As an alternative, Camenzind suggested changing out the silicone strip for a better heat-tolerant material, such as Kalrez, Chemraz, or PEEK. Camenzind also recommended that future missions should not use heat sealing. As an alternative, he advocates bagged tools and samples should use zip-lock bags or "Gerry Tube" used in the food industry for no-leak seals. The report also mentions the Lunar lab's use of Polaroid film and two computers with fans as potential sources of organic contamination.

In the Meteorite laboratory, two contamination sources were mentioned – the use of a polyester tape and the Linoleum type flooring. Camenzind advises changing out the tape for a low-outgassing tape (Avery, 3M, etc.). The Linoleum floor was also recommended to be replaced with a more compatible cleanroom flooring material. In addition, the report comments on the UPW system and the possible presence of bacteria. During low water usage, biofilm growth can be of concern and bacteria may also be present in the Reverse Osmosis (RO) system. Camenzind suggests that routine monitoring of the UPW system for bacteria may be necessary.

In the Genesis laboratory, the Camenzind report listed several major sources for organic contamination:

- Floor Tiles
- ULPA filter potting compounds
- ULPA filter gaskets
- Tygon tubing
- Desiccator door seals
- Plastic Flow meters
- Oven door seals and exhaust manifold
- Floor pedestal rubber material

The report also outlines the Balazs 2000 Genesis cleanroom organic testing results related to these materials. The large amount of plasticizers found, such as TXIB and silicones, suggest outgassing from

vinyl, floor tiles, ULPA filter potting compounds and other materials. As steps for mitigating cleanroom outgassing, Camenzind recommends using carbon filters in the air recirculation system. The report also details an outgassing study conducted by Balazs on the polypropylene shippers that are used for wafer transport and storage. Balazs W.O. 00-02387 study heated a polypropylene shipper to 100°C for 30 min. The outgassing results found antioxidant, di-tert-butyl-4-ethylphenol, and some hydrocarbons with a total outgassing result of 11 ppm. In addition, the report mentions that the use of SafeSkin nitrile gloves number 61013 had a noticeable organic residue during UPW cleaning and an alternative glove material may be needed.   While some of Camenzind's recommendations would benefit from updating as technologies and industry procedures mature, many of these ideas may be worthwhile for future investigations into cleanroom operating procedures.

2.6.3   Outside Air Organic Analysis

JSC is located near large petrochemical plants, including ones that manufacture plastics less than 5 miles away. It is currently unknown how much residual background environmental contamination is entering all curation laboratories. However, the JSC toxicology Lab in B37 analyzed outside and indoor air samples in 2000. Results from air samples from the Genesis Room 1112, Meteorite lab, and outside air near JSC building 31 north (B31N) are shown in figure 25 below.

JSC B37 Toxicology 2000			
	GENESIS 1112 Room Air	Meteorite Lab Room Air	Outside Air JSC B31N
Identified Chemicals	(ng/L)	(ng/L)	(ng/L)
FREON 12	*	6.58	*
ACETALDEHYDE	16.50	13.94	9.08
METHANOL	26.25	26.73	12.64
ETHANOL	45.93	68.36	3.16
ACETONE	13.13	38.88	6.10
ISOPROPANOL	293.20	362.35	*
PENTANE	4.51	7.14	*
FREON 113	*	97.92	*
HEXANE	3.24	4.26	*
TOLUENE	5.73	5.31	*
HEXANAL	4.87	6.06	*
HEXAMETHYLCYCLOTRISILOXANE	77.21	138.86	56.65
OCTAMETHYLCYCLOTETRASILOXANE	50.45	78.35	*
DECAMETHYLCYCLOPENTASILOANE	16.68	1119.99	*
TETRACHLOROETHENE	*	77.50	*
CYCLOHEXANONE	*	5.18	4.49
HEPTANAL	*	6.96	*
BUTANAL	5.31	*	*

Figure 25: JSC toxicology results in 2000 for Genesis lab, Meteorite lab, and JSC outside air.

The outside air sample is lower in all identified chemicals compared to both Meteorite and Genesis laboratories. The cyclohexanone could be contributed to nylon-6 and the hexamethylcyclotrisiloxane with silicone offgassing. However, it is unknown why these are elevated in the outside air sample; possibly due to packaging of the sample prior to analysis. For Genesis and Meteorite labs, the use of IPA wipes and Freon 113 for cleaning can be easily identified. Both labs also show elevated levels of silicone offgassing from cleanroom sealants. Based on these results, outside air does not seem to contribute much contamination to the curation laboratories. However, a full investigation of outside air contaminants has never been conducted and this is the only known measurement of outside air at JSC.

3.0 ORGANIC CONTAMINATION BASELINE 2012

The 2012 organic contamination baseline study focused on testing the molecular organic contamination in current working gloveboxes that house extraterrestrial samples. The study also focused on examining the current cleaning protocols that are used for gloveboxes. Since this organic contamination baseline study had limited funds, the project focused testing only on gloveboxes where historically there exists limited data. In addition, future sample return missions will most likely use a type of isolation containment system similar to a glovebox for sample containment beyond the use of a particulate reduced cleanroom.

Two gloveboxes were chosen for the study: the Advanced Curation Glovebox (ACG) and an Apollo 11 Lunar Curation Glovebox (LCG). The choice was made based on three measurement constraints: (1) test the difference between a working glovebox after a cleaning compared to a cleaned glovebox without samples, tools, and supplies; (2) the need to test current cleaning procedures with the difference of cleaning a glovebox in-situ in the laboratory versus moving a glovebox for cleaning in Preclean; and (3) the measurement of surface molecular organic contamination with methylene chloride could not be done in a working glovebox due to possibility of contaminating lunar samples. The organic contamination testing plan was to clean each glovebox with curatorial technical support procedure (TSP) 23. Afterwards, the following tests would be done:

- Liquid particle counts on UPW rinse water from cleaning
- Scanning Electron Microscope (SEM) particle identification from UPW rinse filters from cleaning
- TD-GC-MS Analysis by Vertical Silicon Wafer Exposure
- TD-GC-MS Analysis by Surface Silicon Wafer Exposure
- TD-GC-MS Analysis by Absorbent Tube Exposure
- Non-volatile residue Fourier Transform Infrared Spectroscopy (NVR/FT-IR) Analysis by Methylene Chloride Surface Exposure (ACG ONLY)
- Gas Chromatography Mass Spectroscopy (GC-MS) Analysis by Methylene Chloride Surface Exposure (ACG ONLY)

The ACG was originally manufactured by Absolute Controls and outfitted by Oceaneering in 2000 for testing advanced curation robotic sample handling techniques for future Mars sample return (figures 26 – 28). The glovebox was specifically designed to house a custom robotic arm for sample processing. The ACG is currently housed in a positive pressure ISO class 5 cleanroom environment in B31, room 2022A. The glovebox is constructed with electropolished 304 stainless steel, glass viewing windows, Viton seals, and four Hypalon gloves. The glovebox is constantly purged at 50-75 scfh with house gaseous nitrogen (GN2), a boil off of grade C LN2. During the testing, only supplies needed for the organic test were located inside ACG and no work was done during exposure times. Possible organic material in ACG included Viton gaskets and Hypalon gloves.

Figure 26: ISO class 5 cleanroom with ACG.

Figure 27: ACG inside the ISO class 5 cleanroom.

Figure 28: ACG after TSP 23 cleaning

The LCG is the original Apollo 11 Lunar processing cabinet #307-41 manufactured by the Stainless Equipment Company in Englewood, Colorado, for the Lunar Curation Processing Laboratory in 1978 and located in the Lunar Pristine Sample Laboratory (PSL) in JSC B31N in an ISO Class 6 cleanroom environment (figures 29 and 30). The glovebox is constructed with 316L stainless steel (fine brush polished), polycarbonate main window, glass PI viewing window, Viton seals, and six neoprene gloves.

Figure 29: PSL inside the Lunar laboratory, B31N.

Figure 30: LCG located in the PSL inside an ISO Class 6 cleanroom environment.

During all organic testing, the following items were situated inside the LCG in addition to tools needed for organic sampling:

- Nylon bags on tools and containers (not sealed in cabinet)
- Teflon bags
- One Teflon glove
- Teflon disks
- One Teflon floor brush
- One small Teflon brush
- Aluminum dust pan
- Two scissors
- 4x4 inch x 2 mil Teflon sheets
- Teflon Deutsch connector covers
- One balance
- One heat sealer
- One adjustment platform (stage)
- Stainless steel chisel, chipping ring and bottom, hammer
- Stainless steel trays/one opened and others in sealed in nylon bags
- Aluminum foil
- Tweezers
- Other tools still in sealed nylon bags
- Aluminum containers
- Four samples bagged in two Teflon bags each
- One sample that was processed
- Stainless steel containers with Teflon lids
- 1 cm and 1 inch direction cubes/black anodized
- Stainless steel corner scale
- Stainless steel 6 inch ruler

It should be noted that normal sample processing was conducted during all organic sampling inside the LCG. This included the use of the heat sealer on Teflon bags. However, it should be noted that nylon and polyethylene bags were not heated sealed during this testing to comply with standard laboratory operating procedures. Possible organic material in LCG include Teflon (in the form of bags, jars, and fittings), nylon tool bags, Viton gaskets, polycarbonate (Lexan) window, neoprene gloves, and silicone rubber strip on the heat sealer.

The following are specific procedures and results from the organic testing. It is important to note that all testing in the advanced curation glovebox was completed with no sample handling and minimal disturbance to the glovebox. In comparison, all testing in the lunar processing cabinet was conducted with maximum sample handling and working inside the glovebox. This was done to ensure a standard baseline sampling of contaminates in a working glovebox.

3.1   Standard Glovebox Cleaning

TSP 23 (March 8, 2011 version) is the standard protocol for cleaning gloveboxes in all curation laboratories with heated UPW (see Appendix III for full procedure). However, historically TSP 23 used Oakite Liqui-DET (phosphates, amine, surfactants, and water miscible solvent) solution with mechanical scrubbing, IPA, nitric acid, and Freon 113 as a degreaser and final rinse for glovebox cleaning (see appendix II).   Federal environmental policies on ozone depleting chemicals phased out chlorofluorocarbon production from 1992 – 1995 and Freon 113 can no longer be used for cleaning at JSC. Today, TSP 23 only uses UPW with a resistivity >18 MΩ, TOC < 5.0 ppb and heated to 70°C. However, it was observed that the actual temperature was 52°C during cleaning of the ACG in Preclean. For both gloveboxes, gaseous nitrogen flows at 50 scfh throughout the glovebox cleaning. The glove ports are covered with Teflon and a slit is cut for PFA tube insertion with a PFA nozzle for rinsing. At least three rinses are done with UPW rinse water being drained through a 47 mm diameter Millipore mixed cellulose ester (MCE) 0.8 µm pore size filter paper for optical particle inspection for cleanliness. For the LCG, lunar material would typically saturate the Millipore filter for the first or second rinse. Therefore, before using the Millipore filters for final rinses, a 185 mm diameter Whatman grade 41 cellulose ashless 20 µm pore size filter paper is used to collect lunar sample material for proper procedural disposal. After each rinse, the filter paper is observed under a Bausch and Lomb optical stereomicroscope with a 4X objective lens to meet military standard (MIL-STD) 1246C cleanliness Level 50 (figure 31).

Level	Particle Size (µm)	Count per 1 ft^2	Count per 0.1 m^2	Counts per Liter
50	5	166	179	530
50	15	25	27.0	230
50	25	7.3	7.88	34
50	50	1.0	1.08	10

Figure 31: MIL-STD 1246C cleanliness Level 50.

The current TSP procedure states that glovebox rinses will continue "until no further significant decrease in particles is attained and there are no more than 50 particles > 10 microns." After the Millipore filter paper meets this requirement, the glovebox is deemed cleaned and placed back into service.

Figure 32: LCG UPW cleaning.

Figure 33: Stereomicroscope particle inspection of filter paper from UPW rinse.

The cleaning history of the LCG is relatively well known. The glovebox was originally degreased in 1978 and periodically cleaned for over 30 years with various curation procedures and degreasing

chemicals. However, the cleaning history of the ACG is generally unknown. The glovebox has been used by several JSC groups and has changed laboratories multiple times. Unfortunately, cleaning certification and other cleaning documentation was not passed on between groups. Typically, the most important cleaning history is in the transition from the glovebox manufacturing facility to a cleanroom. While our team received verbal verification that the glovebox was initially degreased during the procurement process, we do not have any documentation to verify this claim. Prior to this testing, the last glovebox cleaning was on August 7, 2007, under curatorial order 14759 using TSP 23.

For this baseline study, the TSP 23 cleaning procedure remained the same for both glovebox cleaning. The ACG and LCG also passed cleanliness MIL-STD Level 50 verification with optical inspection. The LCG was cleaned in-place inside the Lunar laboratory ISO class 6 cleanroom. The ACG was located in B31, room 2022A in an ISO class 5 cleanroom used for Mars studies. However, since this laboratory does not have a local supply of UPW, the glovebox was transferred to curation Preclean B31 room 243 to conduct TSP 23 and then moved back to room 2022A for organic testing. While in curation Preclean, the glovebox was cleaned outside of the clean tent (Final Clean) area in room 243. The Final Clean area particle filtered tent could not be used due to the large size of the glovebox. Therefore, while the inside of the glovebox was under constant GN2 purge and all glove ports were sealed, the outside of the glovebox was not contained inside a cleanroom. Prior to moving, the Hypalon gloves were removed and clean Teflon was applied to each glove port. The move between room 2022A and 243 was orchestrated by curation technicians working with JSC riggers to cleanly move the glovebox between the cleanroom and Preclean facility. During each move, the glovebox was cleanly wrapped in clean polyethylene sheets and the move was done quickly to mitigate the down time of being under constant GN2 purge.

3.2   Liquid Particle Counts from Glovebox Cleaning

Glovebox drain samples of UPW from the TSP 23 cleaning were collected in Teflon bottles for particle counter analysis for comparison with the optical particle inspection. Each UPW sample was analyzed by a HIAC Liquid Syringe Sampler and Particle Counter in the Genesis Advanced Precision Cleaning Laboratory ISO Class 4 cleanroom. During TSP 23, UPW rinses were stopped once the optical stereomicroscope particle observation reached a Level 50 cleanliness standard. For both gloveboxes, two rinses and a final rinse were collected for analysis. In addition, a UPW baseline control was collected before UPW cleaning. The results for particle counts for each cleaning are shown in figures 34 and 35. Each sample was run on the particle counter three times and the results in the table are the average of these counts. UPW from the Genesis lab was used as a control before and after sample runs to check the accuracy of the particle counter. The particle counts are given in particle size per 10 ml of UPW. For comparison, the MIL-STD Level 50 has also been provided in the tables below.

Advanced Curation Glovebox TSP 23 Cleaning							
UPW Particle Count per 10 ml							
Particle Size (μm)	Genesis Before Control	PreClean UPW Baseline	Rinse 1	Rinse 2	Final Rinse	Genesis After Control	MIL-STD Level
1	27	331.33	104526	4412	13290	45	
3	1	14	21167	533.33	1806.8	3	
5	1	5.67	6503.33	159	707.75	0	5.3
10	1	1.67	492.33	19	26.75	0	
25	0	0.33	4.33	0.33	0.5	0	0.34
50	0	0	0	0	0.25	0	
100	0	0	0	0	0.25	0	
150	0	0	0	0	0.25	0	
Note: all counts are averages of measurements.							

Figure 34: ACG UPW particle counts from TSP 23 cleaning.

Lunar Curation Glovebox TSP 23 Cleaning							
UPW Particle Count per 10 ml							
Particle Size (μm)	Genesis Before Control	Lunar UPW Baseline	Rinse 1	Rinse 2	Final Rinse	Genesis After Control	MIL-STD Level 50
1	2	886.4	3622.67	2005.33	1246.6	4	
3	0	54.8	749.67	394.33	128.8	0	
5	0	15.2	340.33	185.67	40.2	0	5.3
10	0	1.6	101.33	47	6.2	0	
25	0	0	22	0.67	0.6	0	0.34
50	0	0	19.33	0	0.4	0	
100	0	0	18.67	0	0.4	0	
150	0	0	17	0	0.4	0	
Note: all counts are averages of measurements.							

Figure 35: LCG UPW particle counts from TSP 23 cleaning.

The particle count results show that the LCG is much cleaner than the ACG in the lower particle sizes. While both particle count results show that each glovebox passes MIL-STD Level 50 at 25 μm size particles for the final rinse, both gloveboxes fail Level 50 at 5 μm particle size diameter. This can be expected when it is difficult to resolve particles < 25 μm in diameter using a low magnification optical stereomicroscope for particle counts during TSP 23. In addition, the optical microscope technique also allows for the potential for human error. The ACG results show that rinse 2 is lower than the final rinse for particle sizes < 10 μm. Particle count loads at 1 μm particle size diameter also show a dramatic difference between rinses, which is not normal. Usually, a downward trend is seen with lowering particle counts with more rinses until a plateau is reached. A possible explanation is that some type of contamination is still adhering to the glovebox material and not ablating evenly during UPW rinsing. This could potentially mean that the ACG glovebox was never degreased from original manufacturing.

3.3   Scanning Electron Microscope Particle Identification from Glovebox Cleaning

Particle counts provide a quick and inexpensive measure for the amount of particle contamination and effectiveness of cleaning. However, the identity of the particles is largely unknown. Therefore, the filter paper used during TSP 23 UPW cleaning for optical particle inspections were analyzed with a SEM for

particle identification. A JEOL JSM-7600F Field Emission Scanning Electron Microscope (FE-SEM) was used to survey 392 particles with over 450 spot analyses with a low angled backscatter electron (LABe) detector. The final rinse Millipore filters were analyzed for both LCG and ACG TSP 23 cleaning rinses. The 47 mm diameter Millipore MCE 0.8 μm pore size filter paper was cut to fit onto a 1 cm diameter SEM stub and carbon coated. The MCE filter material is a combined cellulose acetate and cellulose nitrate matrix. In addition, a 185 mm diameter Whatman grade 41 cellulose ashless 20 μm pore size filter paper that was used on the first LCG rinse was also analyzed for particle identification of initial large particle release.

A systematic survey of the subdivided sample searched for particles trapped by the filter. Each particle had a SEM image taken as well as a chemical spectrum. On more complex particles, more than one spectrum was taken for chemical identification. After a particle was identified, similar particles with similar spectrum were placed into possible identified material groups and counted. The results are shown in figures 36 to 41 with major groups of particles. Each particle size was also given an average size diameter and each group was given a size range and average size of the group. The particle percentage can be used to compare with the UPW particle count analysis to give a relative contamination load of each glovebox. In addition, a small sample of different types of organic particles images and spectra are shown from this investigation in figures 42-47.

Lunar Curation Glovebox SEM Particle Identification				
Whatman grade 41 cellulose ashless 20 μm pore size filter				
Possible Identified Material Groups	Particle Count	Particle %	Size Range (μm)	Average Diameter Size (μm)
Aluminum Silicate	2	3.51%	100	100
Calcium Carbonate	2	3.51%	25 to 50	38
Fluorine	1	1.75%	100	100
Iron Oxide	12	21.05%	20 to 300	77
Iron Sulfate	1	1.75%	12	12
Lunar Geologic Material	25	43.86%	5 to 100	29
Lunar Geologic Ilmenite	1	1.75%	20	20
Stainless Steel	3	5.26%	5 to 120	15
Organic Compound	9	15.79%	5 to 50	26
Unknown	1	1.75%	200	200
Particle Count Total	57	100.00%		

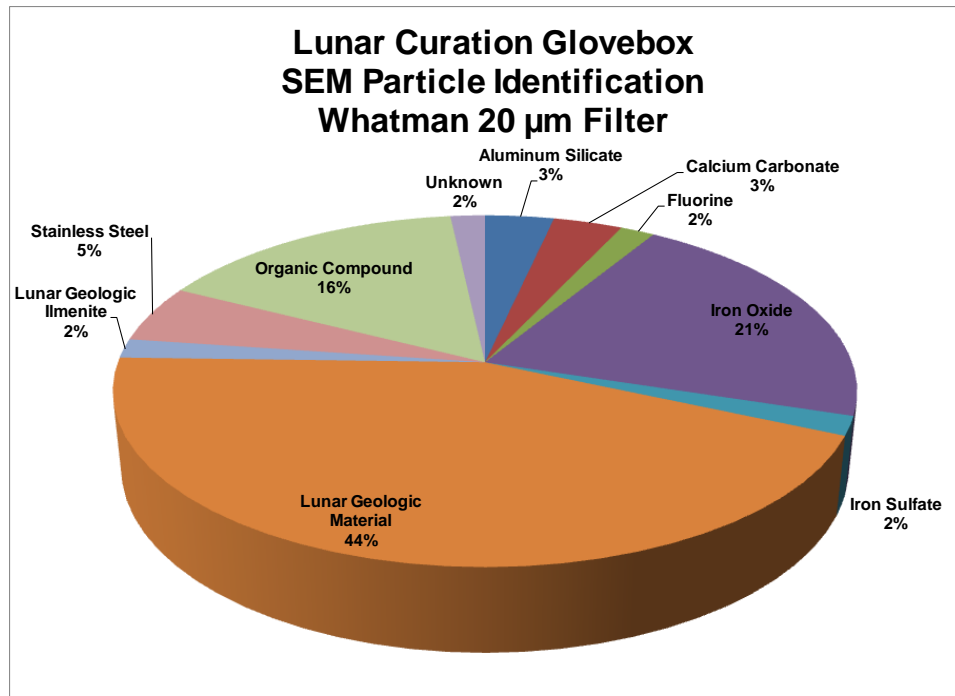**Figure 36: LCG SEM particle identification on 20 micron pore size filter.**

Figure 37: Chart for LCG SEM particle identification on 20 micron pore size filter.

Lunar Curation Glovebox SEM Particle Identification				
Millipore MCE 0.8 µm pore size filter				
Possible Identified Material Groups	Particle Count	Particle %	Size Range (µm)	Average Diameter Size (µm)
Aluminum	1	1.12%	25	25
Aluminum Oxide	1	1.12%	12	12
Iron Oxide	1	1.12%	5	5
Stainless Steel	23	25.84%	2 to 10	5
Lunar Geologic Material	24	26.97%	2 to 15	6
Lunar Geologic Ilmenite	7	7.87%	3 to 8	8
Organic Compound	27	30.34%	2 to 100	16
Hydrocarbon	1	1.12%	10	10
Silicone	4	4.49%	4 to 8	6
Particle Count Total	89	100.00%		

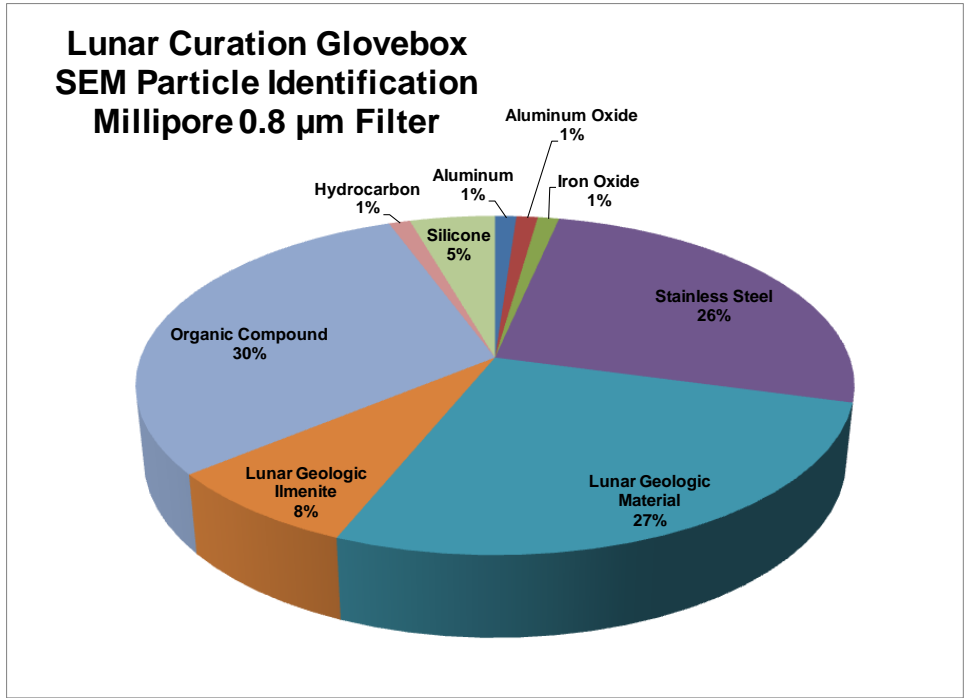**Figure 38: LCG SEM particle identification on 0.8 micron pore size filter.**

Figure 39: Chart for LCG SEM particle identification on 0.8 micron pore size filter.

Advanced Curation Glovebox SEM Particle Identification				
Millipore MCE 0.8 μm pore size filter				
Possible Identified Material Groups	**Particle Count**	**Particle %**	**Size Range (μm)**	**Average Diameter Size (μm)**
Aluminum	4	1.63%	3 to 10	6
Calcium Carbonate	6	2.44%	1 to 5	3
Copper Sulfate	4	1.63%	1 to 5	4
Iron Oxide	17	6.91%	3 to 30	9
Iron Phosphate	2	0.81%	3 to 10	2
Iron Sulfide	2	0.81%	2 to 2	7
Potassium carbonate	1	0.41%	5	5
Geologic Silicate Mineral	51	20.73%	1 to 25	7
Silver Cadmium Oxide	3	1.22%	5 to 10	8
Stainless Steel	16	6.50%	0.5 to 10	4
Fluorosilicone	10	4.07%	1 to 25	6
Hydrocarbon	5	2.03%	5 to 50	24
Organic Compound	95	38.62%	0.5 to 100	18
Silicone	30	12.20%	1 to 25	6
Particle Count Total	246	100.00%		

Figure 40: ACG SEM particle identification on 0.8 micron pore size filter.

Advanced Curation Glovebox
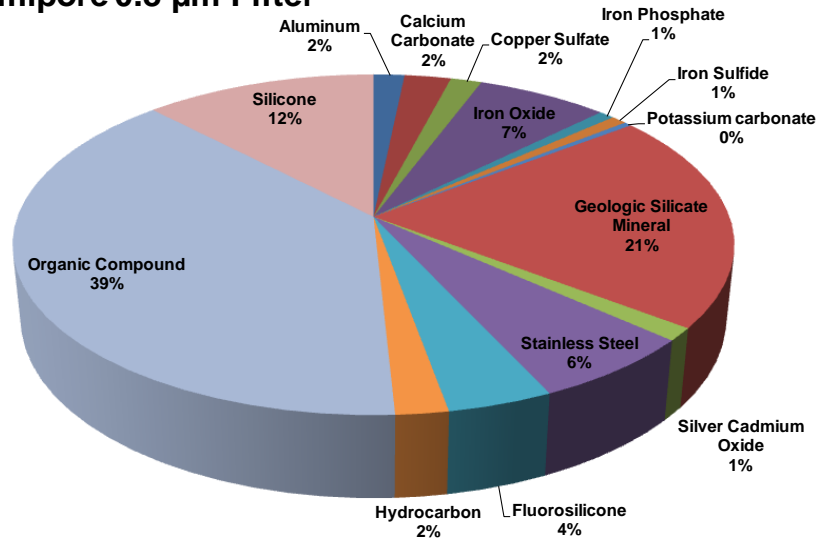**SEM Particle Identification**
Millipore 0.8 μm Filter

Aluminum 2%
Calcium Carbonate 2%
Copper Sulfate 2%
Iron Phosphate 1%
Iron Sulfide 1%
Potassium carbonate 0%
Silicone 12%
Iron Oxide 7%
Geologic Silicate Mineral 21%
Organic Compound 39%
Stainless Steel 6%
Silver Cadmium Oxide 1%
Hydrocarbon 2%
Fluorosilicone 4%

Figure 41: Chart for ACG SEM particle identification on 0.8 micron pore size filter.
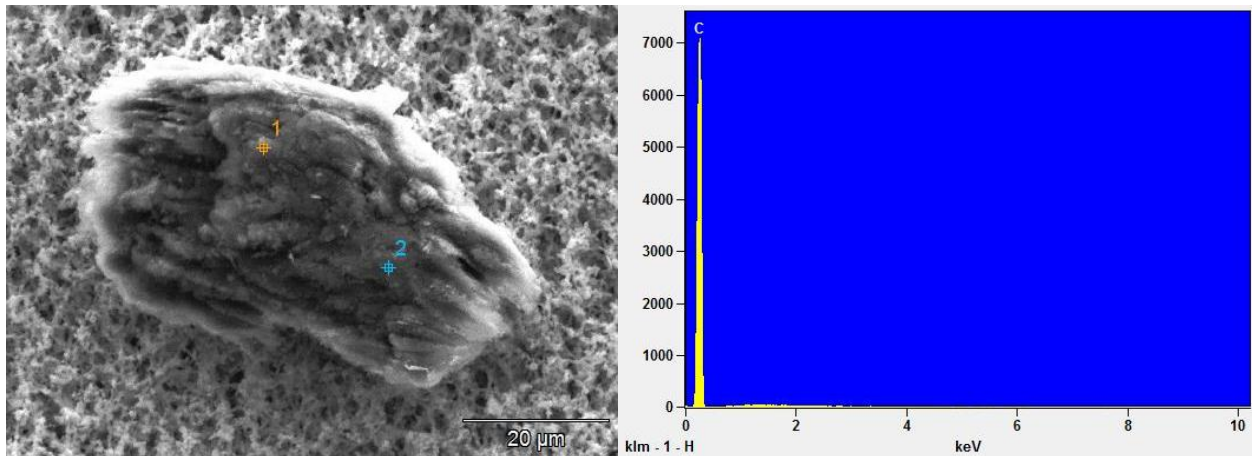

Figure 42: SEM image and chemistry of unknown organic particle with a carbon signature.
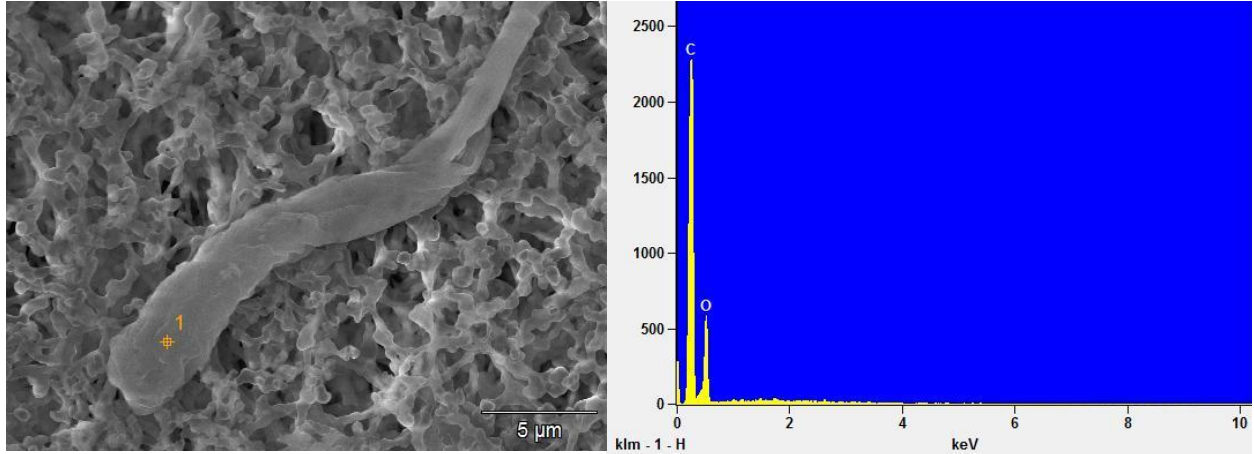
Figure 43: SEM image and chemistry of unknown organic fiber with carbon and oxygen signature.
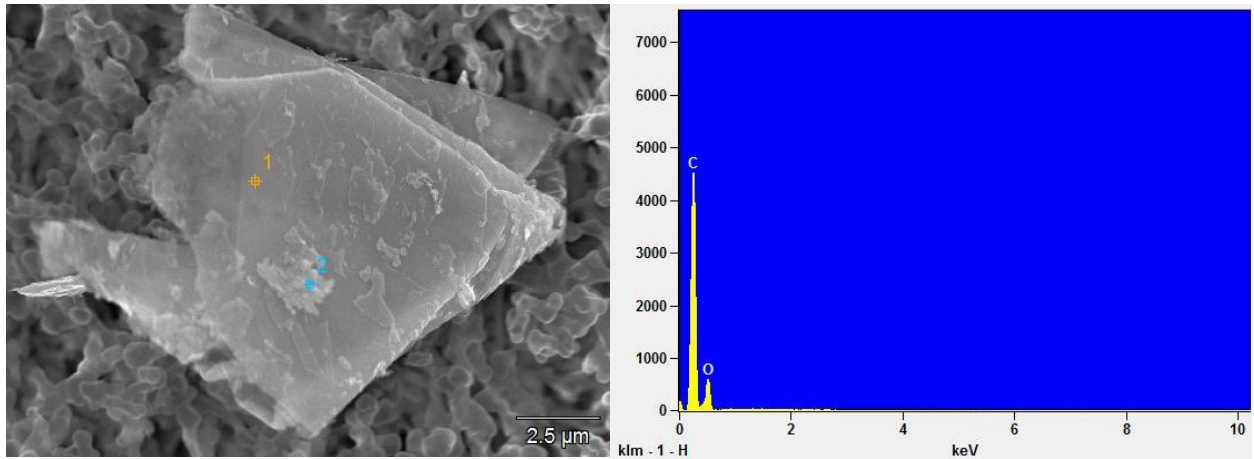

Figure 44: SEM image and chemistry of unknown organic particle with carbon and oxygen signature.
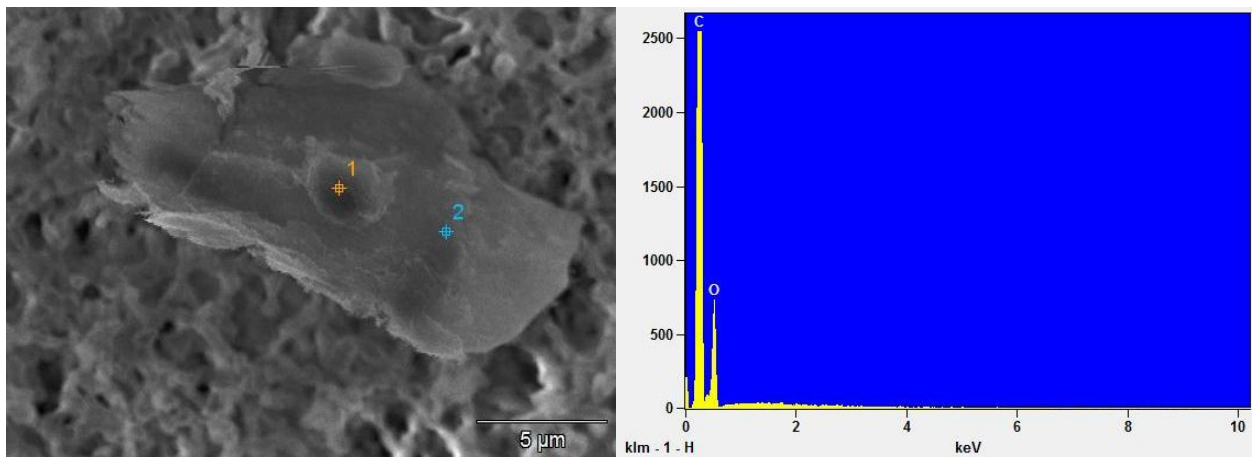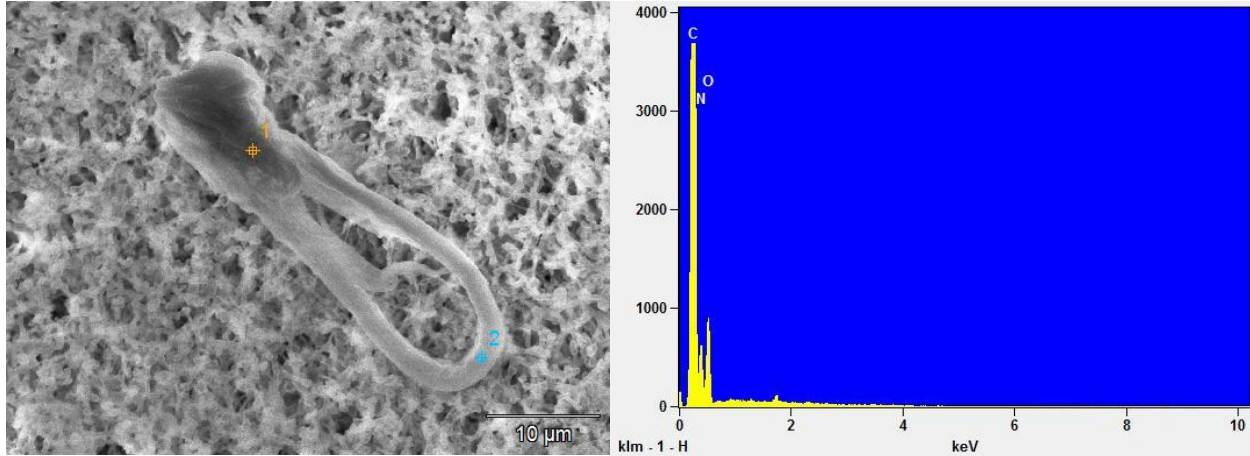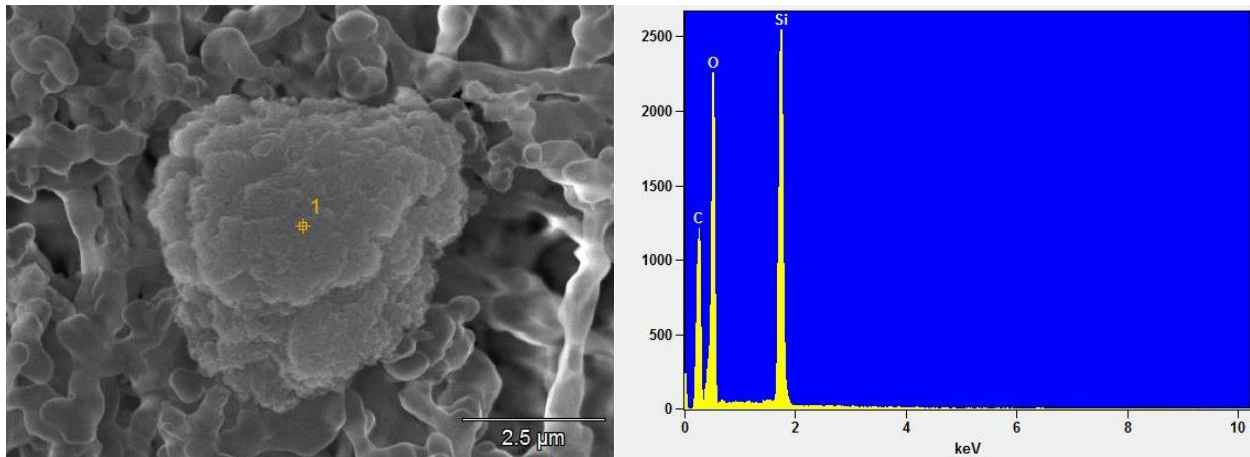

Figure 45: SEM image and chemistry of unknown organic particle with carbon and oxygen signature.

Figure 46: SEM image and chemistry of unknown organic particle/fiber with carbon, nitrogen, and oxygen signature.

Figure 47: SEM image and chemistry of unknown organic particle with silicone, oxygen, and carbon signature; possibly silicone.

The large Whatman LCG filter shows that most of the geologic material was removed from the glovebox on the first few rinses and was reduced in quantity in the final rinse. The Lunar geologic material was mostly plagioclase, pyroxene, olivine, K-feldspar, and ilmenite. Aluminum, aluminum silicate, aluminum oxide, iron sulfate, and fluorine could possibly be geologic in nature. However, some could have been introduced by cross-contamination from the lab as well as the calcium carbonate found. In both LCG analyses, the iron oxide is probably geologic in origin, but could also be from the steel in the glovebox. The organic compounds (figures 42 to 47), silicone, and hydrocarbons are probably from laboratory contamination sources. These organic particles could come from the polycarbonate window, neoprene gloves, Viton seals, and numerous nylon and Teflon bags used in the glovebox. In addition, the heat seal has a silicone strip.

The ACG final rinse filter contained more organic compounds, silicone, fluorosilicone, and hydrocarbons than the LCG samples. Since the ACG processed terrestrial geologic materials, the sample contained a wide range of silicate minerals, calcium carbonate, copper sulfide, iron phosphate, iron sulfide, potassium carbonate, and aluminum. The iron oxide most likely is from the steel in the glovebox and/or could be sample related. The silver cadmium is most likely from the robotic arm electronics that was used inside the glovebox. The two graphs in figure 48 and 49 show a percentage breakdown of organic, geologic

sample material, and metal contamination from the glovebox. Organic contamination is much greater on the ACG than the LCG. If the particle count data for 1 micron particle size is applied to the organic particle identified, the LCG final rinse has about 448 organic particles/10 mL and ACG final rinse has about 7575 organic particles/10 mL. This higher organic load in the ACG could be interpreted that the glovebox was never thoroughly degreased. Other organic sources may include Hypalon gloves and Viton gaskets. Based on the SEM images from this study, it is difficult to directly relate the morphology of the particle to specific organic contamination sources.
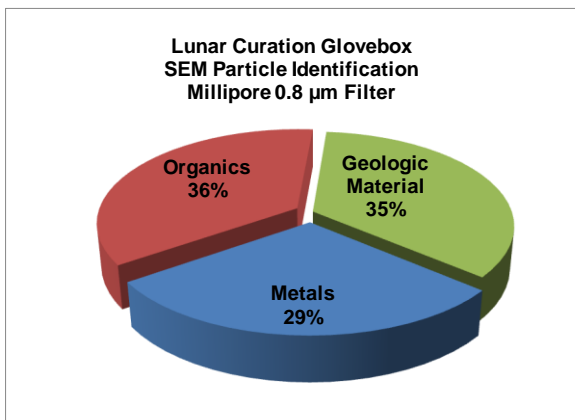
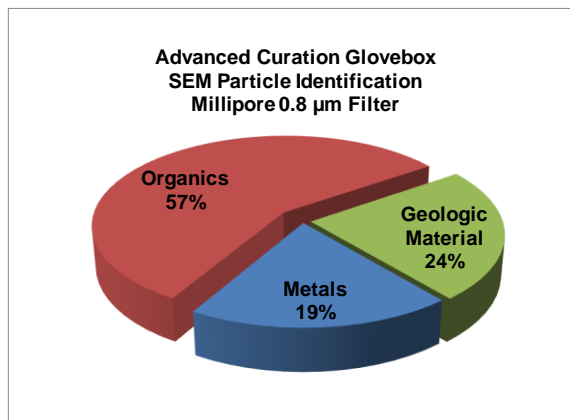**Figure 48:** General chart for LCG SEM particle identification.

Figure 49: General chart for ACG SEM particle identification.

3.4 Vertical and Surface Wafer Exposure Thermal Desorption Gas Chromatography Mass Spectroscopy Analysis

Air Liquide Balazs Nanoanalysis was contracted for molecular organic analysis in both gloveboxes in order to have comparable results to past glovebox investigations. This is the same contractor that has been used since 1998 in JSC curation for organic and inorganic testing. The vertical exposure of 8" or 6" diameter ultra-pure silicon semiconductor wafers for 24 hours and subsequent TD-GC-MS analysis has been historically done at JSC Curation for airborne contamination. For better comparison with previous data sets, we selected the same laboratory sampling procedure for the 2012 organic testing. However, a new sampling technique was added to attempt a better understanding of organic contamination adhering to the surface of the glovebox. This was to expose a second set of silicon wafers, oriented face down, to the surface of the glovebox. ACG and LCG were both sampled with the same method. However, a 6" diameter silicon wafer instead of a standard 8" diameter wafer was used for the ACG due to the size of the glove ports for sample insertion.

For each test in ACG and LCG, two pairs of the pre-baked silicon wafers were sent to JSC. The first set of wafers was exposed vertically for 24 hours. The second set of wafers was also simultaneously exposed vertically for 24 hours and then placed onto the surface of the glovebox for the last 15 min. to attempt to measure surface contamination. The pre-cleaned wafer samples came packaged in three layers of pre-baked aluminum foil and were sandwiched face to face (polished mirror side together). For the LCG, the wafers were introduced to the glovebox through the standard antechamber pass-through door. These wafers were exposed to a working lunar glovebox during testing. For the ACG, the 6" wafers were introduced quickly into the glovebox by the removal of one of the 8" glove ports, since the ACG does not have a sample pass-through door. In contrast to the working lunar glovebox, the ACG was undisturbed throughout the sampling. After sampling, the sampled wafers were wrapped face-to-face in three layers

of pre-baked aluminum foil and shipped back to Balazs for TD-GC-MS analysis along with a shipping control wafers that were never opened (see figures 50 to 54).

Figure 50: Lunar material being processed inside LCG during testing.

Figure 51: 8" silicon wafers exposed during organic testing inside the LCG.
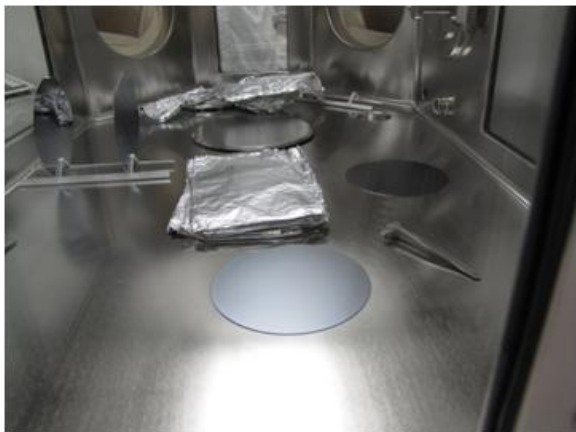
Figure 52: 6" silicon wafer surface exposure.

Figure 53: 6" silicon wafer vertical exposure in the ACG.

Figure 54: Silicon wafer handling during the ACG organic testing.

Balazs supplied JSC with a report and specified the analytical procedure for obtaining the results. At Balazs, the silicon wafers were heated in a GL Sciences SWA-256 full wafer desorption system in a continuously flowing stream of ultra-high purity helium. The sample chamber temperature was increased from ambient to 400°C in 15 min. and maintained 400°C for an additional 15 minutes. Stainless steel sampling tubes containing proprietary adsorbents at near-ambient temperature were used to capture organic compounds from one side of wafer surface. These sampling tubes were then analyzed by TD-GC-MS per Balazs procedure "SEMI MF 1982-1103 Method-B". The GC was equipped with a non-polar poly (dimethylsiloxane) phase capillary column. The GC was programmed with an initial temperature to maintain 35°C for 3.5 min. and then increase at a rate of 10°C/min. to 280°C followed by maintaining the final temperature of 280°C for 10 min. Helium was used as the carrier gas for the GC-MS and an internal standard, toluene-d8, was added to each sampling tube during the analysis.

The results were reported in units of ng/cm^2, which was based on the surface area of one side of the wafers and are expressed by the equivalent n-hexadecane external standard value. Labeled chromatograms were included for each sample. The results were expressed both in terms of the total organics in three different ranges (based roughly upon boiling point) and as individual compounds detected at concentrations above the reporting limit. Identification of each compound detected was first attempted by searching 275,000 mass spectra in a Wiley library. In cases where no matches were found, the Balazs analyst interpreted the mass spectra to give best estimate of the most probable compound or class of compounds. The organic compounds were classified into three boiling ranges, low-boiling ($C_7 - C_{10}$), medium-boiling ($>C_{10} - C_{20}$) and high-boiling ($>C_{20}$), based on comparisons with the retention times of a $C_7 - C_{28}$ n-hydrocarbon external standard. Semiquantitated amounts of the organic compounds in each boiling range were calculated by using the integrated total ion count (TIC) of that boiling range and the response factor for an n-hexadecane external standard. For semiquantitated compounds, amounts of individually identified compounds were estimated using TIC area of that compound and the response factor of an n-hexadecane external standard. The following results were obtained in figures 55 to 60.

| Lunar Curation Glovebox			
Hydrocarbons	**Control Wafer (ng/cm²)**	**Vertical Exposure (ng/cm²)**	**Surface Exposure (ng/cm²)**
Low boilers C7-C10	*	*	0.2
Medium boilers >C10-C20	*	1.8	2.5
High boilers >C20	*	0.1	0.2
Sum >= C7	*	1.9	2.9
Identified Compounds			
Diethylformamide	*	*	*
Diethylacetamide	*	*	*
Alkyl amine	*	*	*
2-Butoxyethyl acetate	*	*	*
Octafluoropentanal(m/z:51,69,100,131,151,181,200,231,281)	*	*	*
2-Cyclohexen-1-one, 3,5,5-trimethyl-	*	0.3	0.3
Dibutylformamide	*	0.2	0.2
Cyclo(Me2SiO)6	*	0.2	0.2
2,6-di-tert-Butylquinone	*	*	*
Cyclo(Me2SiO)7	*	*	*
Cyclo(Me2SiO)8	*	*	0.1
Cyclo(Me2SiO)9	*	0.2	0.3
Dibutyl phthalate	*	*	0.1
Cyclo(Me2SiO)10	*	0.1	0.2
Siloxane	*	0.1	0.1
* Recording Limit = < 0.1 ng/cm²			

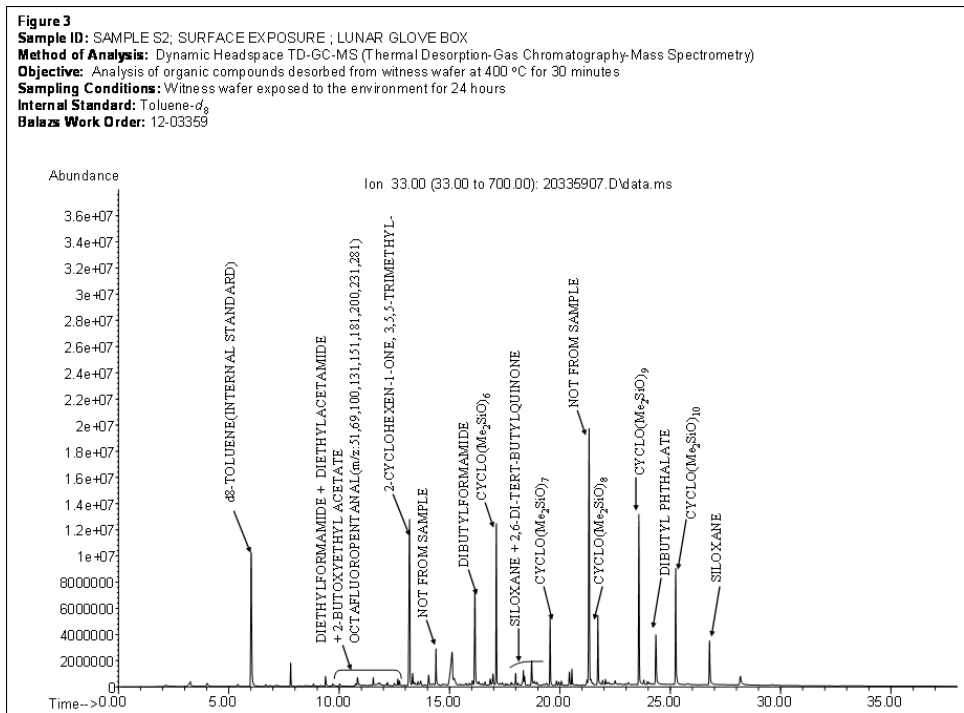**Figure 55: LCG Balazs organic wafer test results.**
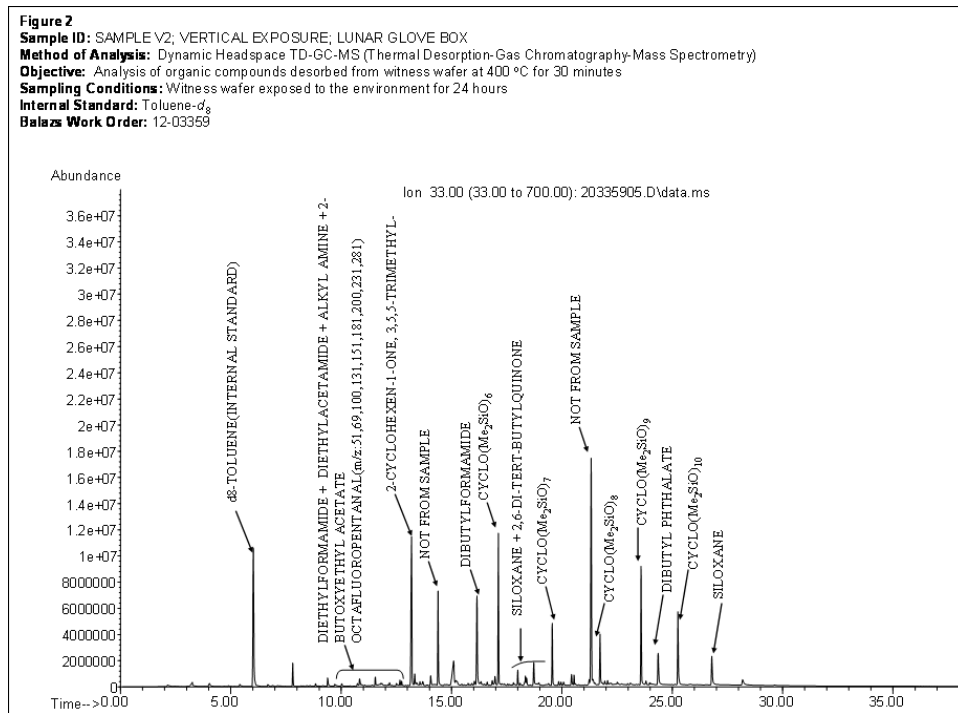
Figure 56: LCG Balazs organic wafer TD-GC-MS plot for vertical wafer exposure.

Figure 57: LCG Balazs organic wafer TD-GC-MS plot for surface wafer exposure.

Several identified chemicals above reporting limit were found for the LCG. The solvent isophorone (2-cyclohexen-1-one, 3,5,5-trimethyl-) was detected and is typically used in printing inks, paints, lacquers, adhesives, copolymers, coatings, finishings, and pesticides. In addition, it can be used as a chemical intermediate and as an ingredient in wood preservatives and floor sealants. Dibutylformamide (DBF) is an additive or reducing agent used in manufacturing of polymers, rubbers, medicines, herbicides, flame retardants in fabrics, solvents, inks, and photo paper. DBP is a common plasticizer used in adhesives, solvents and inks. The LCG results show elevated levels of silicones: cyclo$(Me_2SiO)_6$, cyclo$(Me_2SiO)_8$, cyclo$(Me_2SiO)_9$, cyclo$(Me_2SiO)_{10}$, and siloxane. These can be found in silicone adhesives and cleanrooms sealants. However, the silicones may also be from the heat sealer that was used to seal Teflon bags. The heat sealer has a known silicone rubber strip that clamps down on the bag while heating the material.

Advanced Curation Glovebox			
Hydrocarbons	**Control Wafer (ng/cm²)**	**Vertical Exposure (ng/cm²)**	**Surface Exposure (ng/cm²)**
Low boilers C7-C10	*	0.4	0.4
Medium boilers >C10-C20	*	7.1	9.6
High boilers >C20	*	1.1	1.8
Sum >= C7	*	8.6	11.8
Identified Compounds			
Dibutylamine	*	*	*
N-Formylpiperidine	*	*	0.1
2-(2-Butoxyethoxy)ethanol	*	0.6	1
Caprolactam	*	0.2	0.6
Tripropylene glycol	*	*	*
Dibutylformamide	*	*	0.1
N,N-Dibutylacetamide	*	*	*
Texanol	*	*	*
Dimethyl phthalate	*	*	*
Diisopropyl adipate	*	*	*
2,6-di-butyl-2,5-cyclohexadiene-1,4-dione	*	*	*
2,6-di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one	*	*	*
Cyclo(Me2SiO)7	*	*	*
Diethyl phthalate	*	0.2	0.3
TXIB	*	0.3	0.3
Piperidine, 1,1'-carbonylbis-	*	*	*
Cyclo(Me2SiO)8	*	0.3	0.5
Tri(2-chloroethyl) phosphate	*	0.2	0.2
Benzenesulfonamide, N-butyl- + 3,5-di-tert-Butyl-4-hydroxybenzaldehyde	*	*	*
Benzenesulfonamide, N-butyl-	*	*	*
Isopropyl Myristate	*	*	*
Diisobutyl phthalate	*	0.1	0.1
Cyclo(Me2SiO)9	*	*	0.1
Dibutyl phthalate	*	0.5	0.6
C17-C22 Hydrocarbon	*	*	0.1
* Recording Limit = < 0.1 ng/cm²			

Figure 58: ACG Balazs organic wafer test results.

Figure 2
Sample ID: V1;VERTICAL EXPOSURE,ADVANCED CURATION GLOVEBOX;24 HRS EXPOSURE
Method of Analysis: Dynamic Headspace TD-GC-MS (Thermal Desorption-Gas Chromatography-Mass Spectrometry)
Objective: Analysis of organic compounds desorbed from witness wafer at 400 °C for 30 minutes
Sampling Conditions: Witness wafer exposed to the environment for 24 hours
Internal Standard: Toluene-d_8
Balazs Work Order: 12-04514

Figure 59: ACG Balazs organic wafer TD-GC-MS plot for vertical wafer exposure.

Figure 3
Sample ID: S1;SURFACE EXPOSURE,ADVANCED CURATION GLOVEBOX;24 HRS EXPOSURE + 15 MIN SURFACE
Method of Analysis: Dynamic Headspace TD-GC-MS (Thermal Desorption-Gas Chromatography-Mass Spectrometry)
Objective: Analysis of organic compounds desorbed from witness wafer at 400 °C for 30 minutes
Sampling Conditions: Witness wafer exposed to the environment for 24 hours
Internal Standard: Toluene-d_8
Balazs Work Order: 12-04514

Figure 60: ACG Balazs organic wafer TD-GC-MS plot for surface wafer exposure.

The identified chemicals above reporting limit for the ACG are N-formylpiperidine and 2-(2-butoxyethoxy) ethanol, which are both solvents. Caprolactam was found and is usually associated with nylon-6 bags. DBF, a rubber/polymer additive, was also found. Several plasticizers above reporting limits included DEP, TXIB, DBP, and DIBP. Tri(2-chloroethyl) phosphate can be associated with flame retardant in plastics. Silicones found were $cyclo(Me_2SiO)_8$ and $cyclo(Me_2SiO)_9$ along with $C_{17} - C_{22}$ hydrocarbons.

3.5 Air Absorbent Thermal Desoprtion Gas Chromatography Mass Spectroscopy Analysis

The determination of organics in air was also completed through Air-Liquide Balazs Analytical Services. Balazs provided a sampling kit to JSC curation that contained a sample pump and two stainless steel sample tubes packed with multiple beds of proprietary adsorbents. For both the ACG and LCG, a clean 128 mm long, ¼" diameter stainless steel GN2 tube was connected directly from the main glovebox chamber to the stainless steel absorbent sampling tube. The other end of the absorbent sampling tube was then connected to a Gilian LFS-113 low flow sampling pump set at a flow rate of 100 mL/min (see figures 61 to 63). The sampling pump was run for exactly 6 hours while the glovebox GN2 flow rate was set at a nominal 50 scfh. Afterwards, the absorbent sampling tube was sealed at both ends with the original stainless steel compression fitted ends and then wrapped in clean baked-out aluminum foil for shipping to Balazs for TD-GC-MS analysis. In addition, a shipping control sampling tube was sent with the kit and was never opened at JSC.

Figure 61: Location of adsorbent tube attachment to main chamber of the ACG.

Figure 62: Location of adsorbent tube attachment to main chamber of the LCG.

Figure 63: Gilian sampling pump and adsorbent tube for collecting organics in air.

The following experimental set-up for TD-GC-MS was reported by Balazs. At Balazs, the GC used a non-polar poly (dimethylsiloxane) phase capillary column. The GC was programmed with an initial temperature to maintain 35°C for 3.5 min. and then increase at a rate of 10°C/min. to 280°C followed by maintaining the final temperature of 280°C for 10 min. Helium was used as the carrier gas for the GC-MS and an internal standard, toluene-d8, was added to each sampling tube during the analysis. This test method was designed to analyze semi-volatile organic compounds in the boiling point range of n-heptane (boiling point approximately 100°C) to n-octacosane (boiling point approximately 430°C). Identification of each compound detected was first attempted by searching a Wiley library of 275,000 mass spectra. In cases where no matches were found, mass spectra were interpreted by the Balazs analyst to give best estimate of the most probable compound or class of compounds.

The results were reported as n-decane in units of ng/L along with labeled chromatograms for each sample. The organic compounds are classified into three boiling ranges, low-boiling ($C_7 - C_{10}$), medium-boiling ($>C_{10}-C_{20}$) and high-boiling ($>C_{20}$), based on comparisons with the retention times of a $C_7 - C_{28}$ n-hydrocarbon external standards. Semiquantitative amounts of the organic compounds in each boiling range are calculated by using the integrated TIC of that boiling range and the response factor for an n-decane external standard. Amounts of individually identified compounds were estimated using TIC area of that compound and response factor of n-decane external standard. The following results were given for the ACG and LCG in figures 64 and 65.

Lunar Curation Glovebox				Advanced Curation Glovebox		
Hydrocarbons	Control Blank (ng/L)	TD-GC-MS Results (ng/L)		**Hydrocarbons**	Control Blank (ng/L)	TD-GC-MS Results (ng/L)
Low boilers C7-C10	*	1.2		Low boilers C7-C10	*	0.6
Medium boilers >C10-C20	*	3.8		Medium boilers >C10-C20	*	18.8
High boilers >C20	*	*		High boilers >C20	*	0.1
Sum >= C7	*	5		Sum >= C7	*	19.5
Identified Organic Compounds				**Identified Organic Compounds**		
Cyclo(Me2SiO)3	*	*		Methyl methacrylate	*	*
Ethylbenzene	*	*		Cyclo(Me2SiO)3	*	*
m,p-Xylene	*	*		Cyclo(Me2SiO)4	*	*
o-Xylene	*	*		Limonene	*	*
Cyclo(Me2SiO)4	*	0.2		C3 benzene	*	*
Cyclo(Me2SiO)5	*	*		C10-C14 Hydrocarbon	*	0.2
Methylnaphthalene	*	*		C16-C20 hydrocarbon	*	16.8
Chlorodecane	*	0.3		* Reporting Limit = < 0.1 ng/L		
C12-C16 Hydrocarbons	*	0.3				
* Reporting Limit = < 0.1 ng/L						

Figure 64: LCG Balazs results for adsorbent tube.   **Figure 65: ACG Balazs results for adsorbent tube.**

The determination of organics in air provides a better understanding of the organic cleanliness of the gaseous nitrogen environment and sometimes provides a better VOC load. Unlike the silicon wafers, which collect airborne particles well, the absorbent tube should be better at collecting VOCs in the gaseous nitrogen environment. Conversely, silicon wafers should be better suited for collection of suspended particles. Compared with the silicon wafer tests, the absorbent tubes also provide a better insight into the hydrocarbon load inside the glovebox's main sample processing chamber.

For the identified organic compounds, the LCG has 0.2 ng/L of cyclo(Me$_2$SiO)$_4$ that can be representative of silicone outgassing. The LCG results also show 0.3 ng/L of chlorodecane, which is a plasticizer that is indicative of outgassing of a rubber. The most likely source for the presence of cyclo(Me$_2$SiO)$_4$ and chlorodecane is the use of a heat sealer, which has a silicone rubber strip. Both ACG and LCG results detected hydrocarbons >C$_7$. In comparison, the hydrocarbon load in the LCG is much lower than the ACG, which is almost four times larger. This difference is not understood.

It was proposed that one possibility of the difference in hydrocarbon load could be indicative of the cleanliness level of the nitrogen piping infrastructure between B31 and B31N. In July 2013, a determination of organics of the GN2 supply lines was conducted with Balazs. The LCG, AGC, and a B31, room 215 nitrogen supply lines were tested. B31, room 215 is the future planned location of the OSIRIS-REx Laboratory and the supply line closest to the lab entry door was tested. Each supply line was fitted with two ¼" stainless steel adsorbent tubes with a flow rate of 100 ml/min. for 24 hours. The adsorbent sample tubes and control tubes were sent back to Balazs for TD-GC-MS analysis. All three locations resulted in no organic compounds found and all hydrocarbon loads were below the reporting limit of < 0.1 ng/L for >C$_7$ (figure 66). The same Balazs TD-GC-MS analysis was also conducted on April 12, 2004, for the GN2 supply in Genesis laboratory room 1107 and mechanical room 1108 in B31N. It should be noted that this testing was done prior to the installation of a new LN2 tank in 2006. The results also reported no organics compounds were found and all hydrocarbon loads were below the reporting limit of < 0.1 ng/L for >C$_7$ (figure 24). Therefore, the B31 and B31N nitrogen supply lines are not the cause for elevated organic levels in LCG and ACG. The two separate data points also suggest that

in-house nitrogen does not seem to be a general source for any organic contamination in curation laboratories.

Hydrocarbons	Control Blank (ng/L)	July 2013 Testing		
		GN2 Supply OSIRIS-REx Lab B31 R215 TD-GC-MS Results (ng/L)	GN2 Supply LCG Lunar Lab TD-GC-MS Results (ng/L)	GN2 Supply ACG B31 R2022A TD-GC-MS Results (ng/L)
Low boilers C7-C10	*	*	*	*
Medium boilers >C10-C20	*	*	*	*
High boilers >C20	*	*	*	*
Sum >= C7	*	*	*	*
Identified Organic Compounds				
None	*	*	*	*
* Reporting Limit = < 0.1 ng/L				

Figure 66: Balazs TD-GC-MS results for GN2 supply organic testing in 2013.

The TD-GC-MS analysis adsorbent results can also be used to classify the glovebox air cleanliness according to ISO-AMC air cleanliness class; ISO 14644-8 (figure 67). For example, -12 is the cleanest at 0.001 ng/m^3 Total Volatile Organic Compounds (TVOC) concentration. Based on these TD-GC-MS results, the LCG total hydrocarbons = 5 ng/L = 5000 ng/m^3 and has an ISO-AMC = $-$ 5 (10^4 ng/m^3). For the ACG, total hydrocarbons = 19.5 ng/L = 19500 ng/m^3 and has an ISO-AMC = $-$ 4 (10^5 ng/m^3).

ISO-AMC Class	TVOC Concentration (ng/m^3)
0	10^9
-1	10^8
-2	10^7
-3	10^6
-4	10^5
-5	10^4
-6	1000
-7	100
-8	10
-9	1
-10	0.1
-11	0.01
-12	0.001

Figure 67: ISO-AMC air cleanliness class; ISO 14644-8.

3.6 Surface Methylene Chloride Exposure Non-volatile Residue/Fourier Transform Infrared Spectroscopy and Gas Chromatography Mass Spectroscopy Analysis

In consultation with Balazs, a new methodology was attempted to better understand the organic contamination adhering to the surface of the glovebox in addition to the surface wafer exposure. The new technique would use a highly pure solvent, methylene chloride, to dissolve any surface contamination. The exposed methylene chloride would then be tested by standard GC-MS and NVR/FT-IR analysis. Balazs shipped to JSC pure methylene chloride in a glass vial along with a glass syringe. Methylene chloride was applied to the surface for a few seconds and immediately reacquired with the syringe needle and emptied into a clean vial for shipment back to Balazs (see figures 68 and 69). Two samples were taken for each analytical method. Since methylene chloride could potentially contaminate lunar material inside the LCG, only the ACG was tested by this method.


Figure 68: Application of methylene chloride to the surface of the ACG with glass syringe.

Figure 69: Collection of methylene chloride to the surface of the ACG with glass syringe.

At Balazs, the methylene chloride sample was completely concentrated for NVR/FT-IR analysis. The residue was weighed and transferred to a metal mirror for reflectance mode FT-IR analysis utilizing Nicolet 6700 FT-IR system coupled to Continuum FT-IR microscope. The spectra were collected at 8 cm^{-1} resolution with 64 scans. Background spectra were collected on a clean area of the mirror. The control sample was 0.004 mg and the ACG sample was 0.158 mg. Below is the spectrum for the FT-IR analysis (figure 70).
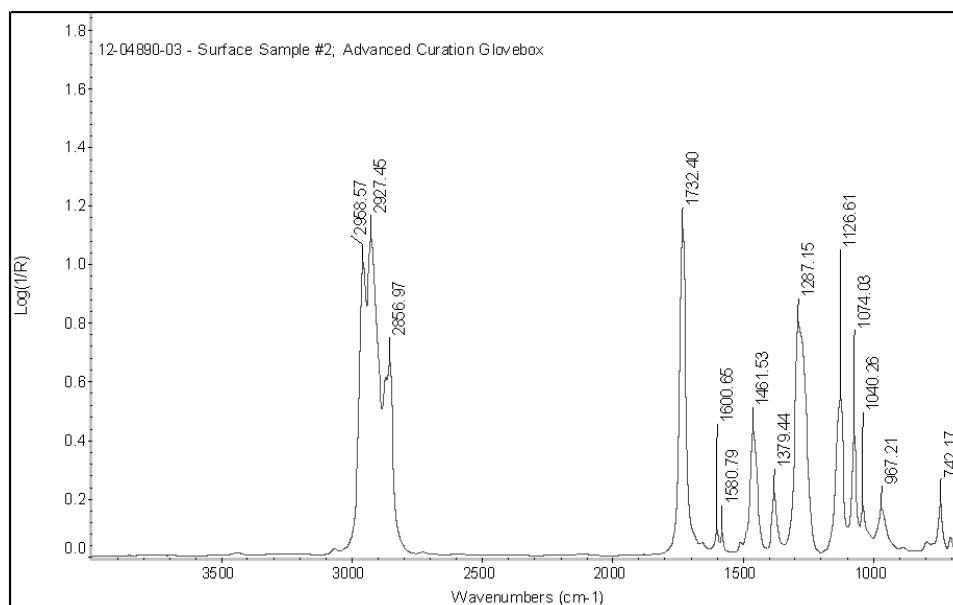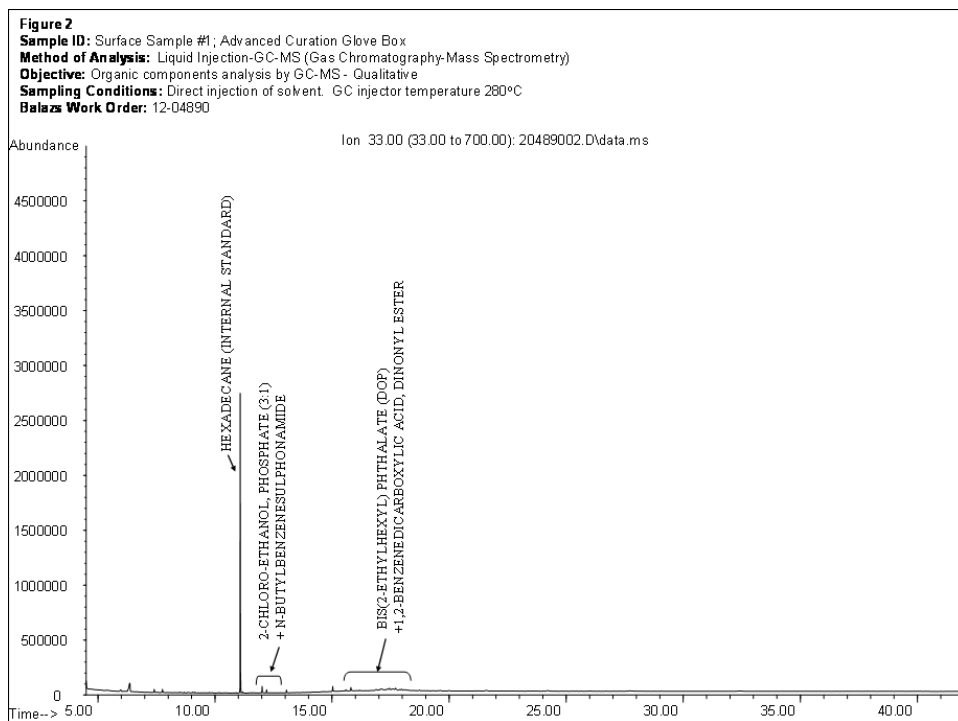
Figure 70: ACG Balazs plot for NVR/FT-IR results.

The infrared spectrum collected on the blank exhibited no significant infrared absorption bands. The infrared spectrum collected on the ACG sample residue exhibited C-H stretching absorption bands at 2958, 2927, and 2856 cm^{-1}, carbonyl stretching absorption band at 1732 cm^{-1}, aromatic ring mode absorption bands at 1600 and 1580 cm^{-1}, C-H bending absorption band at 1461 cm^{-1}, C-H umbrella mode absorption band at 1379 cm^{-1}, C-C-O stretching absorption band at 1287 cm cm^{-1}, and O-C-C stretching absorption band at 1126 cm^{-1}. In addition, C-H in-plane bending absorption band 742 cm cm^{-1} was found and was interpreted as typical for a dialkyl phthalate; e.g. diheptyl or dioctyl phthalate (DOP). The NVR/FT-IR results also show the presence of aromatic hydrocarbons. The carbonyl can be interpreted as indicative of some organometallic complexes. However, the interpretation of the presence of dialkyl phthalate is a common group of chemicals associated with plasticizers and mainly found in the manufacturing of PVC. This interpretation of the results matches closely with the GC-MS analysis below.

At Balazs for GC-MS, the second sample of exposed methylene chloride was concentrated to a minimum amount and an internal standard (Hexadecane) was added for the GC-MS analysis. A HP 7890 GC with a 5975C quadrupole Mass Selective Detector (MSD) was equipped with a non-polar poly (dimethylsiloxane) phase capillary column for the analysis. The GC was programmed to begin with an initial temperature 40°C for 3 min. and then increased at a rate of 20 °C /min. to 280°C and held at 280°C for 30 min. The injection port temperature was 280°C and the sample volume injected was 1.0 µL. Each compound passed down the GC column at a characteristic rate. As each compound exited the CG, it entered the MSD where it was ionized using electron impact ionization (70 eV). The MSD collected a full mass spectrum (10-700 amu) approximately once per second. Each identified compound detected was first searched using the Wiley library of 275,000 mass spectra. In cases where no matches were found, the analyst interpreted the mass spectra to give best estimate of the most probable compound or class of compounds. The results are below in figure 71.

Figure 71: ACG Balazs plot for GC-MS results.

Four chemicals were found by GC-MS. 2-Chloro-Ethanol, Phosphate (3:1) or TCEP – $C_9H_{15}O_6P \cdot HCl$ is commonly used as a reducing agent in biochemistry and in detergents. TCEP has also been widely used as a flame retardant and manufacturing of PVC vinyl, electronics, adhesives, upholstery, carpeting, rubber, plastics, paints, and varnishes. +N-Butylbenzenesulphonamide (NBBS) – $C_{10}H_{15}NO_2S$ is widely used as a plasticizer in industrial chemicals and drugs. NBBS also has antifungal properties and was commonly used on agricultural fields for over 30 years and is now a common contamination in ground water supplies. In addition, NBBS is fairly common building block for industrial chemicals and drugs. Bis(2-ethylhexyl) phthalate (DOP or di-2-ethylhexyl phthalate (DEHP) – $C_{24}H_{38}O_4$) is a common plasticizer in many plastics manufacturing and most common in the outgassing of PVC type materials. DEHP is widely found in the environment and municipal water supplies in low levels from manufacturing of PVC. 1, 2-benzenedicarboxylic acid, dinonyl ester– $C_{26}H_{42}O_4$ or commonly called dinonyl phthalate (DNP) is used primarily as a low efficiency plasticizer for PVC to impart flexibility. DNP can also be found in many types of vinyl from automotive to electrical wiring as well as uses as an additive in lubricating oils.

4.0   SUMMARY

Hydrocarbons, plasticizers, solvents, silicones, and rubbers are the majority of organic contamination found in JSC astromaterials curation cleanrooms and gloveboxes. A list of all organic compounds found in JSC curation (B31 and B31N) to date has been provided in Appendix I. After standard UPW cleaning of the ACG and LCG, both gloveboxes showed relatively low levels of organics when compared to standard laboratories. Hydrocarbon loads ($> C_7$) ranged from 1.9 to 11.8 ng/cm^2 for TD-GC-MS wafer exposure analyses and 5.0 to 19.5 ng/L for TD-GC-MS adsorbent tube exposure (ISO-AMC air cleanliness class – 4 and – 5 respectively). Plasticizers included < 0.6 ng/cm^2 of DBP, DEP, TXIB, and DIBP. Silicones included < 0.5 ng/cm^2 of cyclo(Me$_2$SiO)$_x$ (x = 6, 8, 9, 10) and siloxane. Solvents included < 1.0 ng/cm^2 of 2-cyclohexen-1-one, 3,5,5-trimethyl- (isophorone), N-formylpiperidine, and 2-(2-butoxyethoxy) ethanol. In addition, DBF, rubber/polymer additive was found at < 0.2 ng/cm^2 and caprolactam, nylon-6 at < 0.6 ng/cm^2. All other identified organic compounds were below a reporting limit of < 0.1 ng/cm^2. It is difficult to trace specific sources of organic contamination given that these organic additives and compounds are used in many different types of manufactured products. In some cases, it is unclear whether some of these detected organics are from inside the lab or from the background environment (e.g., common plasticizers released into the Houston air and not filtered through the cleanroom air handling and filtration system). While the one data point from JSC Toxicology measurements in 2000 suggests that the background environment may not contribute much contamination, if any, the subject should be further explored. More importantly, additional individual laboratory material organic testing is required for linking specific sources to contamination. However, the study results demonstrate that organic contamination can be associated to the use of sample and tool bags, glovebox construction materials, laboratory equipment, cleanroom facility construction materials, cleaning chemicals, and personal hygiene products.

Modern modular cleanroom designs used at JSC since 1999 contain a larger variety of complex organic construction products (plastics) and adhesive (silicone) components than previous curation facilities. While these construction products have greatly reduced the particle load and ease of cleaning in the laboratory environment, they have increased the variety of organic outgassing products. As a result, this has also increased the difficulty in linking specific outgassing products and hinders efforts to reduce organic contamination over time. This is not to suggest that previous laboratory construction did not contain large amounts of organics outgassing, but the possible sources of contamination were easier to isolate. The application of new construction materials may have increased chemical outgassing over time when compared with the 1978 constructed Lunar facilities in B31N. In general, most outgassing organic material will decrease contamination levels over time. This observation is illustrated by the comparison of Genesis cleanroom organic results between 2000 and 2011. A closer comparison of individual plasticizers that were found shows that the newer classes of cleanrooms outgassing chemicals are being detected in the ACG, but not in the LCG. This difference could be related to differences in construction materials and the amount of time since original installation. A future experiment could clean the ACG with organic solvents, degreasers, and/or other organic contamination reduction cleaning procedures and retest for organics. The results could determine the presence or absence of cleanroom related chemicals.

The hydrocarbon contamination is most likely a mix of plastic construction components and the use of sample and tool bags (mostly nylon and to a lesser extent Teflon). Based on recent organic tests on nitrogen supply lines in B31 and B31N, the hydrocarbon contamination is not from the supply of nitrogen and is indigenous to the glovebox. Some of the hydrocarbon and plasticizer contamination found in the glovebox tests may originate from the polycarbonate windows, gloves (both neoprene and to a lesser

extent Hypalon) and possibly a small Viton gasket component. The largest contaminating glovebox material is most likely the use of polycarbonate windows. This was observed when the MBraun cold curation glovebox changed from polycarbonate to glass windows for Hayabusa sample containment. The use of a heat sealer to seal Teflon and nylon bags is probably related to the largest component of silicone contamination inside the glovebox and cleanroom. The silicon rubber strip could be changed to a more heat-tolerant product, such as Kalrez, Chemraz, or PEEK, to reduce silicone outgassing contamination. In addition, heat sealing will also produce outgassing of hydrocarbons. Caprolactam, nylon-6, is still detectable in large quantities in the lab over Teflon related products. Many solvents found during testing could be from the daily use of IPA wipes and other cleaning products. In smaller quantities, outgassing of paint products has been detected in the cleanrooms. The overall organic results show a strong possibility that personal hygiene products (e.g., soaps, perfumes, nail polish) have been found in JSC curation laboratories and possibly in lunar gloveboxes diffusing through porous neoprene gloves. Further testing is required of laboratory material and personal hygiene products to provide a direct correlation between the specific contaminate and source.

The TSP 23 UPW cleaning for the LCG and ACG showed that the optical stereomicroscope particle inspection was not as precise as the automated liquid particle counter. In addition, the microscopic inspection has an element of potential human error. JSC Curation should review new practices for cleanliness inspection as well as implement better particle counting standards. Historically, JSC Curation used THC, NVR, black light inspection initiated during the Apollo program. Standard methods for testing cleanliness at other NASA cleaning facilities still use the NVR approach standard in MIL-STD 1246C and TOC collected from rinse solutions or water. However, X-ray photoelectron spectroscopy (XPS) could provide a better approach for quickly assessing organic cleanliness. An XPS method for identifying residual organic contamination on a material surface after precision cleaning was initially researched by Mickelson (2002a). XPS was also used to assess carbon contamination on Genesis solar wind samples (Calaway et al. 2007). XPS has the ability to quantify contamination at or below 10^{15} carbon atoms/cm^2, which has better precision than other standard testing and verification of cleanliness methods. In addition, standards could be manufactured with curation standard material surface with 10^{14} to 10^{15} carbon atoms/cm^2 and used for daily comparison after precision cleaning.

The study of JSC curation cleaning procedures through time shows that procedural changes are not well documented. The selection and deletion of chemicals has not been thoroughly studied and focused cleaning reviews may be required for JSC curation. Specifically, JSC 03243 and TSP 23 glovebox cleaning procedures are in need of further review. It may also be useful to closely study the history of changes over time and chemical substitutions (e.g., JSC 03243 Oct. 1, 1971, and June 1, 1981, cleaning procedures). The two major chemical changes for cleaning were the use of IPA over 3:1 Benzene/Methanol solution and the use of UPW over Freon 113. Freon 113 had the additional benefit of being a useful organic degreasing solvent as well as a good chemical for final rinsing. The addition of Freon 113 to Apollo 11 cleaning procedures significantly helped to reduce organic contamination. A substitute for Freon has not been thoroughly studied and this was also mentioned by several historical reports. New chemicals have replaced Freon for cleaning in other industries (e.g., Dupont Vertrel XF (HFC-4310), 1,1,1,2,2,3,4,5,5,5 – decafluoropentane and 3M HFE-7100DL, a methyl nonafluoroisobutyl ether). The TSP 23 UPW cleaning procedure was recently established to only use UPW and UPW is the choice for final rinsing in the semiconductor industry. However, the semiconductor industry also uses many different cleaning agents before a final UPW rinse to reduce organic contamination. In addition, accepted practices for the semiconductor industry may not directly translate to a cleanliness policy for such a diverse collection of extraterrestrial samples. Nevertheless, UPW has a very high purity, free from

71

inorganic and organic contamination and is much cleaner than most manufactured solvents that require complex distillation purification systems. If UPW is continued to be used at JSC curation, the system should be maintained and have an established monitoring program based on international standards. Established monitoring practices of the UPW systems includes: ASTM D 5127-13, a standard guide for the use of UPW; ASTM D4453 – 11, a standard for handling UPW; ASTM D 5391-99 test method for flowing UPW resistivity; ASTM D 5997-96 test methods for monitoring UPW total organic carbon; and ASTM F 1094-87 test methods for microbiological monitoring of UPW.

Another observation from TSP 23 UPW cleaning was the state of the cleanroom used for cleaning. The Apollo program used ISO class 5 cleanrooms for all cleaning. Today, JSC curation Final Clean laboratory uses a clean tent at about ISO Class 6 to 7. Since many new curation laboratories use ISO Class 4 and 5 cleanrooms, it may be a good practice to match the cleaning facility at the same cleanliness level as the cleanest cleanroom (ISO class 4 in this case). In most modular cleanroom facilities in the semiconductor industry, it is common practice to design the cleanroom for in-situ cleaning and clean everything in-place. A review of the JSC cleaning facility could study the type of cleanroom needed for cleaning curation isolation containment and handling equipment in-place as opposed to outside of the laboratory. In addition, it would be important to look at how the individual laboratories are physically connected to the cleaning process and if detached, how this affects clean products in transit to the lab. The construction of new laboratories should be designed with cleaning in mind of how it will be physically done and provide adequate space to clean equipment and lab. Technicians were also observed wearing lab coat, shoe cover, and hat in the Final Clean lab and inside the Lunar lab during TSP 23. However, most modern precision cleaning is done with full cleanroom suit with hood, masks, and double gloves – especially if you are opening the isolation containment system (glovebox). Any future cleaning facility study should also investigate the prevention of contamination by laboratory cleaning technicians and the appropriate use of cleanroom garments and personnel hygiene requirements. The last in-depth literature reviews on curation cleaning practices were done in 2002 as part of the NASA report series on Mars Return Sample Handling (MRSH). Edward Mickelson (2002a, 2002b, 2002c) provided three reports on cleanliness standards, methods for monitoring cleanliness and best practices for cleaning in a curation laboratory. However, these reports are becoming outdated and a new focused literature study on current state-of-the-art cleanliness standards, method of cleaning, types of materials to use, and monitoring cleanliness would be beneficial to JSC curation.

The organic contamination baseline study also demonstrated the necessity of a focused material review. Sample segregation and material selection are both important for reducing organic contamination. The segregation of samples was highlighted in the Bada Committee final report. Specifically, the isolation and containment of samples from lab personnel and certain materials are important. In addition, the purchasing of approved materials must be carefully monitored. For example, Viton, a DuPont registered trademark fluoroelastomer, is routinely used as a gasket material for gloveboxes in JSC curation. However, DuPont currently sells 37 types of Viton with each having different outgassing and particle shedding properties. While curation may require a Viton material, specific Viton needs to be specified. This becomes more complicated when a secondary company is supplying the Viton part needed for primary curation of samples and this material called "Viton" may not necessarily be manufactured by DuPont. Materials that are purchased by JSC curation should be certified by the manufactures or vendor to reduce the chance that the received product is not counterfeit. Sample segregation for inorganic and organic analysis may need separate isolation containment systems constructed from different material. For example an organic processing glovebox materials list may include:

- Stainless Steel 316L (main chamber)
- DuPont Kalrez seals
- Schott Amiran Anti-reflective Glass
- Honeywell North polyurethane/chlorosulfonated polyethylene gloves
- In-line Hydrocarbon gaseous nitrogen purifier
- In-line Pall 3nm particle gaseous nitrogen filter
- Stainless Steel 316L containers

Inorganic processing glovebox materials list may include:

- Ethylene chlorotrifluoroethylene, Halar from Edlon Inc. SC-2001 non-pigmented (main chamber)
- DuPont Kalrez seals
- Sabic MR10 Lexan (polycarbonate)
- Honeywell North polyurethane/chlorosulfonated polyethylene gloves
- In-line Pall 3nm particle filter
- Teflon containers

Throughout the 40 years of JSC curation, the use of Teflon, nylon and polyethylene bags in labs as well as heat sealing these types of bags for primary sample containment has been a topic for discussion and study. Historically, the Apollo program used only Teflon as the primary sample containment and for handling samples with over-gloves in a glovebox. Nylon and polyethylene are certainly detectable and large contamination sources in curation labs. While the cost of nylon and polyethylene is much lower when compared to the expense of Teflon, more studies are needed to fully understand the short-term and long-term use of these materials as primary containment. In addition, a review of permissible glovebox glove materials and routine replacement is recommended. The LCG organic testing and historical records demonstrated that there might be contamination from personnel hygiene products diffusing through neoprene glovebox gloves in lunar gloveboxes. Neoprene may need to be changed to Hypalon or another comparable material. The lunar gloveboxes use of polycarbonate over glass should also be reviewed. The initial switch to polycarbonate (Lexan) in the Lunar laboratory was never documented or studied. In addition, polycarbonate windows in Lunar lab gloveboxes were observed to be visibly deteriorated (discolored breakdown of the plastic as well as numerous scratches). Routine replacement should be explored for polycarbonate materials (possible every 10 years, which is the recommendation for most Lexan manufactures). While glass windows will reduce organic contamination, glass is prone to break during geologic subdivision with hammering; although the Apollo 15 Lunar processing cabinet still has the original glass window. Safety issues may require polycarbonate or a more complex multiple layered window to accommodate safety and cleanliness may need to be designed and manufactured. All material used in curation must be thoroughly tested before use (e.g., the Viton example above). JSC curation should also keep a good record of material testing or the manufacturer's material tests. In addition, modular cleanroom construction materials and facility maintenance (e.g., new floors, walls, GN2 piping, etc.) materials need to be studied thoroughly before installation.

Facility maintenance and routine cleaning documentation was observed to be absent in the JSC curation data center and difficult to trace. While the Apollo program once used contractor TSP reports and kept adequate records, this is currently not done today. Each glovebox, cabinet, and sample handling tools

should have a documented cleaning history, easily assessable and known. In addition, each glovebox, cabinet, and sample handling tools should have a minimum standard for cleaning and be placed on a schedule for recleaning at an established shelf-life (possibly annual). Tools and samples that are bagged are prone for bag material degradation over time and each bag should be on a cleaning and re-bagging schedule. Laboratory furniture, instrumentation, floor, and wall cleaning should be regular and have a documented cleaning history. While procedures and schedules exist for cleaning certain curation labs, thorough documentation does not exist of what was cleaned or when. For gloveboxes, each material component should have a life-span and replacement schedule. For example, Viton gaskets and polycarbonate (Lexan) windows manufacturers typically recommend replacement every 10 years, and glove manufacturers typically recommend replacement every 5 years. The GN2 piping infrastructure must be routinely inspected for possible sources of cross-contamination between laboratories and isolation contaminant systems. New GN2 piping also must be carefully documented such that each pipe and valve is certified cleaned. Any new augmentation to the system must have proper materials and be cleaned in-house or certified cleaned from the manufacturer. GN2 filters and purifiers should also be placed on a replacement schedule. Most manufacturers typically recommend annual replacement or when a specified gas volume has passed through the filter. As filtration systems improve, GN2 filter upgrades are recommended (e.g., Lunar lab has old 60 μm filtration and today filtration can be readily available at 0.3 nm filtration). For reducing organics in the GN2 system, in-line point-source hydrocarbon traps could be added to the GN2 system at specific gloveboxes or storage systems. As part of a regular facility maintenance schedule, routine inorganic and organic monitoring of all curation laboratories would benefit from early detection of contamination and potentially help understand point sources of contamination.

The JSC curation story of Xylan contamination raised several potential lessons learned that should be studied for progressing modern curation practices and mission planning. The rapid schedule and lack of resources for material testing in the early 1970s started the use of Xylan in the labs without being thoroughly investigated. The initial testing was never completed as required by the contamination control committee. In addition, the committee changed personnel and the committee itself was eventually dissolved without closing tasks and actions. A long period of time is observed between when Xylan contamination was officially noticed by the contamination control officer to actual laboratory actions (1986 to 1990). A breakdown in communication due to interoffice politics and management prolonged actions to investigative scientific study. The Xylan study also recognized that polyamides in the gloveboxes could potentially give a false biochemical signal. It was suggested that polyamides in the Xylan could possibly affect research analyses of amino acids and proteins. However, only JSC curation internal memos documented this hypothesis and this interpretation of the data set was not noted in the final Xylan reports. This would later be noted in the study of nylon bags, almost a decade later. If Xylan was researched thoroughly in the 1970s and early 1980s, the increased use of nylon and caprolactam organic contamination may have been avoided.

Administrative procedures and employee training can help reduce organic contamination in JSC curation laboratories. Annual training on cleaning and working in cleanrooms could be used to help employees remember protocols and introduce new standards. Many NASA wide cleanroom certification training classes are a one-time occurrence and do not meet cleanroom training requirements needed for cleanrooms rated below ISO class 7. At JSC, the curation facilities house the cleanest facilities at JSC. The training should be tailored to curation cleanroom requirements and not rely on NASA-wide training. It is suggested that a NASA training policy for all workers in curation laboratory be well established and each employee should learn how to be vigilant toward contamination sources. During the historical literature search, it was found that official memoranda were widely used prior to 1995. This type of

interoffice reporting was critical for understanding historical curation decisions or changes in procedures. However, with the advent of email, there is no system or memos to document historical changes to curation facilities or procedures. A new archiving system is required to track this information for future generations to understand past laboratory and procedural changes.

In the past, JSC Curation used a full-time CCO who monitored the laboratories and routinely would report to CAPTEM. Today, the CCO is a full-time researcher with a low percentage of time dedicated to curation contamination oversight. The idea of the CCO as a full-time job to focus on monitoring contamination in all curation laboratories should be carefully reviewed. The CCO could also be used to maintain a robust research program on material testing, cleaning technologies, and infrastructure improvements. CAPTEM should also review the idea of a contamination subcommittee with a dedicated chair, which could also be the CCO. The new contamination control subcommittee would be comprised of a member from each collection subcommittee. Scheduled lab inspections and documentation for contamination, similar to the safety inspections, could be conducted routinely by lab leads (weekly), CCO (monthly) and CAPTEM (annually). Each curation collection could be mandated to keep documentation on cleaning history and monitoring data for review by the CCO.

The Apollo program was the last sample return mission that made specific requirements for organic contamination. The Lunar mission required an organic cleanliness level of < 1 ng/g, which was the detection limit of the time. However, today NASA does not maintain organic cleanliness policies or requirements for future sample return mission beyond the basic requirements from the Planetary Protection Office. Future mission planning would benefit from basic requirements for organic contamination and cleanliness levels from a scientific perspective. These requirements could be established by the planetary science subcommittee and CAPTEM under the NASA Advisory Council. The requirements could then be administered as NASA Policy Directives through the Astromaterials Acquisition and Curation Office at JSC. If today's scientific community requires an organic free environment for future sample return missions that are better than the observed organic loads in JSC Curation, more can be done on choosing better materials as well as modifying current handling and cleaning procedures.

The organic contamination baseline study has produced the most comprehensive study on organic contamination in NASA JSC Astromaterials Acquisition and Curation Office laboratories. The historical perspective and testing results can be used as a benchmark to plan new sample return mission requirements that wish to preserve extraterrestrial organic material from sample collection to the curation facility. The results of this study highlight current procedures and requirements that will require improvement to match the cleanliness of the Apollo program and even further innovations to meet the requirements for future sample return missions. The study also provides more avenues of research on contamination monitoring and control in a curation facility. While this report is a comprehensive review of organic contamination that has been done to date at JSC, the recent contamination monitoring has mainly focused on organic contamination $> C_7$ hydrocarbons and compounds. Future research and monitoring will need to extend the organic baseline study to include light organics C_1 to C_6 that will be increasingly important for future missions. In addition, the nature of terrestrial organic contamination from PAHs, bacteria (DNA and RNA), amino acids, and other biological studies will be paramount for future exploration missions that focus on astrobiology. This new line of research will take several more years of study and progress JSC curation's ability to further understand the role of organics and mitigate contamination.

5.0   APPENDIX I

Identified Organic Compounds in Johnson Space Center Curation Laboratories

This is a list of all identified organics compounds found in JSC Curation B31 and B31N from 1998 to 2013:

1-(2-Butoxyethoxy) ethanol
2-(2-Butoxyethoxy) ethanol
2-(2-Butoxyethoxy) ethanol + Cyclo (Me2SiO)7
2-(2-Butoxyethoxy) ethanol + Cyclo(Me2SiO)5
2, 6-di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one
2, 6-di-butyl-2,5-cyclohexadiene-1,4-dione
2, 6-di-tert
2, 6-di-tert-Butylquinone
2-Butoxypropanol
2-Ethylhexanol
2-Nitropropane
2-n-Octyl-3 (2H)-lsothiazolone
2-Octyl-3-isothiazolinone
2-Propanol, 1-(2-methoxypropoxy)-
3, 5-di-tert-Butyl-4-hydroxybenzaldehyde
4-(hydroxymethlethyl)-acetophenone
Acetaldehyde
Acetone
Acetonitrile
Acetophenone
Acetophenone derivative
Acetyl acetophenone
Acetyl phenyl propanol
Acrolein
Adipic acid derivative
Alkyl acrylate
Alkyl ester + Cyclo(Me2SiO)6
Alkyl esters
Alkyl nitrile
Alkyl phthalate
Alkylphenol
Benzene
Benzaldehyde
Benzoic acid + 2-(2-butoxy ethoxy) ethanol
Benzoic acid + Decanal
BHT-aldehyde
BHT-quinone-methide + Ethanone, 1-[4-(1-hydroxy-1-methylethyl) phenyl]-
Butanol
Butanol + benzene
Butene
Butoxy ethanol
Butoxyethoxy ethanol
Butoxypropanol
Butyl benzyl phthalate

Butyl hydroxy toluene (BHT)
Butylbenzoquinone
Butyraldehyde
C3 – benzene + dipropylene glycol
C7 Ketone
C7 Saturated aliphatic hydrocarbons
C6 Hydrocarbons
C8 Hydrocarbons
C9 Aromatic Hydrocarbon
C12 Hydrocarbon + Unknown(m/z:97,110)
C14 Saturated aliphatic hydrocarbons
C20 Hydrocarbon
C5 – C9 Hydrocarbons
C6 – C10 Hydrocarbons
C6 – C7 Hydrocarbons
C6 – C9 Hydrocarbons
C8 – C23 Hydrocarbons
C8 – C25 Hydrocarbons
C8 – C9 Saturated aliphatic hydrocarbons
C8 – C9 Saturated and unsaturated aliphatic hydrocarbons
C10 – C11 Saturated aliphatic hydrocarbons
C10 – C12 Saturated aliphatic hydrocarbons
C10 – C13 Saturated aliphatic hydrocarbons
C10 – C25 Hydrocarbons
C11 – C18 Hydrocarbons
C16 – C20 Hydrocarbon
C18 – C27 Hydrocarbons
C20 – C24 Hydrocarbons
C21 – C25 Hydrocarbons
C21 – C26 Hydrocarbons
Caprolactam
Carbon disulfide
Carbon monoxide
Carbonyl sulfide
Cyclic tetramehtylene adipate
Cyclo (Me2SiO)3
Cyclo (Me2SiO)4
Cyclo (Me2SiO)5
Cyclo (Me2SiO)6
Cyclo (Me2SiO)7
Cyclo (Me2SiO)7 + 2,6-di-tert-butyl benzoquinone
Cyclo (Me2SiO)8
Cyclo (Me2SiO)9
Cyclo (Me2SiO)10
Cyclo (Me2SiO)11
Cyclododecane
Cyclooctasiloxane, hexadecamethyl-
Decamethylcyclopentasiloxane
Di(2-ethylhexyl)adipate
Diacetoxy butane
Diacetyl acetophenone
Diacetyl benzene

Dibutyl phthalate (DBP)
Dibutylamine
Didecyl ester of decanedioic acid
Didecyl sebacate
Diethyl phthalate (DEP)
Difluorodimethyl silane
Diisobutyl phthalate
Diisopropenyl benzene
Diisopropyl adipate
Diisopropyl phenol
Dimethyl benzyl amine
Dimethyl phthalate
Dimethylcyclohexanol
Di-n-octyl phthalate
Dioctyl adipate
Dioctyl phthalate (DOP)
Dipropylene glycol methyl ether
Dipropyleneglycol
Dodecanamide
Dodecanenitrile
Ethanol, 2-(2-butoxyethoxy)- + Cyclo(Me2SiO)5
Ethyl benzene
Ethyl hexanol
Fluorocarbons
Hexadecamethylheptasiloxane
Hexamethylcyclotrisiloxane
Hexamethyldisiloxane
Hexanedioic acid, bis(2-ethylhexyl) ester
Hydroxymethylethyl-acetophenone
Isobutyraldehyde
Isopropanol
Isopropenyl acetophenone
Isopropenyl acetophenone + Cyclo (Me2SiO)6
Isopropenylbenzene
Isopropyl alcohol
Isopropyl myristate
m, p-Xylenes
Methoxypropoxypropanol
Methyl isobutyl ketone (MIBK)
Methyl isopropyl ether
Methyl naphthalene isomers
Methyl palmitate
Methylethylketone
N, N-dimethyl formamide
Naphthalene
Naphthalene + Butoxethoxy ethanol + Cyclo (Me2SiO)5
NMP
N-N-dibutylacetamide
Nonanal
Octamethylcyclotetrasiloxane
Octasulfur
Other siloxanes

o-Xylene
p-Acetyl acetophenone
p-Acetyl-isopropenylbenzene
p-Diacetylbenzene
PGMEA
Phenols
Possible fluorochlorocarbons (m/z: 85, 101, 135,151)
Propoxypropanol
Propylene glycol glyme isomers
Siloxane
Styrene
Sulfur dioxide
Surfynol
Tetrachloroethylene
Texanol
Toluene
Trichloroethylene
Triethyl phosphate
Triphenyl phosphate
Tripropylene glycol
TXIB
TXIB + Diethyl phthalate
Undecanenitrile
Unknown (43, 71, 115, 145, 160)
Unknown (m/z: 111, 125, 140)
Unknown (m/z: 115, 145, 160)
Unknown (m/z: 115, 158)
Unknown (m/z: 138, 208)
Unknown (m/z: 153, 183, 198)
Unknown (m/z: 41, 55, 84,100, 129)
Unknown (m/z: 43, 161, 176)
Unknown (m/z: 43, 163)
Unknown (m/z: 43, 55, 115, 127)
Unknown (m/z: 43, 55, 127, 155, 183)
Unknown (m/z: 43, 55, 71, 95)
Unknown (m/z: 43, 56, 71, 173)
Unknown (m/z: 43, 57, 101, 127)
Unknown (m/z: 55, 84, 112, 142)
Unknown (m/z: 55, 84, 99, 173)
Unknown (m/z: 55, 97, 150)
Unknown (m/z: 55, 99, 173)
Unknown (m/z: 55, 99, 173, 221)
Unknown (m/z: 57, 165, 267, 282)
Unknown (m/z: 70, 77, 105,112, 123)
Unknown (m/z: 71 , 83, 101 , 113, 119)
Unknown (m/z: 76,104,149,193)
Unknown (m/z:43, 55, 71, 97, 110)
Unknown (m/z:43,57,71,83,101,113,119,132, 147)
Unknown (m/z:43,71,91,115,145,160) + Cyclo(Me2Sio)6
Unknown (me/: 43, 163)
Xylenes

6.0   APPENDIX II

Johnson Space Center 03243 Glovebox Cleaning Procedure: 1981

Lunar Sample Curatorial Facility Cleaning Procedures for Contamination Control: JSC 03243, June 1, 1981 (supersedes JSC 03243). Except from CP-1 pages 4-7:

CP-l

1.0 PROCEDURE FOR CLEANING LUNAR SAMPLE CABINETRY

1.1 PROCEDURE

A. This procedure shall be followed to clean stainless steel GN2 cabinetry for processing and storage of lunar samples. This procedure may also be followed to clean cabinetry for other events requiring this level of cleanliness

B. Degreasing - Degreasing is required on all interior surfaces of new cabinets during first cleaning. Degreasing on previously cleaned cabinets is required only when visual inspection indicates need, or when called for on work request.

C. New cabinets, not previously cleaned, will be given an initial acid wash to remove lead contamination derived from the fabrication process. After the first cleaning, acid wash will not be required unless operations dictate otherwise. Acid wash will be specified on the Clean Room Work Request (SOG) when required.

1.1.1 PREPARATION

A. Personnel involved in cleaning will wear clean-room clothing when working in cabinetry.

B. Make up 1% Liquidet solution using facility distilled water, meeting particle count requirements of table IV. Certify daily.

C. Acid Wash (when required) - Make up 2% nitric acid solution using reagent grade acid and facility distilled water.

1.1. 2 Cabinet Cleaning

A. Degrease according to Para. 1.1.3 when called for on Work Request.

B. Completely wash all areas inside of each cabinet with Liquidet solution. Use stiff nylon brush, and nonabrasive scouring pads to scrub and polish the cabinet surfaces. Remove all visible rust and stains with Scotch Brite pads or stainless steel toothbrush.

C. Remove all solution from cabinet. Use vacuum flask with liquid pickup, lint-free wipes, and squeegee as needed.

D. Rinse all areas with distilled or deionized water. Use drain or vacuum to remove the solution.

E. Repeat water rinses and removal until all of the detergent is gone. Rinse with isopropyl alcohol and purge with GN2 until dry.

Examine all interior surfaces with a black light inside the cabinet. If there is no fluorescence, proceed to the next step. If there is fluorescence:

1. Reclean the fluorescent areas.

2. Reexamine with black light. If there has been no change in the fluorescence, proceed to the next step. If there is a change in the fluorescence, repeat cleaning and rinsing until there is no further reduction.

NOTE

NEVER LEAVE WATER IN CABINET FOR EXTENDED PERIODS OF TIME, AS THIS WILL PROMOTE RUST. IF ANY SEQUENCE IS INTERRUPTED AND A DELAY OCCURS, REMOVE WATER FROM CABINET WITH ISOPRDPYL ALCOHOL RINSE AND PUT CABINET UNDER GN2 PURGE.

F. Using an unfiltered Millipore can at 85 psig, spray interior of cabinet with 1% Liquidet and water solution.

G. Repeat water rinses and removal until all of the detergent is gone.

NOTE

PLACE TEFLON OR POLY GLOVE PORT COVERS IN POSITION. COVERS MAY BE REMOVED TO PROVIDE ACCESS FOR CLEANING, BUT SHOULD BE REPLACED WHEN ACCESS IS NOT REQUIRED. PERSONNEL WILL WEAR TEFLON FEP GLOVES ON ALL SUBSEQUENT STEPS REQUIRING OPERATIONS INSIDE THE CABINETS.

H. Immediately after water rinse, rinse all areas with isopropyl alcohol (IPA) (85 psig pressure) to remove water.

I. Remove all solution from cabinet. Use vacuum flask with liquid pickup and squeegee as needed. Dry cabinet with GN2 purge.

J. Acid wash per Para. 1.1.4 only when specified on Work Request .

K. Rinse all areas with a minimum of 500 ml redistilled Freon per square foot of cabinet surface. Freon shall be at 85 psig pressure.

L. Remove all Freon from cabinet. Use vacuum flask with liquid pickup and squeegee if needed.

M. Use a 5 gallon stainless steel pressurized (85 psig) spray can of redistilled Freon for final verification of cabinet cleanliness. Before flushing, take 1000 ml Freon base sample. Flush .the interior of the cabinet with a minimum of 100 ml per square foot of surface area. Collect a minimum of 700 ml representative sample and another 1000 ml sample at end of flushing cycle.

N. Perform a particle count on the 1000 ml sample. Deliver the base sample and 700 ml sample to lab for total hydrocarbon count (THC & NVR) analysis. The particle count and THC or NVR of final flush shall meet table IV requirements.* The base sample shall meet table I* requirements for THC or NVR. Any failure to meet these requirements is cause for rejection.

O. Visually inspect interior of cabinet for particulate matter and rust.

    1. If particulate matter is found, repeat Steps M and N until cabinet is free of particulates.

    2. If rust is found, use wipes and Freon to remove. Repeat Steps M *and* N until cabinet is free of particulates.

P. After verification of cleaning, put a positive purge on the cabinet with gaseous nitrogen meeting table III* requirements.

*Appendix

1. 1.3 DEGREASING PROCEDURE – Only when called for in work request or when necessary

A. Use high pressure Freon spray on all interior surfaces of cabinet.

B. Scrub floor and walls of cabinet with Teflon brushes or other non-abrasive scrubbers.

C. Repeat high pressure Freon spray on all interior surfaces.

D. Drain Freon and dry cabinet with nitrogen purge to reduce introduction of moisture.

1. 1.4 ACID WASH - Only when called for on work request. Acid wash only floor of the cabinet

A. Prepare adequate 2% nitric acid solution to completely cover floor of cabinet to a depth of approximately ¼". Use reagent grade acid: $69 - 71 \%$ HNO_3 to prepare solution.

B. Plug all drain lines and carefully pour acid solution over floor of cabinet. Let sit 30 minutes. Agitate solution with squeegee after 15 minutes.

C. Drain acid from cabinet.

D. Rinse all areas of cabinet with water.

E. Repeat step "B" and "C".

F. Rinse all interior surfaces of cabinet with distilled water until sample caught at drain pipe is neutral.

G. Rinse all surfaces with pressurized isopropyl alcohol. This will facilitate removal of water.

H. Immediately after alcohol rinse, start GN_2 purge of cabinet. Continue purge until cabinet is dry.

I. Continue with CP – l cleaning.

1.1.5 PRECLEANING OF CABINET EXTERIOR AND STAND

Preclean exterior of cabinet and stand to remove all stains, finger prints, grease and soiled areas. Remove exterior rust with stainless steel brushes, Scotch Brite, etc. This includes underside of cabinet and stand.

<div align="center">NOTE</div>

RUST AND DISCOLORATION FROM WELDS ARE CONSIDERED DIFFERENT AND SEPARATE PROBLEMS. THIS PROCEDURE REFERS ONLY TO RUST, NOT DISCOLORATION FROM WELDS. CLEAN ROOM SHOULD COORDINATE WITH CURATORIAL TOOL AND EQUIPMENT MONITOR ON PROBLEMS.

1.1.6 PREPARATION FOR TRANSFER TO CURATORIAL FACILITY

After final GN_2 purge, tighten all fittings and caps on penetrations to prevent introduction of moisture and loss of nitrogen. After interior and exterior are clean, bag in poly for transfer to building 31 or 31A/Curatorial Facility.

<div align="center">*APPENDIX</div>

<div align="center">TABLE I – BASE SAMPLE</div>

PARTICLE COUNT*	THC**	NVR***
10μ to 25μ - 15	2μg/100 ml	0.2mg/100ml
25μ to 50μ - 2		
50μ to 100μ - 1		
> 100μ - zero		

*Total number of particles in 100 ml sample.
**Total hydrocarbon contamination as determined by gas chromatograph.
***Nonvolatile Residue

TABLE II – FINAL FLUSH

PARTICLE COUNT*	THC**	NVR***
0µ to 10µ - unlimited	$3µg/ft^2$***	$1.0mg/ft^2$
10µ to 25µ - 100	NVR & THC not applicable to plastics , rubber, other elastomers	
25µ to 50µ - 10		
50µ to 100µ - 5		
100µ to 175µ - 1		
> 175µ - zero		

*Total number of particles in 100 ml sample.
**Total hydrocarbon contamination as determined by gas chromatograph.
***This works out to be 3µg/100 ml based on sampling rate of $100 ml/ft^2$.
****NVR - Nonvolatile Residue

TABLE III – LIQUID NITRDGEN SPECIFICATION

CONTANINANT	MAX ALLOWABLE (PPM)
Argon	20
Oxygen	10
Carbon Monoxide	10
Carbon Dioxide	10
Hydrogen	10
Moisture	10
Methane	1

TABLE IV – PARTICLE COUNT AND THC LIMITS

PARTICLE COUNT*		THC
0µ to 175µ	unlimited**	($10µg/ft^2$ for xylan coated items)
175µ to 700µ	6	
>700µ	zero	
Fibers;***		NVR
700µ to 1500µ	1	$1.0mg/ft^2$
>1500µ	zero	

  * Total number of particles in 1000 ml sample.
  ** Unlimited means that particles in this range are not counted; however, any obscuring
    of the filter grid lines shall be cause for rejection.
  *** Fibers - a particle whose length is 10 times its width (minimum length of 100µ).
  *** May be waived by Contamination Control Officer.

7.0   APPENDIX III

Technical Support Procedure 23 – Glovebox Cleaning: version March 8, 2011

6.   PROCEDURE

Preparations for cleaning the cabinet should be done on the day before the cabinet is scheduled for cleaning (sections 6.1.1 through 6.1.7) so that cleaning can be started at the beginning of the following day with washing done continuously, with no breaks, until completion and the cabinet is completely dry.

Allowing water to remain in the cabinet will promote rusting of the stainless steel by the UPW.

6.1   Prepare cabinet for cleaning

6.1.1   Processor will remove all samples and equipment, except the balance and heat sealer, from cabinet.

   NOTE: Remainder of procedure will be done by CTOG.

6.1.2   Lock down balance and remove along with heat sealer.

6.1.3   Dry vacuum the air lock.

6.1.4   Set cabinet flow at 50 SCFH or higher to maintain positive pressure in the cabinet. Remove gloves and install clean cover sheets one at a time.

6.1.5   If gloves are to be analyzed for biological contamination keep "in cabinet" portion interior and twisted closed and place in a clean bag.

6.1.6   Tilt the cabinet so that the water will run towards the drain.

6.1.7   Connect the rinse line to the UPW manifold.

6.1.8   Verify that the water is ready

   a)   Resistivity readings should be > 18 mega ohms (verify by checking the readings taken that day or check reading on the instrument in 1108)

   b)   Hot water heater should be "ON".

6.1.9   Connect the GN2 spray line.

6.1.10 Connect nozzle and wand to rinse line.

6.1.11 Using a Jerri can as a catchment reservoir, connect the drain line to the pump and then on to the drain. In PSL the drain line will go into drains located on the floor in either 2107 or 2107A.

6.1.12 Spray water into a sink, available container, or drain until the air is out of the line and the line is rinsed thoroughly.

NOTE: When the water is hot determine if protection from the heat is needed. A teflon outer layer should be used over any item going into the cabinet.

6.1.13 While the water is still flowing, and if specified on the CO, take baseline water samples using bottle provided. Label containers "Baseline, hot water" with date and time. Appendix A specifies limits for UPW cabinet rinse.

6.1.14 Sampling UPW for the particles Base Line

   a)   Rinse the clean vacuum filtration device with certified UPW.

   b)   Assemble the vacuum filtration device less funnel/filter holder top.

   c)   Using forceps, remove membrane filter (Millipore, 0.8 microns, preferably black) from container and place on filter holder base.

   d)   Attach funnel/filter holder to base.

   e)   Using a pen, mark area on the pad to indicate area actually filtered.

   f)   Rinse the funnel/filter holder with water to remove all particles.

   g)   Turn on vacuum pump and begin pouring sample into the funnel.

   h)   Allow vacuum pump to run approximately 10 - 20 seconds after all liquid has been filtered. Turn off vacuum pump.

   i)   Remove funnel; using forceps place filter pad in clean petri dish.

6.1.15 Counting Procedure for Assaying the Sample.

   a)   Verify that the microscope is calibrated for the magnification being used.

   b)   Place petri dish on microscope stage and adjust lamp for maximum particle definition. Adjust the microscope to the magnification required.

   c)   Count the pad for particles >10 microns. There must be no more than 50 particles. Appendix B explains criteria for particle count limits.

   d)   Initiate a Clean Room Work Request and record particles counted on each step of the cabinet cleaning. The Clean Room Work Requests are located on Ganymede\Cleaning Work Request\SOG's.

6.1.16 If water meets particulate requirement, proceed with cleaning the cabinet.

6.2   Clean the cabinet

6.2.1 Maintain a positive purge on the cabinet at all times. Insert the sprayer and wand through a slit in the port cover.

6.2.2   Clean drain port.

Before rinsing floors and walls, flush hot water through the drain port and discard.

6.2.3   If water samples are to be collected and analyzed, attach approximately 2 ft. of 3/8" clean PFA tubing to the drain port and cap.

6.2.4   Rinse the cabinet walls with hot water. If hands or arms must extend into the cabinet cover with clean Teflon over-gloves or bags to prevent the hot water from depositing plastics in the cabinet. This is especially important if cleaning the Mars meteorite cabinet.

6.2.5   Collect water samples, if specified on the CO. Label collection container "First Rinse" with date and time.

6.2.6   Continue rinsing using squeegee, Teflon brushes or foam wipes (if allowed) to sweep particles from floor and into drain.

6.2.7   Empty drain water container if used.

6.2.8   Use the wet vacuum only as necessary in short intervals.

6.2.9   Rinse entire cabinet until walls are warm to enhance drying. Sample the water per 6.1.14 and 6.1.15 until no further significant decrease in particles is attained and there are no more than 50 particles > 10 microns.

6.2.10 If specified on the CO, take "Final Rinse" water samples in the bottles provided and label with date and time.

6.2.11 Remove the rinse line from the UPW source and connect it to the clean GN2 line. Blow the water off the top and sides of the cabinet and then towards the drain. (Use the wet vacuum in short intervals.) Continue blowing water out and towards the drain until it is completely dry.

6.2.12 Install the cover sheets over the glove ports and set a high purge on the cabinet.

6.2.13 Thoroughly dry the PFA tubing with GN2 to prevent microbial growth and cap ends.

6.2.14 If water samples were taken, have analysis done.

Evaluate water analysis results as compared with criteria on Appendix A.

6.2.15 Glove cabinet and prepare for processing.

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13. ABSTRACT *(Maximum 200 words)*
Future robotic and human spaceflight missions to the Moon, Mars, asteroids, and comets will require curating astromaterial samples with minimal inorganic and organic contamination to preserve the scientific integrity of each sample. 21st century sample return missions will focus on strict protocols for reducing organic contamination that have not been seen since the Apollo manned lunar landing program. To properly curate these materials, the Astromaterials Acquisition and Curation Office under the Astromaterial Research and Exploration Science Directorate at NASA Johnson Space Center houses and protects all extraterrestrial materials brought back to Earth that are controlled by the United States government. During fiscal year 2012, we conducted a year-long project to compile historical documentation and laboratory tests involving organic investigations at these facilities. In addition, we developed a plan to determine the current state of organic cleanliness in curation laboratories housing astromaterials. This was accomplished by focusing on current procedures and protocols for cleaning, sample handling, and storage. While the intention of this report is to give a comprehensive overview of the current state of organic cleanliness in JSC curation laboratories, it also provides a baseline for determining whether our cleaning procedures and sample handling protocols need to be adapted and/or augmented to meet the new requirements for future human spaceflight and robotic sample return missions.

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