

N93-10854

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

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### 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-SiO<sub>2</sub>-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/cm<sup>2</sup>). 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/cm<sup>2</sup>. 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  $\mu\text{m}$ . 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  $\sim 4$  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  $\sim 100$  ppm of Ca contamination in the Al surface layer. There was evidence of possible Na, K, F and Cl contamination at the  $\text{SiO}_2/\text{Si}$  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  $1 \text{ mm}$  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  $1500 \text{ cm}^2$  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<sup>+</sup> 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.

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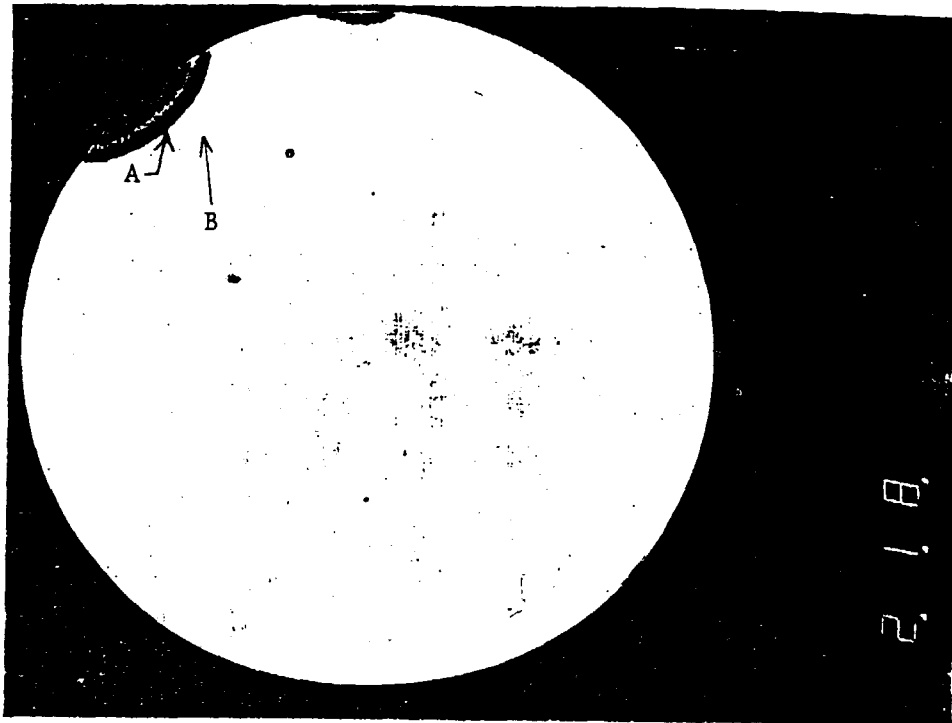


Fig. 1. (a) Post-flight photograph of an IDE sensor from the Earth End tray. Area "A", which symmetrically surrounds the sensors unshielded electrical leads on the wafer perimeter, is a thick layer of in-flight deposited C/O/Si rich contamination. Area "B" is covered with a much thinner layer of the 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.

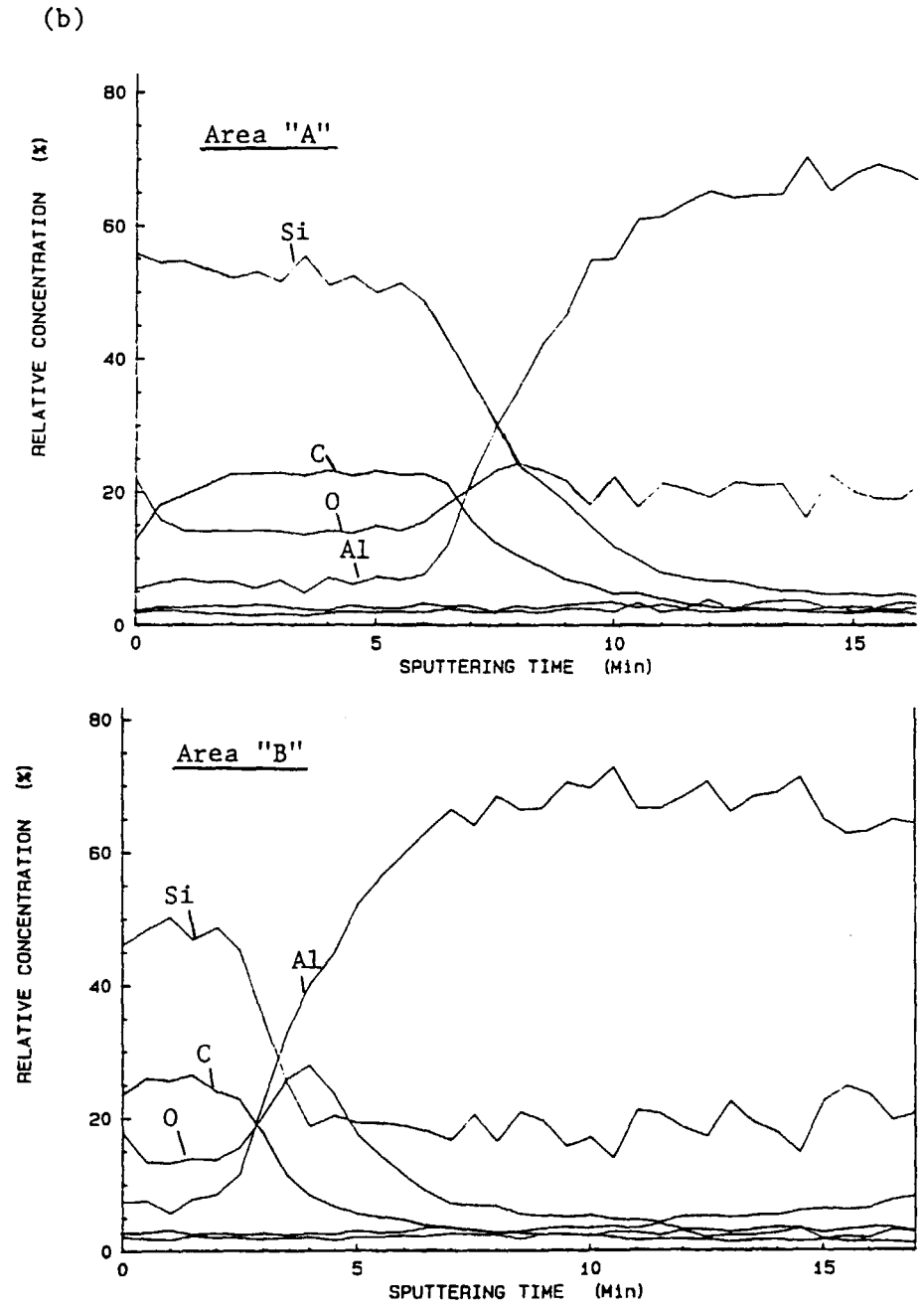


Fig. 2. (a) SEM micrograph of a pressure induced "blank" discharge on an IDE flight sensor. An ultra-pure silicon shard was pushed into the surface of the powered sensor (60 V) until the 1.0  $\mu\text{m}$  thick  $\text{SiO}_2$  insulator layer broke down and the sensor discharged. Bits of the Si shard 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)

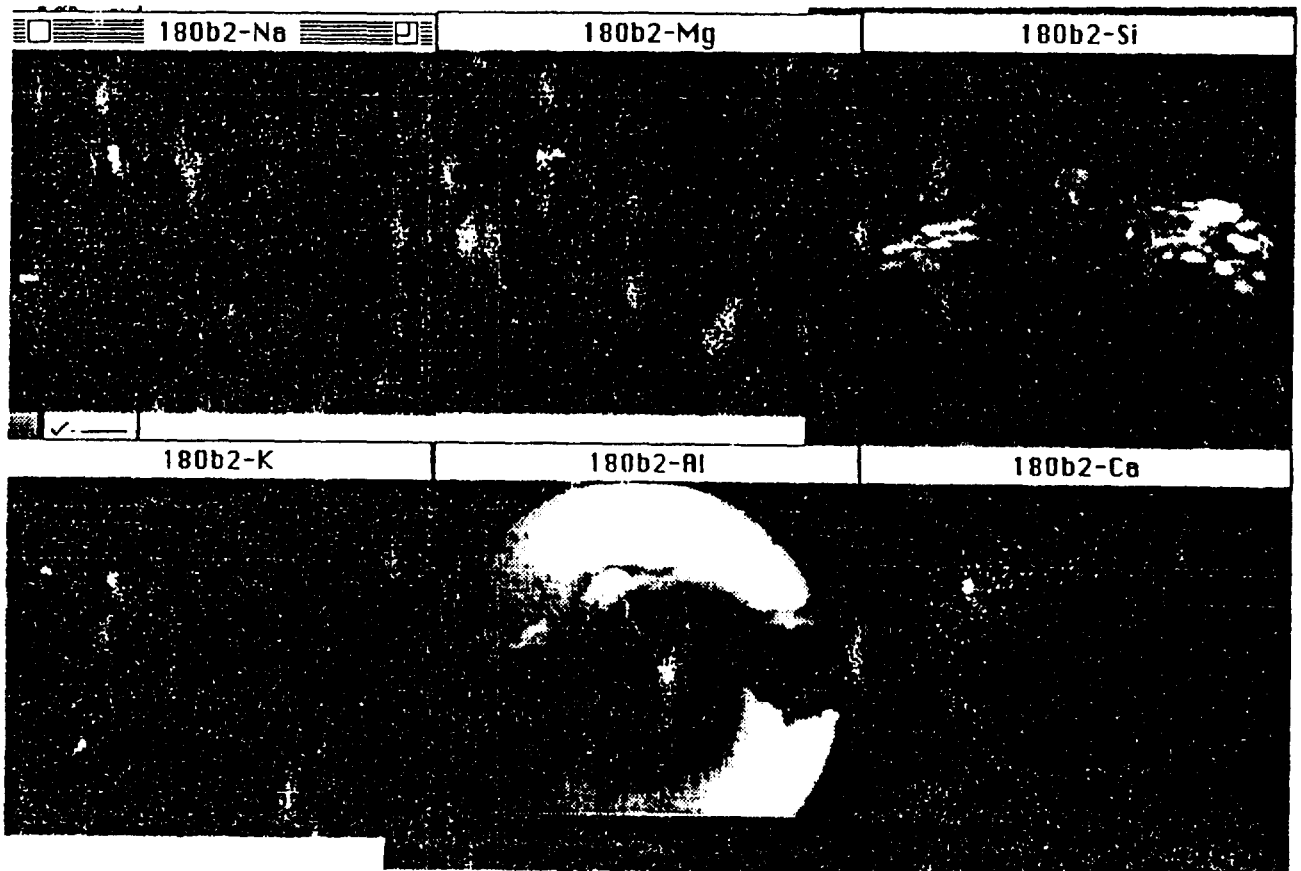
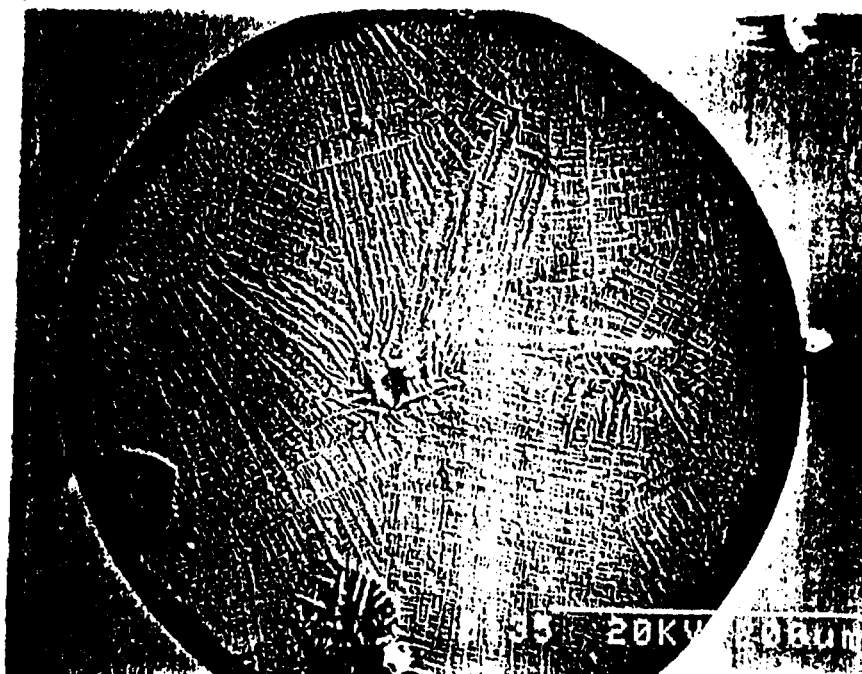
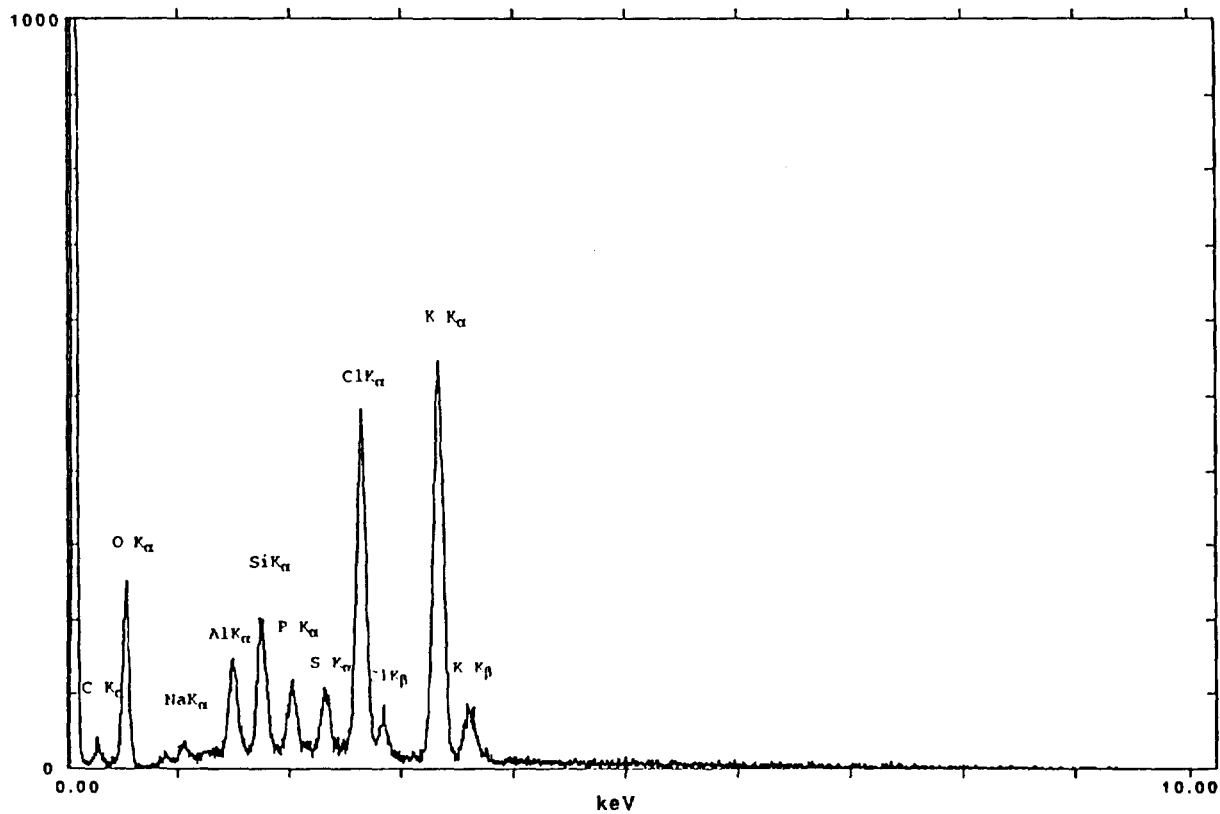


Fig. 3. (a) SEM micrograph of a suspected wastewater droplet residue found on an LDEF sample. (b) EDS spectrum of the central crystals in (a).

(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