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**Principal:
Investigators** **D.P. Griffis and J.J. Wortman**

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Organization: **North Carolina State University
P.O. Box 7911
Raleigh, North Carolina 27695**

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Work under this grant is separated into two parts : (1) The development of analytical procedures for identifying the chemical composition of residue from impacts that occurred on the Interplanetary Dust Experiment (IDE) detectors during the flight of LDEF and the carrying out of actual analysis on IDE detectors and other witness plates and (2) provide analytical support to NASA personnel for the analysis of impacts on various witness plates and other LDEF surfaces. The results of the work by NASA personnel as indicated in (2) above is reported elsewhere and is not discussed in this report.

Semiannual Status Report

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To date, 79 impact craters on sensors from six sides of LDEF have been analyzed for morphology and chemistry studies based on procedures developed earlier as part of this grant. These craters have been classified as to origin based on their chemical and morphological characteristics.

Optical and field emission Scanning Electron Microscopy (SEM) were used to locate impact craters and features on the IDE sensors. Energy dispersive x-ray (EDS), Secondary Ion Mass Spectroscopy (SIMS) and Auger Spectroscopy were used for the chemical analysis of these craters. EDS analysis was limited by the relatively small concentrations of residue in the craters. Contamination issues have greatly affected the chemical analysis. Solid particles, liquids-introduced during shuttle waste dumps and condensates including ultraviolet rays, atomic oxygen and catalyzed polymerization reactions have been recognized as some of the sources of in-flight contamination. EDS was used in analyzing some of these contamination spots. Auger analysis was also performed on dark areas near the electrodes of the sensors and it was observed that these areas have a much thicker contamination layer than areas away from the electrodes. This tends to support the theory that higher electric fields (near electrodes) will attract more particles to the surface and thicken the contamination layer.

All SIMS analysis was done on a CAMECA-3f Ion microscope equipped with oxygen and cesium beams. A protocol was developed earlier to record SIMS data for the IDE sensors and the Ge witness

plates to generate positive and negative elemental maps. To date 79 impact craters have been analyzed: 36 from tray C-9 (Leading), 18 from C-3 (Trailing), 12 from B-12 (North), 4 from tray D-6 (South), 3 from tray H-11 (Space) and 6 from tray G-10 (Earth). All SIMS elemental maps have been electronically developed into a quantitative format and used to make bargraphs and two-dimensional maps of the crater distributions for the different elemental compositions. The ion maps were displayed on the computer screen and electronic boxes were drawn around specific areas of interest. Since each pixel of the ion map represents an intensity level, the enclosed box area provides a fairly accurate value of element intensity. The central crater regions, rims and other bright spots present in and around the crater were quantified through the above method. This data was then normalized to silicon and adjusted for the relative sensitivity factors (RSF). This data was then used to generate bar graphs of intensity levels of different elements present in each crater. All 79 impact craters have gone through this data reduction method. Impactor classification for determining a ratio of manmade to natural particles was also applied to these craters. This impactor classification was based on the two-dimensional maps, relative ion abundance values generated by the electronic manipulation and contamination present in and around the crater site. The criterion followed the guidelines of the Meteoroid and Debris SIG. Particles were labeled natural if they had chondritic or interplanetary dust particle composition (Mg,Si,Fe,S,Ca,Ni and Na). Manmade particles were identified by the presence of Ti,Zn,Cr,Cu or Ag. Four craters containing only Na, K and

Mg were classified as manmade under the assumption that the impactors were paint particles composed of silicate or magnesium oxide pigments. The craters that did not fit any of the above categories were classified as indeterminate. Many of these craters had no detectable residue. This could be the result of impactors composed of Al, O or Si which cannot be separated from sensor materials. As more insight into the contamination levels and impact physics is gained the above classifications are subject to change. Details of particle classification can be found in reference [1].

In addition to impact craters, control areas have also been analyzed to get an estimate of the composition of the background levels on these sensors. Several spots and splatters observed on surfaces have also been analyzed by SIMS. Many of these spots have been traced to paint particles and other man-made debris including human debris. Very few of such areas are believed to be of natural origin. To study the effect on this contamination layer under a simulated impact, several blank discharges were performed by applying pressure on the capacitor surface using Si and a diamond point. It was found that the contamination layer was completely removed from the blank crater. This would imply that if residue is seen at the bottom of the crater it would belong to the impactor. For the future we plan to perform a depth profile down to the SiO₂-Si interface. This will be achieved by an electron flood gun retrofitted with the Cameca 3F instrument. Details of the electron flood gun are described in the following section. These depth profiles should reveal the presence of bulk and interfacial contaminants. Depth profiles through the top Aluminum layer has shown that Calcium is a

major contaminant in Al. This hampers the detection of Ca in crater residue. Contamination issues are discussed in reference [2].

Electron Flood Gun Status

Integration of the electron flood gun system for charge neutralization into the Cameca IMS-3f continues. In initial tests of the system, an electron beam of over 20 micro amperes, significantly more than will be required for charge neutralization, was measured at the cameca sample electrode. Further confirmation of the proper operation of the system was confirmed by the mass spectral measurement of hydrogen desorbed from a metal sample using the electron flood gun. Testing of the electron beam control system showed that current could be controlled over a broad range using filament current for coarse current control and an external control voltage (0 to 10 volts to be provided by the Cameca control computer) for fine current adjustment. Work remaining includes some redesign of the focussing system electronics to provide better control of the beam density impinging on the sample, improved layout of power supply components to allow operation at up to 10KeV and improvement of the electron flood beam deflection system to allow more precise positioning of the electron beam. Work is also in progress on final interfacing the flood gun control to the Cameca control computer in order to provide integrated software control of the flood system with other aspects of Cameca operation such as mass switching and primary beam control thus providing automated charge neutralization.

Future Studies

- 1) Further chemical analyses and data reduction of impact craters on IDE sensors.
- 2) More contamination analyses via SIMS depth profiling to the Si-SiO₂ interface. Background contamination level study via SIMS and Auger Spectroscopy.
- 3) EDS and Auger analysis of heavy deposits of particle residue to determine the composition and interference of these species.

Publications/Presentations under this grant

- 1). C.G. Simon, J.L. Hunter, D.P. Griffis, V. Misra, D.A. Ricks, J.J. Wortman, D.E. Brownlee, "Elemental Analyses of Hypervelocity Microparticle Impact Sites on Interplanetary Dust Experiment Sensor Surfaces", Presented at the Second Long Duration Exposure Facility Post-Retrieval Symposium, June 1992, manuscript to be published in Conference Proceedings.

- 2) C.G. Simon, D. Batchelor, D.P. Griffis, J.L. Hunter, V. Misra, D.A. Ricks, J.J. Wortman, "Contaminant Interferences with SIMS analyses of microparticle impactor residues on LDEF surfaces", Presented at the COSPAR Conference, 1992, manuscript to be published in Conference Proceedings.

ELEMENTAL ANALYSES OF HYPERVELOCITY MICROPARTICLE IMPACT SITES ON
INTERPLANETARY DUST EXPERIMENT SENSOR SURFACES.C. G. SimonInstitute for Space Science and Technology
Gainesville, FL 32609J.L. Hunter, D.P. Griffis, V. Misra, D.A. Ricks, J.J. Wortman
Analytical Instrumentation Facility, North Carolina State University
Raleigh, NC 27695D.E. Brownlee,
Astronomy Department, University of Washington
Seattle, WA 98195

ABSTRACT

The Interplanetary Dust Experiment (IDE) had over 450 electrically active ultra-high purity metal-oxide-silicon impact detectors located on the six primary sides of the Long Duration Exposure Facility (LDEF). Hypervelocity microparticles (~0.2 to ~100 μm diameter) that struck the active sensors with enough energy to breakdown the 0.4 or 1.0 μm thick SiO_2 insulator layer separating the silicon base (the negative electrode), and the 1000 \AA thick surface layer of aluminum (the positive electrode) caused electrical discharges that were recorded for the first year of orbit. The high purity Al-SiO₂-Si substrates allowed detection of trace (ppm) amounts of hypervelocity impactor residues.

After sputtering through a layer of surface contamination, secondary ion mass spectrometry (SIMS) was used to create two-dimensional elemental ion intensity maps of microparticle impact sites on the IDE sensors. The element intensities in the central craters of the impacts were corrected for relative ion yields and instrumental conditions and then normalized to silicon. The results were used to classify the particles' origins as "manmade", "natural" or "indeterminate". The last classification resulted from the presence of too little impactor residue, analytical interference from high background contamination, the lack of information on silicon and aluminum residues, or a combination of these circumstances.

Several analytical "blank" discharges were induced on flight sensors by pressing down on the sensor surface with a pure silicon shard. Analyses of these blank discharges showed that the discharge energy blasts away the layer of surface contamination. Only Si and Al were detected inside the discharge zones, including the central craters, of these features.

Thus far a total of 79 randomly selected microparticle impact sites from the six primary sides of the LDEF have been analyzed: 36 from tray C-9 (Leading [ram], or East, side), 18 from tray C-3 (Trailing [wake], or West, side), 12 from tray B-12 (North side), 4 from tray D-6 (South side), 3 from tray H-11 (Space end), and 6 from tray G-10 (Earth end). Residue from manmade debris has been identified in craters on all trays. (Aluminum oxide particle residues were not detectable on the Al/Si substrates.)

These results were consistent with the IDE impact record which showed highly variable long term microparticle impact flux rates on the West, Space and Earth sides of the LDEF which could not be ascribed to astronomical variability of micrometeorite density. The IDE record also showed episodic bursts of microparticle impacts on the East, North and South sides of the satellite, denoting passage through orbital debris clouds or rings.

I. Introduction

The Interplanetary Dust Experiment (IDE) had approximately 450 high purity MOS type detectors mounted on the six primary sides of the stabilized spacecraft. The sensors were constructed from 2 inch diameter, 250 μm thick, boron-doped ultra high-purity silicon wafers covered with either a 0.4 or a 1.0 μm thick layer of thermally grown SiO_2 insulator, and coated with $\sim 1000\text{\AA}$ of high-purity aluminum. The location and identification of microparticle hypervelocity impacts on the formerly active detectors was facilitated by the presence of 50 μm wide "discharge zones" in the Al top layer surrounding each impact (see Figs. 1-3). It is also suspected that the negatively biased Si electrode surface exposed in the impact cratering event enhanced the collection efficiency of positive ions formed from impactor materials in the impact plasma.

The objective of the chemical analysis study is to empirically determine the manmade-to-natural microparticle population ratio of impactors that struck the LDEF satellite while in orbit. The study takes advantage of the purity of the IDE substrates and their location on all six primary sides of the satellite. Data from this study will be added to the growing pool of orbital hypervelocity impact site analyses produced from studies of the Solar Max, Palapa B and LDEF satellites.

II. Experimental

The detailed analysis protocol developed specifically for the IDE samples is described elsewhere.¹ Optical microscopy and field-emission scanning electron microscopy (SEM) were used to locate and record the morphology of microparticle impact sites. Energy dispersive x-ray spectroscopy (EDS) and secondary ion mass spectrometry (SIMS) were used to look for and map the distributions of residual impactor debris in and around the impact craters. The presence and relative abundances of elements found in the craters were used to classify impactors as "manmade", "natural" or "indeterminate". Examples are presented in section III.

EDS analyses of microparticle impact sites on the IDE sensor were limited in scope due to the concentrations of residue ($\sim 1\%$) required to produce detectable signals using EDS compared to the (ppm) concentrations needed to yield semi-quantitative results using the far more sensitive SIMS techniques. EDS and Auger electron spectroscopy (AES) were used to further analyze high concentration deposits of material (residues and contaminants) that were identified in and around impact sites with SIMS.

As previously described¹, all SIMS data was collected with a Cameca IMS 3F using $^{16}\text{O}^+$ or $^{16}\text{O}^-$ ion beams. The instrument was used in the ion microscope mode and data was recorded as two-dimensional elemental positive ion maps with lateral resolution of 1-2 μm . Pixel intensities were used to calculate relative element abundances (section II.C).

Briefly, the SIMS analytical protocol involves the following steps:

- 1.) Each impact site was first sputtered with the oxygen beam while monitoring the concentrations of C, Na and Mg in order to assure removal of the bulk of the surface contamination layer ubiquitous to LDEF.
- 2.) Next, an energy filtered bargraph type mass spectrum was recorded.
- 3.) Then, a dual channel-plate/ccd-digital-camera detector system was used to record high resolution ($M/\Delta M = 3,000-4,000$) elemental positive ion maps for C, O, Na, Mg, Si, Al, K, Ca, Ti, Cr, Ni, Fe, Cu, Zn, Ag and Au, and molecular ion maps for $^{56}\text{Si}_2$ and $^{58}\text{Si}_2$. (Images were not recorded if there were less than ~ 4 ion counts/min at the observed mass.)

- 4.) If there was enough of the IDE sensor's 1000Å Al top layer remaining around the impact site to prevent sample charging, negative elemental ion maps were recorded for H, C, O, F, Si, Al, S, Cl and Au.

Analysis of impacts on Ge witness plates flown on tray B-12 as part of the IDE experiment has been suspended. A summary of the work done to date on two of the Ge wafers, including crater counts and dimensions, description of contamination problems, and SIMS and/or EDS analyses for 13 impact sites, was presented in the LDEF First Post-Retrieval Symposium Proceedings¹. Contamination feature counts, crater counts, and representative photographs were recorded for all other witness plates mounted on LDEF tray B-12 along with the Ge plates. These included three 1" square Si plates from Washington University (Expt AO187) and ten zirconia, quartz and sapphire plates from NCSU with a total surface area of ~4 in². Results from these other witness plates showed clearly that the Ge witness plates were exposed to a major pre-flight contamination event.

A. The IDE Microparticle Impact Sample Set

The sample set for the study was composed of impacts selected from the 215 IDE sensors that have 1.0 µm thick insulator layers. These sensors were selected over the ones with thinner insulators because their electronically sturdier structure resulted in the majority of them remaining active for the entire 5.77 year LDEF orbital lifetime. Thus, no time bias was introduced into the sample set. The only selection criterion used was size. Impact craters with spall dimensions less than 30 µm were the focus of the study, but a few larger craters were also analyzed.

In order to gather data from a statistically significant fraction of this microparticle impact sample set, the total number of these impacts on each sensor group located on the six primary sides of LDEF was determined. Then, using 10% statistics, the total number of analyses required to achieve a significant fraction was calculated. This technique assumes that the statistics of a randomly selected group of 10% of the samples in a large, random sample set will, to first order, represent the statistics of the entire sample set.

The microparticle impact sample sets on the West, Space and Earth end IDE sensors are comprised of 290, 600 and 330 impact sites, respectively. Analyses of 122 impacts would provide 10% statistics for these three sample sets.

The above logic was iterated a second time for the extremely large sample sets represented by the impacts on IDE sensors that were located on the East, North and South sides of LDEF. Optical scanning of 3 out of 32 sensors from each of these groups provided estimates of the sample set sizes of 10,000, 4,600 and 4,400 impact sites, respectively. Clearly, the resources were not available to analyze 2,000 samples. However, since the sample sets were so large, it seemed logical to select 10% of the sensors from each location and analyze 10% of the samples on each sensor. This yielded the more practical goal of 200 analyses. Thus, analyses of a total of ~320 impact sites on IDE sensors would provide a first order statistical look at the manmade/natural microparticle population ratio.

To date 79 impact sites on IDE sensors have been analyzed with SEM/EDS and SIMS. Manmade or natural classifications have been assigned to 40 of the residues (see section III below), or ~ 50%. An extensive background and blank discharge study required to establish the level of contamination and other analytical interferences has been conducted, but more work is required in this area. Although there are significant analytical interferences associated with elemental analyses of impact sites on the ultra high-purity IDE detector surfaces, most of these can be mitigated through recognition. The details and results from the contamination study will be the subject of a future paper.

B. Impactor Classification

The impactor classifications listed in Table 2 (section III) were assigned after reviewing all available data and are subject to the described limitations. Decisions were based on:

- 1) the element distributions depicted in the two dimensional ion maps described above,
- 2) the relative (to Si) ion abundance values calculated for each species in the central craters of the impact features, and
- 3) the local contamination environment in and around the impact feature.

Because the IDE detectors were constructed from silicon and aluminum, these two important elements could not be identified in impactor residues. Thus, aluminum oxide particle residues were undetectable, and the Si in natural impactor residues was also undetectable.

Identification of natural meteoroid residues followed the guidelines of the Meteoroid and Debris SIG. Residues were labeled natural if they had elemental compositions that were similar to common components of chondritic meteorites or interplanetary dust particles (IDP's). Most IDP's of micron size have solar elemental abundance ratios for Mg, Si, Fe, S, Ca, Ni and Na in decreasing order of abundance. The atomic abundances of Mg, Si and Fe are roughly equal in most IDP's and are an order of magnitude more abundant than Ca, Ni and Na. In practice, residues were labeled as natural meteoroids if they had high Mg and Fe abundances and either lacked or contained low abundances of elements not common in primitive meteoritic materials. Relative ion sensitivity factors, "RSF" (see below) were taken into account when estimating compositions from ion intensity maps.

Manmade particle residues were identified by the presence of relatively high concentrations (>100 ppm in most cases) of metals such as Ti, Zn, Cr, Cu or Ag. Manmade classifications were also assigned to 4 residues (out of the 79) containing only Na, K and Mg under the assumption that these were the remains of impacts with paint particles that used silicate or magnesium oxide pigments. This assumption is subject to change as more insight into possible Na, K and Mg contamination is gained. All 4 of the impacts were located on Leading edge sensors.

Indeterminate classifications were assigned to 39 residues that did not fall into either of the above categories. These included sites that contained only traces of Na and/or K. A subset of the indeterminate classification, labeled "clean", was composed of impact sites with no detectable residues. These may be the result of aluminum oxide particle impacts, a likelihood for impacts on the leading (East) and the North and South sides, or the result of impacts from very high velocity submicron interplanetary dust particles that completely vaporize, a statistical likelihood for impacts on the trailing (West) and Space end trays. As the study progresses, some of the indeterminate classifications may change.

Consideration of all the analytical data was complex and subject to interpretation. As a result, some impactor classifications may change as further insight into the analytical contamination and background issues is gained. For example, H, F and Cl were present in all central craters. This has been traced to ppm level contamination from HF and HCl during sensor fabrication. Na, K, and Mg to a lesser extent, were present in the majority of impacts and may be from residual background contamination. The presence of these elements is reported since there is no verification of background contamination at this time, and there were many impact sites with little or no detectable Na, K or Mg. The Cameca instrument has been retrofitted with an electron flood gun that will permit depth profile studies of the IDE sensor surfaces through the insulating SiO₂ layer. These depth profiles should reveal the presence of bulk and interfacial contaminants in the SiO₂ and Si.

Depth profiles through the conductive aluminum layer have already shown that this material is contaminated with ~10-100 ppm of Ca. This severely limits the ability to identify Ca in impact sites. Calcium was detected all around the areas surrounding nearly all impact discharges, but was absent from

most central craters, or present at concentrations much lower than the background. The few instances where Ca was found in the impact craters at higher than background levels are reported.

Differential sputtering of the contamination layer from the highly textured impact sites was unavoidable and was considered when interpreting the SIMS data. The phenomenon results from beam shadowing effects caused by the craters, ridges, and even the smaller "hills and valleys" of the vapor deposited Al surface layer. In practice, ion images of control areas in the vicinity of the impacts, both before and after oxygen beam sputter cleaning, provided an estimate of the level of "background" concentrations for these areas. Images of impact areas (after sputter cleaning) were interpreted with these values in mind, and only after all sites on a given sensor were examined.

In order to gain insight into the distribution of the material in the surface contamination layer after an impact induced discharge occurred, a series of "blank discharges" were induced on a flight sensor using an ultrapure Si shard. SIMS analyses of these "blanks" showed that the C, Na, Mg, K, Ca bearing contamination layer was blown away from the central craters and surrounding zone of vaporized Al by the discharge energy. Only Si and Al were detected within the discharge craters and vaporization zones of these analytical blank discharges.

C. SIMS Data Reduction Method

Besides the obvious visual information, each pixel of the element ion maps contains digitized intensity information that can be reduced to a semi-quantitative number relative to the Si signal. The following steps were employed in this process:

- 1.) Ion maps were displayed on a computer screen individually and a rectangular box was electronically scribed around the same area of interest on each map.
- 2.) The cumulative pixel intensity data within the box was summed.
- 3.) Relative ion sensitivity factors (RSF) for species implanted in Si were used to correct the intensity values (see Table 1, Ref. 6).
- 4.) The corrected ion intensity values were normalized to the Si ion signal recorded for the same area.
- 5.) Data from individual craters were normalized for the number of pixels summed, the beam intensity during data collection, and the detector conditions during data collection.

Table 1 Relative Sensitivity Factors (RSF's) for species implanted in silicon.^{2,3} In general the values are applicable for elemental concentrations up to ~1%.

<u>Ion</u>	<u>RSF</u>	<u>Ion</u>	<u>RSF</u>
C ⁺	0.007	Cu ⁺	1.61
Na ⁺	139	Zn ⁺	0.054
Mg ⁺	18.0	Ag ⁺	0.694
Al ⁺	36.0		
Si ⁺	1.00	H ⁻	0.602
K ⁺	125	C ⁻	0.161
Ca ⁺	38.5	F ⁻	102
Ti ⁺	13.9	Al ⁻	0.250
Cr ⁺	7.69	S ⁻	5.10
Fe ⁺	1.85	Cl ⁻	26.3
Ni ⁺	1.35	Au ⁻	0.658

The reduced data have several limitations. First, RSF values for species implanted in Si were not appropriate for species deposited in or on aluminum or for deposits that were massive enough to form their own matrix. They are valid only for elements implanted in Si up to concentrations of ~1%. The assumption that the negative Si electrode exposed in the central crater region of impacts on the IDE sensors acted as an ion trap was the reason for selecting these RSF values. This assumption was based on the knowledge that positive ion pairs act as the charge carriers in the IDE discharge event and would theoretically be implanted in the Si. It should be noted that, in general, the RSF values for species in other matrices follow the same relative trend.

The second major limitation of the semi-quantitative data was the result of an artifact of the Cameca 3f operational protocol. This instrument could only collect data for one mass at a time. Up to ~50Å of material was sputtered away during each ion imaging step. Thus, the data for each element was from a different layer within the residue. For example, several hundred angstroms of material was removed between the imaging of Mg and Fe. This is a significant limitation on the ability to deduce impactor chemical composition from the scant residues.

Examples of semi-quantitatively reduced SIMS data are included in this report. More detailed interpretations will be presented in a future report after analysis of several ground based hypervelocity microparticle impact induced discharge features on retrieved IDE sensors is completed, and a more thorough understanding of contamination issues is gained.

III. RESULTS AND DISCUSSION

A. Overview

To date, 79 impacts on IDE sensors have been analyzed with SIMS. These include 36 impacts on two IDE sensors from LDEF tray C-9, (leading, or east side) 18 impacts on four different sensors from tray C-3 (trailing, or west side), 12 impacts on one sensor from tray B-12 (north side), 4 impacts on one sensor from tray D-6 (south side), 6 impacts on one sensor from the earth end tray G-10, and 3 impacts on one sensor from the space end tray H-11. Of the 79 impacts, 57 were formed from particles estimated to have been <3 μm in size, 18 were formed from particles estimated to have been 5-20 μm in size, and 3 were formed from particles estimated to have been 30-50 μm in size.

Microimpactor residue classifications are listed in Table 2. Elements identified at concentrations significantly higher than the background are listed for each impact site. The term "trace" refers to less than 10 ppm concentration, relative to Si, for all elements except Na and K, where the term refers to <100 ppm. Examples of impact feature morphologies, SIMS elemental ion maps, and quantitatively reduced SIMS data are presented in Figs. 1-3.

Minimum crater size of IDE impact features is ~10 μm due to the electrical discharge damage caused when the capacitor sensor was triggered¹. The sensors responded to hypervelocity particles ~0.5 μm or larger (assumed density of ~3 g/cm³). Observed spall zone sizes for small particle impacts into the crystalline IDE sensor surfaces were typically ~3X the size of the central craters¹ (Table 2). The central crater size of microimpacts in crystalline materials typically approximate the impactor size.⁴ Thus, it was impossible to estimate impactor size in the range of 0.5 to ~3 μm from the crater morphology on active IDE sensors.

The formation mechanism for craters ~10-25 μm in size on active IDE sensors was dominated by the impactor's kinetic energy (KE) transfer, but the discharge energy caused the entire crater and spall area to melt and fuse. "Crater" dimensions listed are for this fused area, but are more representative of spall zone size. Impactor size for these features was estimated to have been ~1/3 of the fused crater/spall size.

Formation of larger impact craters ($>30 \mu\text{m}$) was totally dominated by the impactor ΔKE and there were frequently shock induced spall zones around the craters. These larger impact sites had the typical morphology of hypervelocity impacts in crystalline material and impactor size was estimated to have been slightly less than the central crater size. The spall sizes listed in Table 2 are for the maximum dimension of the associated spall zones.

Impact identification Nos. in Table 2 refer to the IDE sensor number followed by a crater number (i.e. 1176-C3). Locations of all impacts were recorded for future reference. Craters were not always sequentially numbered since SIMS analyses were not performed on all craters that were labeled for further study in the initial optical scan. This was primarily due to the inability of the SIMS beam to reach every crater on a given surface without venting and reloading the sample in a different orientation, and in no way affected the randomness of the micro-impact site selections.

Considering all of the limitations described above, the impactor classifications cannot be taken as absolute, but there is moderate confidence in their accuracy within the described limitations of the study. Limits can be ascribed to the manmade/natural ratios based on the results to date. *Future adjustments, resulting from better understandings of contamination issues and impactor residue deposition mechanisms, and from additional analyses of orbital impact sites, may alter the statistical distribution of manmade and natural impactor classifications deduced from currently available data.* Additionally, the combination of this data set with data from other LDEF investigators should provide a more accurate assessment of the microparticle population ratio in LEO.

B. Tray C-3 (Trailing [wake], or West side)

There was an average of 10 impacts per sensor on tray C-3. Impactor residues in 18 impact sites on four different sensors were classified as: 5 manmade, 3 natural and 10 indeterminate. Four of the manmade residues had Ti and/or Zn in high concentrations and were assumed to be from paint particles. Two of these particles were $<3 \mu\text{m}$ in size, and the other two were ~ 20 and $\sim 40 \mu\text{m}$ in size. Residue from a fifth manmade impactor ($<3 \mu\text{m}$ in size) was identified by the presence of significant amounts of Cr along with Mg and Fe.

Figure 1a shows a SEM micrograph of impact No. 1382-C2 from tray C-3 with its $22 \mu\text{m}$ wide central crater and its $65 \mu\text{m}$ wide spall zone. SIMS ion maps for Na^+ , Mg^+ , Si^+ , K^+ , Ti^+ and Zn^+ are shown in Fig. 1b. The black box in these images outlines the image area that was selected for quantitative data reduction. A bar graph of the calculated concentrations, relative to $\text{Si}=1.0$, is shown in Fig. 1c and provides an example of the type of data that can be evaluated further as the study progresses. It should be possible to derive significant information about the chemical composition of the non-volatile components of many impactors from these type of data after contamination interferences are better understood.

The three natural micrometeorite residues on tray C-3 sensors were all identified by the presence of Mg and Fe. Two of the impacts were made by small ($<3 \mu\text{m}$) particles and had Na, Mg, K, Fe and Mg, and Ca, Fe, Ni present in residues. The third impact (No. 1336-C4) had a $23 \times 28 \mu\text{m}$ central crater (as described above) with no additional spall zone. A residue containing Na, Mg, K, Ca and Fe was found in the crater. Probable impactor size was estimated to have been $\sim 10 \mu\text{m}$. Figure 2a is an optical micrograph of this impact. SIMS ion maps are shown in Fig. 2b, and Fig. 2c shows a bar graph plot of the reduced image data for the central crater region.

Ten of the 18 impact sites had insufficient debris remaining to be positively identified above the background levels. This situation could be the result of natural microimpactors that had very high encounter velocities ($>>10 \text{ km/s}$), or impacts from aluminum oxide particles which were not detectable in the Al/Si substrate. Central craters in these impacts ranged in size from 10 - $25 \mu\text{m}$. Figure 3a shows an example of a medium size impact in the "clean" category, No. 1359-C6. Probable impactor size was estimated at $\sim 10 \mu\text{m}$. Figures 3b shows some of the ion maps associated with this impact, and Fig 3c shows a bar graph of the reduced SIMS data for the central crater. It is anticipated that further analysis of

this type of data in "clean" impact sites will lead to quantitation of background contamination levels and allow more accurate assessment of chemical compositions of the non-volatile impactor components.

If all 10 of the "clean" impact sites are assumed to have been caused by small, high speed natural particles, the manmade/natural ratio equals $5/13=0.38$. This microparticle value is significantly higher than the assumed ratio of 0.1 for all impactors striking the trailing edge of satellites in low earth orbit (LEO) and could be the result of contamination interferences. However, the IDE data showed that the long term average flux of particles $>0.5 \mu\text{m}$ in size varied drastically during the nearly 6 year long mission.⁵ Of the total of 290 impacts on these sensors, 186, or 64% occurred during the first year. The overall mission flux rate measured by the sensors matched that measured by other investigators.⁶ It is possible that orbital debris impacts caused the enhanced rate during the first year. (This topic is discussed in more detail in Ref. 5) The chemical analysis data collected thus far, subject to the stated limitations, seem to support this scenario.

C. Tray C-9 (Leading [ram], or East side)

There was an average of 311 impacts/sensor on tray C-9. Using the same criteria described above, impactor residues in 36 impact sites on 2 different sensors were classified as: 11 manmade, 5 natural and 20 indeterminate. If 19 of the 20 "indeterminate" impactors (those that were "clean" or had only Na and K present in the craters) are assumed to have been Al_2O_3 particles, then the manmade/natural ratio would equal $30/5=6.0$. This microparticle ratio is somewhat lower than the assumed ratio of 10 for all impactors on the leading edge of satellites in LEO, but considering the limitations of the current study, this preliminary result is reasonable. It should be noted that the long term impact flux measured by these leading edge sensors did not vary substantially and matched the flux rates measured by other LDEF investigators.⁶

Of the 11 manmade impactors, 9 were particles that were $<\sim 3 \mu\text{m}$ in size and 2 were particles estimated to have been 30-40 μm in size. Of the 9 small particle residues, one had only Ti and a trace of Na and K, three residues contained Cu in addition to Na, K and Mg, one contained Cu along with Na, K, Mg, Fe and traces of Ti and Cr, and four residues contained only Na, K and Mg.

The two largest manmade debris impacts examined have significant amounts of impactor residue. Residue from an $\sim 30 \mu\text{m}$ particle contained Na, Mg, Ti, Cr, Fe, Cu, Zn and Ag and could be from a small piece of electrical component with paint. Residue from a 40 μm particle contained high concentrations of H, C, Ti, Cr and Fe and could have been a piece of painted plastic or a paint particle with an organic binder. (This was the only high concentration H, C residue found in the 79 impact sites.)

All 5 of the natural impactors were identified by the presence of Mg and Fe. Only one residue had Ca above background. One particle was estimated to have been $<\sim 3 \mu\text{m}$ in size, and the other 4 were estimated to have been $\sim 5-10 \mu\text{m}$ in size.

Of the 20 "indeterminate" impactors, 16 were $<\sim 3 \mu\text{m}$ in size, and 4 were $\sim 4-8 \mu\text{m}$ in size. This could support the assumption that most of these impactors were small aluminum oxide spheres (from solid rocket motor exhaust). Zinner, et al., have reported that 8 out of 11 small particle impact craters examined on Ge capture cells from LDEF tray E-8 (near leading edge) contained only Al and O residues.⁷

D. Tray D-6 (South side)

There was an average of 137 impacts/sensor on tray D-6. Impactor residues in 4 craters examined on one sensor were classified as: 1 manmade (Na, K, Mg, Cu) and 3 indeterminate. All craters were formed by particles $<\sim 3 \mu\text{m}$ in size. These results are too preliminary to draw any conclusion other than the obvious, expected result that orbital debris did strike the North side of the satellite. Cu was the indicator for the manmade impactor residue. Al_2O_3 particles, or small high speed natural particles could have caused the other impacts.

E. Tray B-12 (North side)

There was an average of 143 impacts/sensor on tray B-12. Impactor residues in 12 craters examined on one sensor were classified as: 4 manmade, 6 natural and 2 indeterminate (clean). Natural impactors were all identified by the presence of Mg and Fe. Only one of these had significant Ca. Three of the 6 natural impactors were $< \sim 3 \mu\text{m}$ in size, and three were $\sim 5 \mu\text{m}$ in size. The two indeterminate impactors were both $< \sim 3 \mu\text{m}$ in size.

Three of the 4 manmade impactors were $< \sim 3 \mu\text{m}$ in size and the fourth was $\sim 6 \mu\text{m}$ in size. Residue from the largest impactor contained Fe, Cu and Zn along with Na, K, and Mg. One of the 3 smaller impacts contained Na, Mg, K and traces of Cu and Ag, one contained Na, Mg, K, Ti and Zn, and one contained Na, Mg, Fe and Cu.

F. Tray G-10 (Earth end)

There was an average of 10 impacts/sensor on tray G-10. Two out of 6 small particle ($< \sim 3 \mu\text{m}$) impactor residues analyzed on one sensor were classified as manmade based on the presence of Fe and Ti in one and Ti and Cr in the other. The other four impactors were classified as indeterminate since only traces of Na and K were found in the craters. The only conclusion that can be drawn from these data is the expected result that orbital debris did strike the Earth end of the satellite. It is interesting to note that the entire impact set on the Earth end sensors was formed by particles $< 4 \mu\text{m}$ in size. (The sensors were shielded from highly oblique ($< 4^\circ$) grazing impacts.)

G. Tray H-11 (Space end)

There was an average of 21 impacts/sensor on tray H-11. Three impacts on one sensor were analyzed and classified as: 2 manmade and 1 natural. The natural impactor, estimated to have been $\sim 8 \mu\text{m}$ in size, left a residue containing Na, Mg, K, Ca and Fe. Only Ti and Zn were detected in the residue from one small manmade particle ($< \sim 3 \mu\text{m}$). The second manmade particle, estimated to have been $\sim 6 \mu\text{m}$ in size, also left a residue containing Ti and Zn, but a trace of Na and K were detected in the crater. Both particles were probably pieces of paint. No conclusions can be drawn from this small sample set on the Space end tray, but the early results indicate that there may have been more orbital debris strikes on the Space end than expected.

H. Comments

The presence of Cu in 5 of the 11 manmade impactor residues on sensors from the East panel, and 4 of the 5 manmade impactor residues found on sensors from the North and South sides of LDEF, is unexpected. This may be due to higher than normal, heterogeneously distributed background levels of Cu, or some other unidentified mass interferent. However, a review of all residue compositions shows that Cu was only detected in impact sites on the East, North and South sides of the satellite. The IDE impact record shows that the LDEF passed through several orbital debris clouds during its first year in orbit that affected only these three sides of the spacecraft. Thus, it is possible that Cu bearing debris may be a significant component of these debris clouds. If the Cu is shown not to be a contaminant in future work, this could point to a specific source type for this debris. The other manmade impactors were presumably paint particles as discussed above.

Remaining resources for this study will be utilized for the following tasks:

- 1) continued analysis and interpretation of data collected to date in order to further define the nonvolatile chemical composition of impactors,
- 2) continued contamination studies including depth profiles down to the Si substrate that will address background contamination levels for Na, Mg, K and Cu.

- 3) EDS and Auger spectroscopic studies of heavy deposits of impactor residues and surface contamination features in order to determine the composition and possible cross interference of these species
- 4) analyses of several simulated (Fe hypervelocity particles) impact sites on an active flight sensor, and
- 5) analysis of as many flight impact sites as possible until the optimum number of 320 is reached.

IV. SUMMARY

To date, 79 impacts on IDE sensors have been analyzed with SIMS. These include 36 impacts on two IDE sensors from LDEF tray C-9, (leading, or east side) 18 impacts on four different sensors from tray C-3 (trailing, or west side), 12 impacts on one sensor from tray B-12 (north side), 4 impacts on one sensor from tray D-6 (south side), 6 impacts on one sensor from the earth end tray G-10, and 3 impacts on one sensor from the space end tray H-11. Of the 79 impacts, 57 were formed from particles estimated to have been $<3 \mu\text{m}$ in size, 18 were formed from particles estimated to have been $5\text{-}20 \mu\text{m}$ in size, and 3 were formed from particles estimated to have been $30\text{-}50 \mu\text{m}$ in size. Residue from manmade debris, mostly paint particles and metal bits, has been identified in craters on all trays. (Aluminum oxide particle residues were not detectable on the Al/Si substrates.)

Preliminary estimates of the manmade/natural microimpactor population ratio for the East and the West sides of LDEF were calculated assuming that unknown impactor residues were all manmade or all natural, respectively. The calculated ratios were 0.80 for the East and 0.28 for the West. These values are subject to change as more information on contamination interferences, and more analyses impact sites is collected. Additionally, the combination of this data set with data from other LDEF investigators should provide a more accurate assessment of the microparticle population ratio in LEO.

Quantitative analyses of impactor residue chemical composition is underway, but results will not be reported until a better understanding of contamination issues is gained.

Cu was detected in 9 out of 16 "manmade" impacts on sensors from the East, North and South sides of LDEF, but was not detected in any of the 9 "manmade" impacts on sensors from the West, Space and Earth ends of the satellite. If, after further investigation, the Cu is shown not to be a contaminant, this could point to a specific source type for this debris.

The results to date are generally consistent with the IDE impact record which showed highly variable long term microparticle impact flux rates on the West, Space and Earth sides of the LDEF which could not be ascribed to astronomical variability of micrometeorite density. The IDE record also showed episodic bursts of microparticle impacts on the East, North and South sides of the satellite, denoting passage through orbital debris clouds or rings.

References

1. Simon, C.G., Hunter, J.L., Griffis, D.P., and Wortman, J.J., NASA CP 3134, pp. 529-548 (1991).
2. Wilson, R.G., Stevie, F.A., and Magee, C.W., Secondary Ion Mass Spectrometry - A Practical Handbook for Depth Profiling and Bulk Impurity Analysis, J. Wiley & Sons, p. E-17 (1989).
3. Ibid, p. E-22.
4. Cour-Palais, B.G., *Geochimica et Cosmochemica Acta*, Vol. 3, pp. 2451-2462 (1974).
5. Mulholland, J.D., Simon, C.G., Cooke, W.J., Oliver, J.P., Misra, V., and Kassel, P.C., NASA CP , pp. - (1992) [paper of this compilation].
6. Simon, C.G., Mandeville, J.C., McDonnell, J.A.M., Mirtich, M., Walker, R.W., "M&DSIG Microcrater Committee Report", NASA CP- , pp. - (1992). [paper of this compilation].
7. Amari, S., Foote, J., Simon, C. G., Swan, P., Walker, R., and Zinner, E., NASA CP3134, pp. 503-516 (1991).

Table 2. Microparticle residue classifications for 79 impacts on IDE sensor surfaces based on SIMS analyses. (See text for explanation of crater and spall zone sizes.) *Na not looked for in all sites.

Impact No.	Size (μm)		Elements Detected with SIMS	Impactor Classification		
	Crater	Spall		manmade	natural	indeterminate
LDEF Tray C-3 (Trailing [wake], or West side)						
1300-C1	36x54	138	(Na, Mg, K, Ca)--(Ti, Fe)	X		
1300-C2	13x18	-	clean (trace Na)			X
1300-C3	12	-	Na, Mg, K, Fe		X	
1300-C4	13	-	clean			X
1300-C5	11	-	Na, K, Mg, Cr, Fe	X		
1300-C6	10	-	clean			X
1300-C7	12	-	Na, K, Ti	X		
1300-C8	12	-	Na, Mg, K, Ti	X		
1336-C1	10	-	clean (trace Na)			X
1336-C4	23x28	-	Na, Mg, K, Ca, Fe		X	
1359-C4	10	-	clean			X
1359-C5	9x12	-	clean (trace Na, Mg)			X
1359-C6	18x25	42	clean			X
1359-C7	12	-	clean			X
1382-C2	22	65	Na, Mg, K, Ti, Zn	X		
1382-C4	9	-	(trace Mg, Ca, Fe, Ni)		X	
1382-C5	10	-	clean			X
1382-C9	15x20	-	clean (trace Mg)			X
LDEF Tray C-9 (Leading [ram], or East side)						
1176-C1	23	-	Na, Mg, K, Fe		X	
1176-C2	9	-	clean (trace Na, K)			X
1176-C3	9	-	Na, K			X
1176-C4	11	-	Na, K, Cu	X		
1176-C5	32	212	Na, Mg, Ti, Cr, Fe, Cu, Zn, Ag	X		
1176-C6	23x37	-	Na, K			X
1176-C7	50	138	H, C, Ti, Cr, Fe	X		
1176-C8	9	-	Na, Mg, K	X		
1176-C9	12x16	-	Na, Mg, K--(Fe)			X
1176-C10	9	-	Na, Mg, K, Cu	X		
1176-C11	9	-	Na, K			X
1176-C12	10	-	Na, Mg, K	X		
1176-C13	9	-	Na, Mg, K, Cu	X		
1176-C14	9	-	Na, K			X
1176-C15	9	-	Na, K			X
1176-C16	10	-	Na, K			X
1176-C17	11	-	Na, Mg, K, Fe, Cu (trace Ti, Cr)	X		
1176-C18	22x25	-	Na, Mg, K, Fe		X	
1176-C19	11	-	Na, Mg, K	X		
1176-C20	11	-	Na, Mg, K	X		
1293-C1	13x17	-	*clean			X
1293-C2	24x31	-	*Mg, K, Fe		X	
1293-C3	18	-	*Mg, K, Ca, Fe		X	
1293-C4	12	-	*Mg, Fe		X	

Table 2. [continued] Microparticle residue classifications for 79 impacts on IDE sensor surfaces based on SIMS analyses. (See text for explanation of crater and spall zone sizes.) *Na not looked for in all sites.

Impact No.	Size (µm)		Elements Detected with SIMS	Impactor Classification		
	Crater	Spall		manmade	natural	indeterminate
LDEF Tray C-9 (Leading frame, or East side) {continued}						
1293-C5	22x28	-	*clean			X
1293-C7	12	-	*clean			X
1293-C8	10	-	*clean			X
1293-C12	12	-	Ti (trace Na, K)	X		
1293-C13	9	-	clean			X
1293-C14	9	-	clean			X
1293-C15	11	-	clean			X
1293-C16	11	-	clean			X
1293-C17	9	-	clean			X
1293-C18	11	-	clean			X
1293-C19	13	-	clean			X
1293-C20	11	-	clean			X
LDEF Tray D-6 (South side)						
1252-C3	10x13	-	Na, Mg, K, Cu	X		
1252-C4	10	-	clean (trace K)			X
1252-C5	10	-	clean (trace K)			X
1252-C9	10	-	clean (trace K)			X
LDEF Tray B-12 (North side)						
1298-C1	11x19	34	Na, Mg, K, Fe		X	?
1298-C2	10	-	clean			X
1298-C6	15x20	38	Na, Mg, K, Fe		X	
1298-C7	10	-	Na, Mg, K, Ca, Fe		X	
1298-C8	16x20	30	Na, Mg, K, Fe, Cu, Zn	X		
1298-C9	15	-	Mg, Fe		X	
1298-C10a	10	-	Na, Mg, K (trace Cu, Ag)	X		
1298-C10b	10	-	Na, Mg, K, Ti, Zn	X		
1298-C11	11	-	clean			X
1298-C12	9x13	-	Na, Mg, Fe		X	
1298-C13	10	-	Na, Mg, Fe		X	
1298-C14	10	-	Na, Mg, Fe, Cu	X		
LDEF Tray G-10 (Earth end)						
1172-C5	9	-	Na, Mg, Ti, Fe	X		
1172-C6	9	-	clean (trace Na, K)			X
1172-C7	11	-	Na, K			X
1172-C8	10	-	clean (trace Na, K)			X
1172-C10	9	-	clean (trace Na, K)			X
1172-C11	10	-	Na, K, Ti, Cr	X		
LDEF Tray H-11 (Space end)						
1255-C1	20	32	Ti, Zn (trace Na, Mg)	X		
1255-C2	23x27	-	Na, Mg, K, Ca, Fe		X	
1255-C4	11	-	Ti, Zn	X		

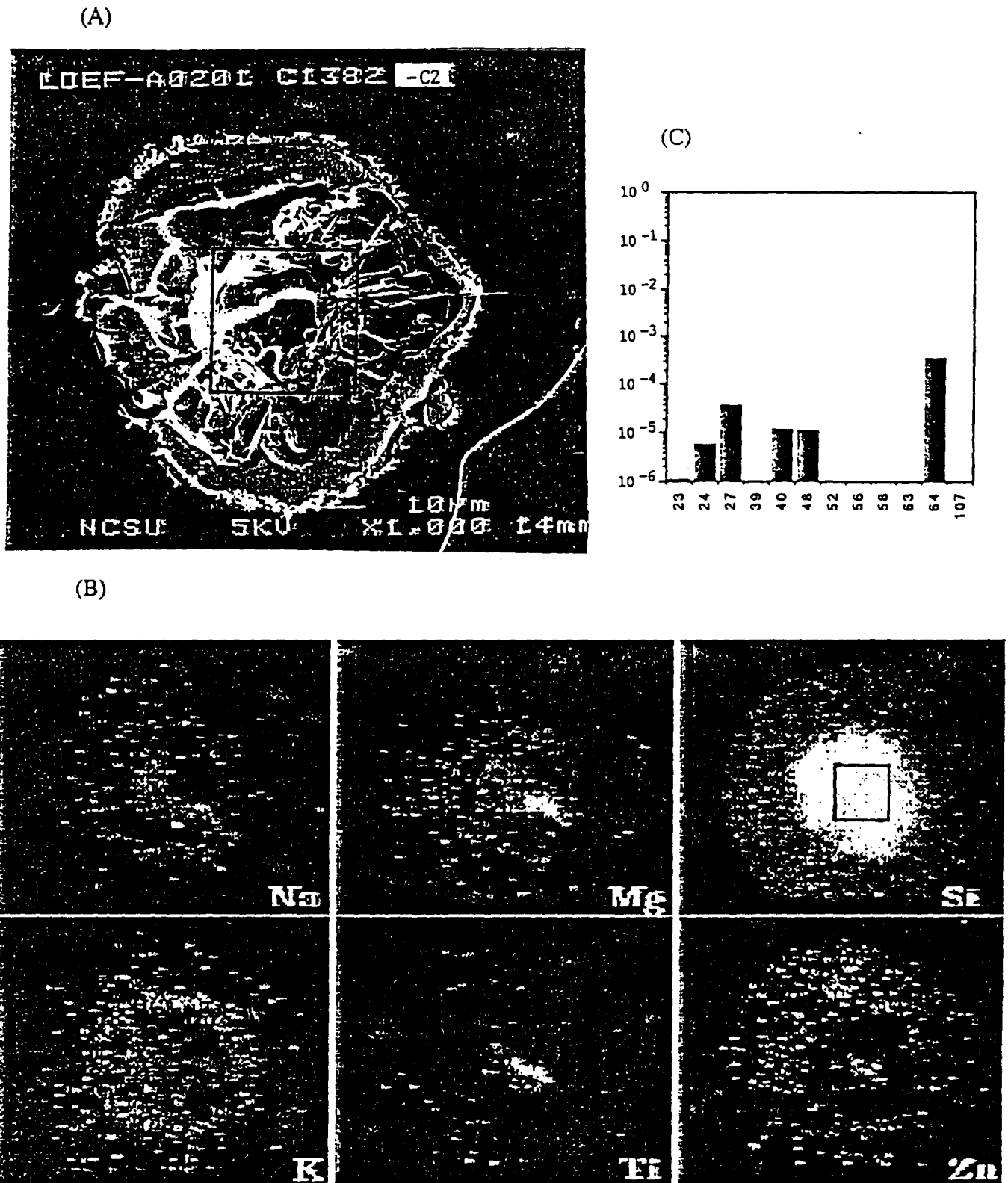


Figure 1. Example of a manmade debris impact (1382-C2) on an IDE sensor mounted on LDEF tray C-3 (Trailing or West side). (A) SEM micrograph. (B) Secondary positive ion images of impact area. Imaged area is 150 μm in diameter. Intensities are uncorrected for relative ion yields. Note exposed area of Si and SiO_2 defined by the Si^+ map. (C) Bar graph plot of corrected ion intensity data for boxed area.

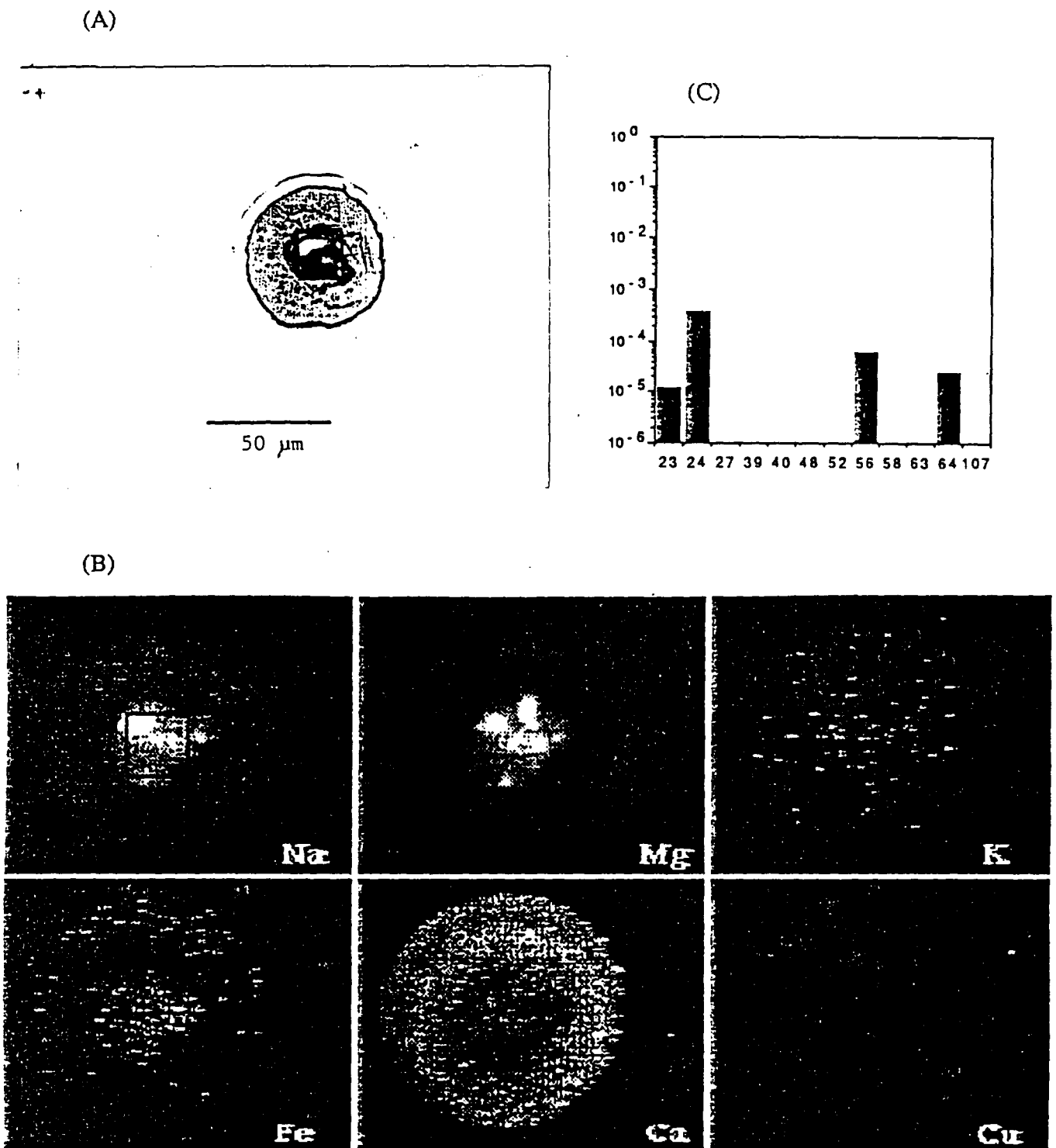


Figure 2. Example of a natural micrometeorite impact (1336-C4) on an IDE sensor mounted on LDEF tray C-3 (Trailing or West side). (A) Optical micrograph. (B) Secondary positive ion images of impact area. Imaged area is 150 μm in diameter. Intensities are uncorrected for relative ion yields. (C) Bar graph plot of corrected ion intensity data for boxed area. Note the low intensity for mass 64 (Cu^+) in the ion image and the relatively high concentration value displayed in the bar graph. This methodological artifact raises the minimum detectable Cu level to the 100 ppm range. The high Ca^+ background intensity surrounding the impact has been traced to contamination in the top layer of aluminum on the substrate.

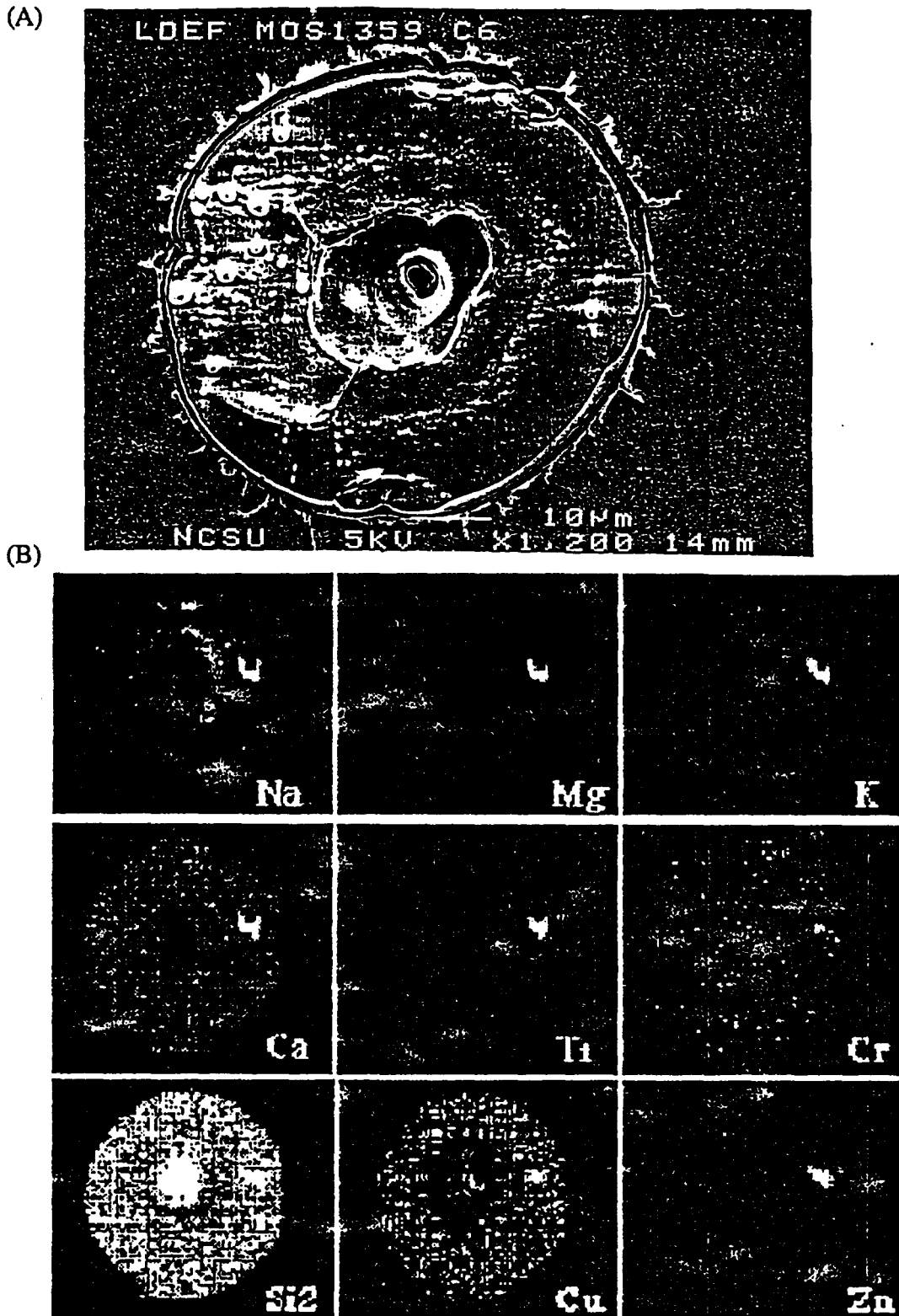


Figure 3. Example of an indeterminate impact (1359-C6) on an IDE sensor mounted on LDEF tray C-3 (Trailing or West side). (A) SEM micrograph. (B) Secondary positive ion images of impact area. Imaged area is $150\ \mu\text{m}$ in diameter. Intensities are uncorrected for relative ion yields. Note central crater area defined by the Si_2^+ map. Bright spot of Na, Mg, K, Ca, Ti, Zn is a contaminate well outside of the impact crater.

CONTAMINANT INTERFERENCES WITH SIMS ANALYSES OF MICROPARTICLE IMPACTOR RESIDUES ON LDEF SURFACES

C.G. Simon**, D. Batchelor*, D.P. Griffis*, J.L. Hunter*, V. Misra*, D.A. Ricks*
and J.J. Wortman*

**Institute for Space Science and Technology, Gainesville, FL 32609-3530 USA

*North Carolina State University, Raleigh, NC 27695-7916 USA

ABSTRACT

Elemental analyses of impactor residues on high purity surfaces exposed to the LEO environment for 5.8 years on LDEF has revealed several probable sources for microparticles at this altitude, including natural micrometeorites and manmade debris ranging from paint pigments to bits of stainless steel. A myriad of contamination interferences were identified and their effects on impactor debris identification mitigated during the course of this study. These interferences included pre-, post- and in-flight deposited particulate surface contaminants, as well as indigenous heterogeneous material contaminants. Non-flight contaminants traced to human origins, including spittle and skin oils, contributed significant levels of alkali-rich carbonaceous interferences. A ubiquitous layer of in-flight deposited siliceous contamination varied in thickness with location on LDEF and proximity to active electrical fields. In-flight deposited (low velocity) contaminants included urine droplets and bits of metal film from eroded thermal blankets.

INTRODUCTION

The Long Duration Exposure Facility satellite (LDEF) was deployed in low earth orbit (LEO) on 7 April, 1984 and after 5.77 years of space exposure was retrieved on 26 January, 1990. The gravity gradient stabilized, non-spinning satellite carried 57 scientific and engineering experiments that gathered information on the LEO environment and its effects on spacecraft materials and systems.

One major task of the LDEF mission was to measure the fluence and composition of the small particle environment in LEO. This population is composed of several microparticle species which include a) natural micrometeorites from asteroidal, cometary and other interplanetary and interstellar dust sources, and b) manmade orbital debris particles that can be linked to rocket fuel exhaust, paint flakes, wastewater dumps, cargo bay debris, and spacecraft materials

that are released in catastrophic events such as satellite explosions. Essentially all natural particles will intercept spacecraft in LEO at hypervelocity speeds, creating impact craters and blasting away many times their own mass in target material that is ejected from the crater in a spray of small particles. (This is one mechanism of microparticle population growth in LEO.) Manmade debris particles also intercept spacecraft in LEO at hypervelocity speeds and create impact craters. However, manmade microparticles released during satellite deployment and retrieval missions can intercept the involved spacecraft at very low velocities (no craters) and contribute to the particulate surface contamination. Particles arising from shuttle operations include wastewater/condensate dumps, hydraulic losses and contaminant particles from the cargo bay.

Several active and inactive experiments on LDEF were designed to record hypervelocity impacts from manmade orbital debris and natural micrometeorites. Impact craters on these surfaces are being examined by the scientific community with microanalytical techniques in a search for impactor debris or residue. We have carried out an extensive series of such analyses using Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM/EDS) and Secondary Ion Mass Spectrometry (SIMS) techniques developed for surfaces from two LDEF micrometeorite experiments: Expt. AO201, the Interplanetary Dust Experiment (IDE), and Expt. AO187-1, the Chemistry of Micrometeoroids Experiment (CME). We report here on contamination interferences that were discovered during the course of our studies and describe the recognition and mitigation practices developed to date. Detailed descriptions of the analytical methodology and results of microcrater analyses are presented elsewhere /1-4/.

EXPERIMENTAL

Sample Selection

The extreme sensitivity of SIMS (ppm for most species) makes it a valuable tool in the search for sparse impactor residues, but it also makes the technique susceptible to interference from trace levels of contamination. This a major concern when using SIMS to look for impactor residues. Only craters in very high purity substrates were selected for analysis in order to minimize interferences from the substrate matrix.

The active IDE experiment consisted of several hundred 51 mm diameter metal-oxide-silicon (MOS) capacitor type impact detectors that were mounted on the six primary sides of LDEF (rows 3, 6, 9, 12, and Earth and Space ends). The detectors discharged when they were impacted by a particle (and then recharged within a few seconds) and recorded the time of the impact event on a magnetic tape. The objective of this experiment was to measure the flux and spatial distribution of microparticles (and their orbits where possible) with respect to time. Because ultra high purity (electronic grade) materials were used to construct the Al-SiO₂-Si detectors, and because they were located on all 6 primary sides of LDEF, they were selected as appropriate surfaces to search for impactor debris in craters using SIMS.

Twelve 32 mm diameter germanium witness plates were also flown on LDEF (row 12) as a part of the IDE. These Ge plates were single crystal, ultra-high purity, (0.99999) and ultra-smooth (<50Å). They were intended to provide a surface on which even very small impact craters (<0.1 μm) could be found, and also to collect surface

contaminants associated with the mission. These surfaces were also selected for SIMS analysis.

A third LDEF surface type selected for SIMS analysis was the high purity gold (0.9999) plates from the CME that had been mounted on row 3 (trailing side) of LDEF. Horz, et al., have reported results of extensive SEM/EDS analyses of impact sites on these surfaces /3,4/. The Au plates were mounted in a protective clamshell enclosure (to limit particulate contamination) that did not open until several days after deployment. Although the clamshell system was designed to close before LDEF retrieval, the extra long stay in orbit (5.8 years compared to a planned 9 months), resulted in its being open upon retrieval. We attempted to look for sparse impactor debris in craters on these surfaces that would have been undetectable using SEM/EDS procedures.

Analytical Procedures

Optical micrographs of each IDE sensor were taken before and after flight, providing a comparative record of pre-flight and in-flight/post-flight features. Surfaces were first scanned with an Olympus stereo optical microscope at 125X in order to locate features for further study. Optical micrographs were taken of some features and/or fiducial marks (scratches) were made in order to assist in relocating the microfeatures during subsequent analyses. The feature locations were also mapped on the whole-sensor micrographs.

SEM/EDS analyses were performed using either a JEOL Model JSM 6400F cold field emission SEM equipped with an Oxford EDS with an ultrathin window, or an Hitachi S-530 scanning electron microscope equipped with thick-window Tracor-Northern TN5500 EDS. Auger Electron Spectroscopy (AES) was used to determine the bulk composition of a surface layer of contamination that was on all LDEF surfaces. Depth profiles of this layer were made with the Auger spectrometer by sputtering away (destructively) the sample with an Ar ion beam while monitoring spectral lines associated with C, O, Na, Mg, Si and Ca. Profiles of two visibly different areas of the contaminant layer on an IDE sensor were analyzed. One area was located in an arc shaped zone surrounding the exposed electrical leads on an IDE detector, and the other area was ~ 5 mm away from this dark zone on the same detector (see Figure 1).

Ge witness plates were scanned as described above, but no pre-flight photos of these witness plates were taken. During the course of the optical scanning, an unusually large number of surface contaminants was noted (~400/cm²). Many of these contamination spots, apparently residues from splatters and droplets, were analyzed using SEM/EDS, and a few were analyzed with SIMS. They were found to be alkali-rich siliceous materials with inclusions (spots) of hydrocarbon based materials. Several other witness plates (Si, quartz and Zirconia) that were mounted concurrently and coincidentally with the Ge plates were secured from other LDEF investigators and optically scanned. The surface particulate counts on these witness plates ranged from 2-20/cm². Thus, it was concluded that the Ge witness plates had been contaminated before being mounted on the LDEF. This unfortunate circumstance greatly complicated SEM scanning of the Ge for microcraters and severely limited the confidence of SIMS analyses of craters for impactor debris.

The Au samples were received from the CME team premounted on SEM stubs and had already been carefully

documented with SEM micrographs and EDS spectra. These samples were placed in the SIMS without further treatment.

All SIMS data was collected with a Cameca IMS 3F using $^{16}\text{O}^+$ or $^{16}\text{O}^-$ ion beams. The instrument was used in the ion microscope mode and data was recorded as two-dimensional elemental positive ion maps with lateral resolution of 1-2 μm . Pixel intensities were used to calculate relative element abundances. The SIMS analytical protocol is described in detail in reference /1/.

Briefly, the SIMS protocol involved the following steps:

(1.) Each impact site was first sputtered with the oxygen beam while monitoring the concentrations of C, Na, Mg (and Si on the Ge and Au samples) in order to assure removal of the bulk of the surface contamination layer ubiquitous to LDEF.

(2.) Next, an energy filtered bargraph type mass spectrum was recorded.

(3.) Then, a dual channel-plate/ccd-digital-camera detector system was used to record high resolution ($M/\Delta M = 3,000-4,000$) elemental positive ion maps for C, O, Na, Mg, Si, Al, K, Ca, Ti, Cr, Ni, Fe, Cu, Zn, Ag and Au, and molecular ion maps for $^{56}\text{Si}_2$ and $^{58}\text{Si}_2$. (Images were not recorded if there were less than ~ 4 ion counts/min at the observed mass.)

(4.) On some samples, negative elemental ion maps were recorded for H, C, O, F, Si, Al, S, Cl and Au.

RESULTS

Three categories of contamination were noted on the LDEF samples. The types of contamination found during the course of this study and the interference mitigation procedures developed are described below.

Substrate Contamination

This category included homogeneous bulk matrix contamination, heterogeneous bulk matrix contamination (such as inclusions), and subsurface interfacial contamination.

The IDE sensors had ~ 100 ppm of Ca contamination in the Al surface layer. There was evidence of possible Na, K, F and Cl contamination at the SiO_2/Si interface, but this situation awaits verification using charge-compensated depth profiling techniques. (The equipment required to perform such an analysis has only recently been installed in our laboratory's SIMS instrument.) These substrate contaminants raised the effective lower limits of detection for these species to the hundreds of ppm level.

Pressure induced "blank" discharges were produced on retrieved sensors [under power] using diamond and silicon shards. SIMS analyses of these "blanks" showed that the Al matrix contaminants and the layer of surface contamination (discussed below) were blown clear of the discharge zone by the energetic event (see Figure 2). However, until the matrix can be more carefully characterized, and until SIMS analyses are performed on hypervelocity impact sites on flight retrieved sensors using impactors with known compositions in ground based

facilities, the lower limits of detection for the species in question will remain high. No conclusions on orbital impactor origins will be reached that rely solely on the presence of these species in impact sites. It should be noted that out of 79 impact sites on IDE sensors examined with SIMS, 38 have either no detectable residue, or only have traces of Na and K present in the impact sites.

The Ge samples had no detectable bulk matrix contaminants and were not subject to interfacial contamination since they were single crystal substrates.

The Au samples had bulk Cu and Ag contamination levels in the hundreds of ppm range. An interfacial layer of multi-element contamination was found $\sim 1 \mu\text{m}$ below the surface when doing a depth profile of the Au matrix adjacent to an impact crater. The layer was $\sim 2 \mu\text{m}$ thick and was rich in C, Na, Mg, Al, Si, K, Ca, Ti, Cr, Fe, Cu, Zn and As. This was traced to the manufacturer's practice of covering the Au plate with a $1 \mu\text{m}$ thick Au leaf in the final processing step in order to produce a smooth surface texture. The presence of As (frequently found with Au ore deposits) in this layer was used as a tracer for the contamination. The 1 mm thick Au leaf was clearly visible in micrographs of impact craters, and the exposed contamination layer could be morphologically identified. These two techniques essentially eliminated false identification of impactor debris from this source, but the presence of the contamination severely limited the utility of SIMS in identifying impactor sparse debris that could not be detected with EDS.

Particulate contamination

This included all surface particles. These could be traced to pre- and post-flight sources such as clothing fiber, paper fiber, starch grains, pollen, sawdust, spittle, fingerprints, bits of metal, plastic and rubber, etc.; inflight sources from shuttle operations during deployment and retrieval; and self-generated sources from environmental degradation (especially atomic oxygen [AO] erosion) of LDEF surfaces and specimens. The atomic oxygen exposure generated ash on some materials, eroded the polymer from metal backed films leading to the release of bits of thin metal foils, and eroded organic binders in some paints leading to the release of small, inorganic paint particles (pigments). There is also surface debris from the molten ejecta of impacts. A detailed survey of particulate contamination is the subject of several reports from the LDEF community /5-8/.

Some surface particulate contamination features possess the basic symmetry of an impact crater and can be mistakenly identified by inexperienced operators. A particular example of this type of interference is an apparent residue from a droplet of wastewater. As can be seen in Figure 3, the residue is circular and appears to have a central crater. However, stereoscopic examination and line profilometry have verified that these are surface deposits. EDS analyses of the crystalline deposits in these spots reveals a pattern that closely resembles human urine /9/. These features are relatively rare and easily identified by experienced researchers. We have identified less than 10 in optical scans of over 1500 cm^2 of highly smooth LDEF surfaces. It should be noted that other LDEF and Solar Max investigators have reported these feature on retrieved surfaces /9,10/.

Samples were handled in clean rooms or laminar flow hoods during optical examination in order to minimize

accumulation of post-flight surface particulate debris. Much of the surface particulate debris was blown off of sample surfaces using a filtered, pre-purified nitrogen stream. This procedure was repeated each time a sample was removed from its protective case, and just prior to insertion into the SEM or SIMS instruments. No solvent rinsing or washing procedures have been used to date.

Interference from particles in or near impact features that were imaged with SIMS were determined by careful SEM/EDS examination of the impact site. Particles that were not associated with the impact event could be recognized by their morphology. If there was no evidence that the particle had undergone melting, it was assumed to be a contaminant. Salt crystal (NaCl and KCl) and bits of metal (Al and stainless steel) were the major particulate interferences. Purely organic based particles were not a significant problem since they could be easily recognized by their composition. In general, the best method of mitigation for particulate interferences was recognition, which translated into operator experience.

As mentioned above, the Ge samples were contaminated with high levels of surface particulates before flight. These particles were apparently residues from droplets and splatters of some liquid, and could not be blown off the surface with nitrogen. It may be possible to clean these samples using solvent rinsing or washing techniques, but these procedures could add or relocate contamination. (However, cleaning the surface debris from the ultra-smooth Ge may permit effective SEM scanning of the surfaces for very small craters.)

In addition, the impact features on the Ge witness plates generally had high aspect central crater ratios with very jagged walls and inner spall zones. These jagged central crater walls led to beam shadowing during the SIMS analysis where the primary ion beam is prevented from reaching the bottom of the crater due to the rough contours of the crater walls. Due to this effect, residues at the bottom of the crater could not be extracted at their true levels. The combination of this limitation and the high level of surface contamination made it very difficult to study the impact craters on Ge plates with our SIMS instrument, and work has been suspended on this sample set.

Surface contamination layer

A layer of C/O/Si rich contamination covers essentially all exposed LDEF surfaces to some degree. Various sources for this layer include outgassing products from organic based paint and silicone based room-temperature-vulcanizers (RTV's), and possibly from silizane based waterproofing agents used on shuttle tiles /11,12/. The thickness of the layer is dependent on the particular surfaces position relative to the various outgassing sources, the amount of ultraviolet (UV) light exposure, and the proximity to electric fields. Coloration of the layer varies from transparent to dark brown, and is related to the thickness in a given area. In general, this contamination layer was darker on surfaces that had low exposure to atomic oxygen (AO). SIMS depth profiles of the contaminant layer showed that C was present at concentrations 10 to 100 times higher on sensors from the backside of LDEF (row 3) versus sensors from the front side of the spacecraft (row 9). Thus, it is assumed that the contamination layer color is due to carbon-carbon bond conjugation (C=C). It should be noted that the overall thickness of the layer did not appear to be related to AO exposure.

It was noted that on most IDE sensors there was a dark, arc shaped zone of contamination around the unshielded electrical leads (Au wires) on the upper surface. The sensors were bonded to their Al holders with silicone RTV, and there were also some areas of darker contamination near the edges of the MOS wafers. As shown in Figure 1, Auger depth profiles of this contamination layer in a dark arc near the electrical leads on one sensor, and in a "light" colored area adjacent to this zone, showed that the layer was twice as thick in the dark area (~700 Å compared to ~350Å).

During SIMS analyses, the contamination layer over an impact site, which varied in thickness depending on impact location and age, was sputtered away using the O⁺ beam while monitoring the concentration of C, Na and Mg (and Si on Ge and Au surfaces). (Na and Mg were present in this layer in amounts detectable to SIMS but not to EDS or AES.) When the ion signals for these species dropped sharply, the layer was assumed to be essentially gone. However, residual material from this layer can expect to be sputtered more slowly from the valleys and troughs associated with the local surface topography. (This is known as differential sputtering and is an effect of beam shadowing.) Thus, careful interpretation of SIMS data was still required, and the utility of C,O and Si isotopic ratios in suspected impactor debris (not performed by this group) is severely restricted /13/.

SUMMARY

Contamination issues clearly have significant effects on the chemical analyses of the micrometeoroid experiments on LDEF. Secondary Ion Mass Spectrometry (SIMS) analyses of microimpactor residues on LDEF surfaces is subject to interference from three general classes of contamination.

[1] The most difficult interference comes from indigenous contamination of target materials. This can take the form of granular inclusions, subsurface layers and bulk matrix impurities. Careful compositional characterization of target substrates allows SIMS operators to define realistic lower limits of detection, identify tracer ion species or ion ratios associated with specific contaminants, and develop other contaminant recognition criteria.

[2] A myriad of particulate surface contaminants can be found on LDEF surfaces. Small particles that are lodged in or near impact sites will give large signals during SIMS analysis. These interferences are best dealt with through careful SEM/EDS analysis and recognition of morphologies not associated with hypervelocity impact events.

[3] A C/O/Si rich contamination layer covers all LDEF surfaces to varying degrees. This layer is sputtered away before analyzing the impact site for impactor residue. However, differential sputtering of this layer from the highly variable topography associated with impact craters can still interfere with C/O/Si compositional analyses and severely restrict the utility of isotopic ratios of these species in suspected impactor debris.

REFERENCES

1. C.G. Simon, J.L. Hunter, D.P. Griffis and J.J. Wortman, "Ion microprobe elemental analysis of impact features on Interplanetary Dust Experiment sensor surfaces.", *NASA CP 3134*, 529-548 (1991).
2. C.G. Simon, J.L. Hunter, D.P. Griffis, V. Misra, D.A. Ricks, J.J. Wortman, and D.E. Brownlee, "Elemental analyses of hypervelocity microparticle impact sites on Interplanetary Dust Experiment sensor surfaces", presented at the Second LDEF Post-Retrieval Symposium (1992) *NASA CP* (in press).
3. F. Horz, R.P. Bernhard, J. Warren, T.H. See, D.E. Brownlee, M.R. Lurance, S. Messenger and R.B. Peterson, "Preliminary analysis of LDEF instrument AO187-1 'Chemistry of Micrometeoroids Experiment'", *NASA CP 3134*, 487-501 (1991).
4. R. Bernhard and F. Horz, "Compositional analysis of projectile residues on LDEF instrument AO187-1", presented at the Second LDEF Post-Retrieval Symposium (1992) *NASA CP* (in press).
5. E.R. Crutcher and W.W. Wascher, "Particle types and sources associated with LDEF", *NASA CP 3134*, 101-120 (1991).
6. E.R. Crutcher, L.S. Nishimura, K.J. Warner and W.W. Wascher, "Migration and generation of contaminants from launch through recovery: LDEF case history", *NASA CP 3134*, 121-140 (1991).
7. E.R. Crutcher, L.S. Nishimura, K.J. Warner and W.W. Wascher, "Quantification of contaminants associated with LDEF", *NASA CP 3134*, 141-154 (1991).
8. E.R. Crutcher and K.J. Warner, "Molecular films associated with LDEF", *NASA CP 3134*, 155-178 (1991).
9. D. Humes and D. Batchelor, private communication (1992).
10. J.L. Warren, H.A. Zook, J.H. Alton, U.S. Clanton, C.B. Dardano, J.A. Holder, R.R. Marlow, R.A. Schultz, L.A. Watts and S.J. Wentworth, "The detection and observation of meteoroid and space debris impact features on the Solar Max satellite", *Proceedings of the 19th Lunar and Planetary Science Conference*, 641-657 (1989).
11. G.A. Harvey, "Organic contamination on LDEF" *NASA CP 3134*, 179-198 (1991).
12. G.A. Harvey, "Silizane to silica", presented at the Second LDEF Post-Retrieval Symposium (1992) *NASA CP* (in press).
13. S. Amari, J. Foote, C. Simon, P. Swan, R. Walker and E. Zinner, "SIMS chemical analysis of extended impact features from the trailing edge portion of experiment AO187-2.", *NASA CP 3134*, 503-516 (1991).

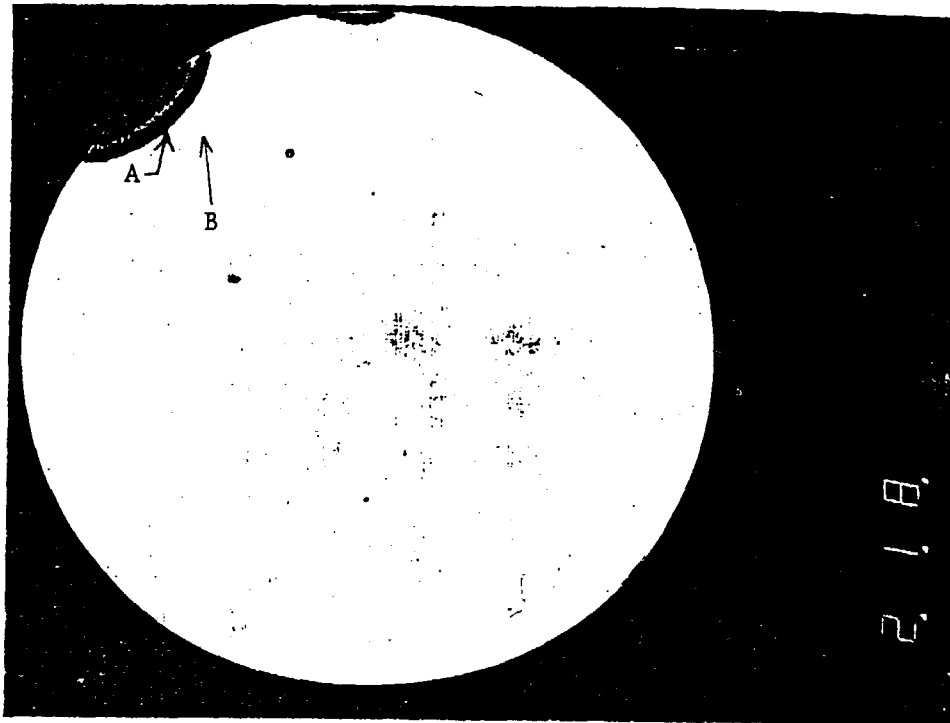


Fig. 1. (a) Post-flight photograph of an IDE sensor from the Earth End tray. Area "A", which symmetrically surrounds the sensors unshielded electrical leads on the wafer perimeter, is a thick layer of in-flight deposited C/O/Si rich contamination. Area "B" is covered with a much thinner layer of the same contamination. (b) Auger depth profile of areas "A" and "B" on a sensor from LDEF row 3 (trailing side). One minute of sputter time is equivalent to $\sim 100\text{\AA}$ depth.

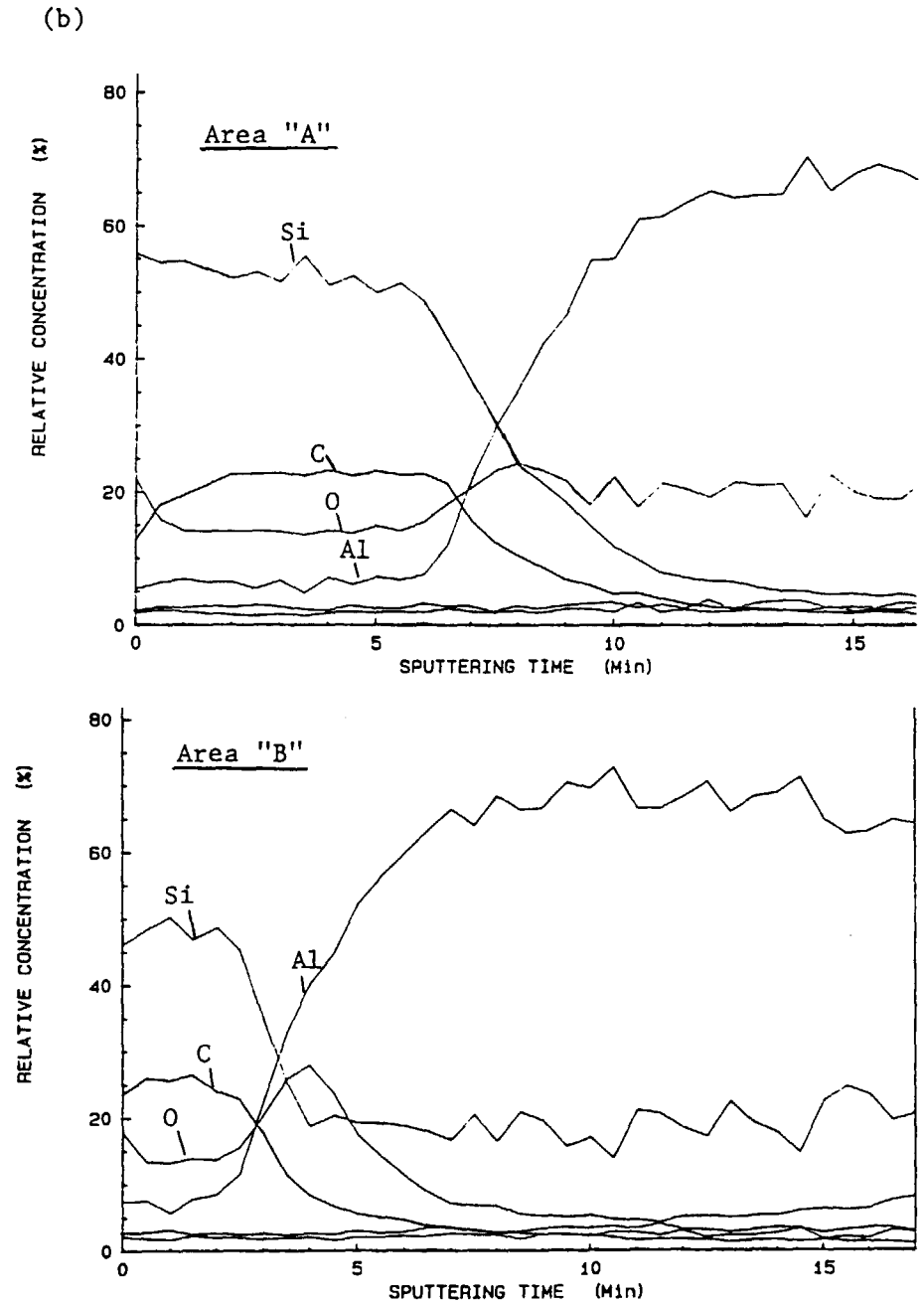


Fig. 2. (a) SEM micrograph of a pressure induced "blank" discharge on an IDE flight sensor. An ultra-pure silicon shard was pushed into the surface of the powered sensor (60 V) until the 1.0 μm thick SiO_2 insulator layer broke down and the sensor discharged. Bits of the Si shard can be seen in the central portion of the region cleared by the discharge. (b) SIMS elemental positive ion maps of the feature pictured in (a) showing that the layer of surface conatmination was blown clear of the discharge zone.

(a)



(b)

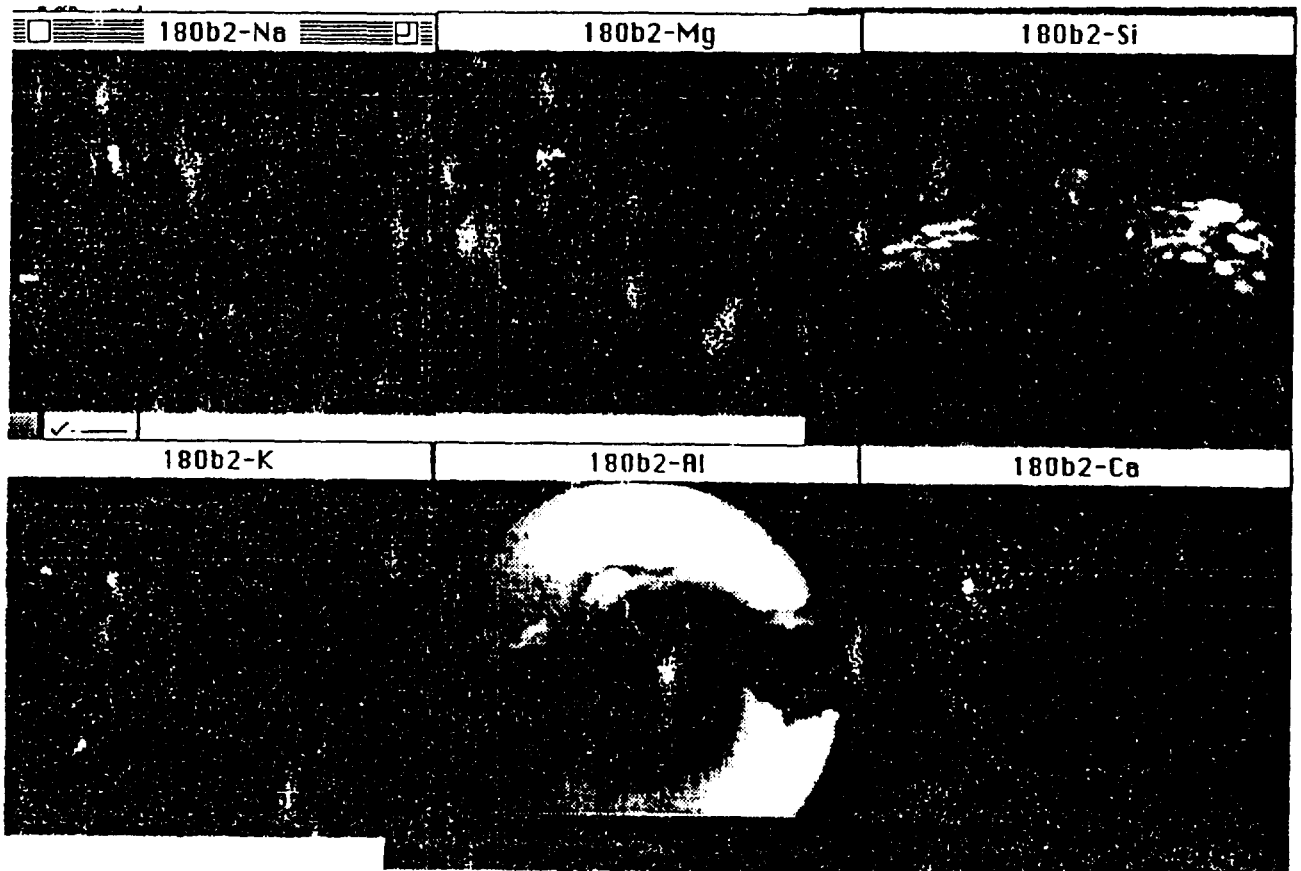
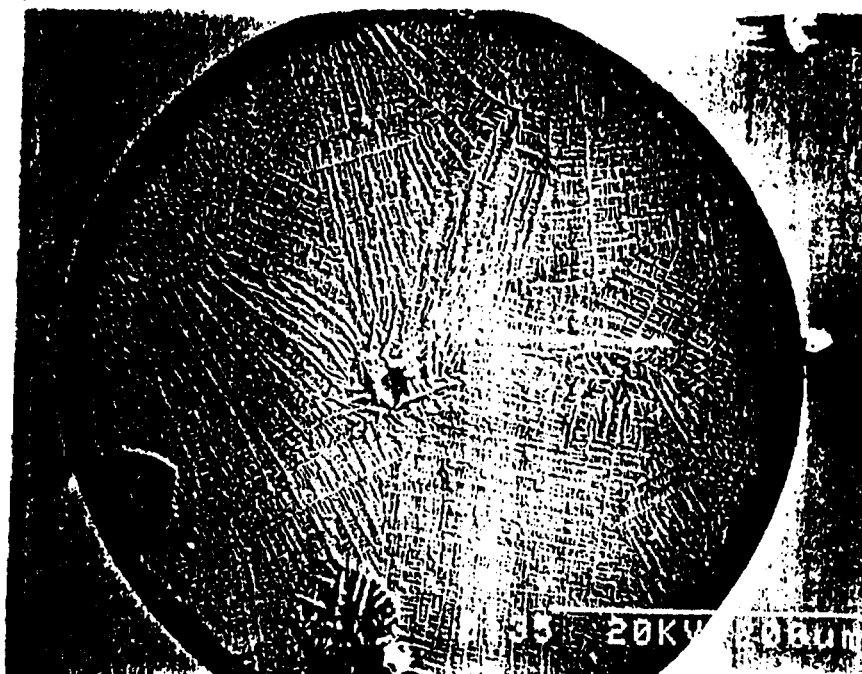
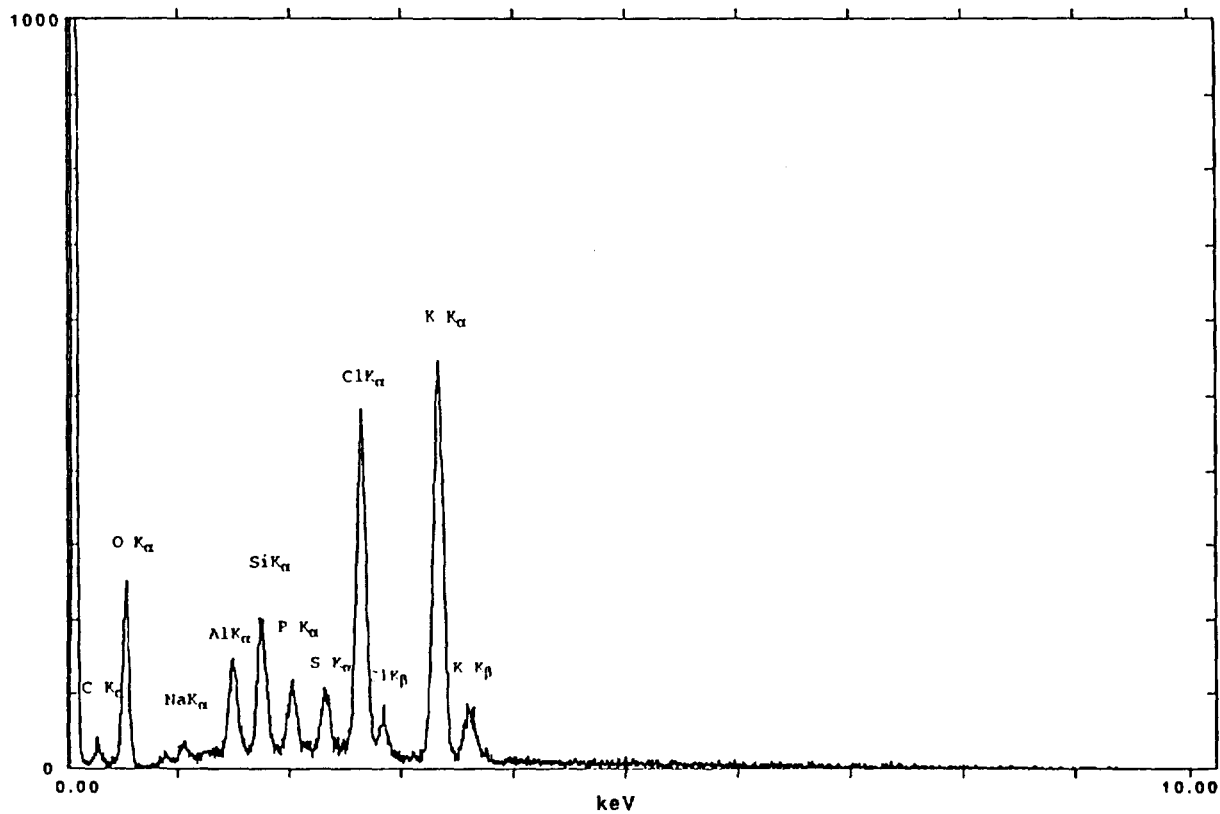


Fig. 3. (a) SEM micrograph of a suspected wastewater droplet residue found on an LDEF sample. (b) EDS spectrum of the central crystals in (a).

(a)



(b)



NASA LDEF Targets

H-11 1226 B1 10kv 14kx central crystals

Analyst: Dale Batchelor keV: 10.00 Current: 1000.00 Live Time: 200.00 eV/Channel= 5.00

Detector Resolution: 133.00 eV Take-off angle= 40.00