

# Atmospheric Electron-Induced X-ray Spectrometer Development

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*Abstract.* The progress in the development of the Atmospheric Electron X-ray Spectrometer (AEXS) described. The AEXS is a surface analysis tool based on the excitation of characteristic x-ray and luminescence spectra at ambient pressure using an electron beam. *In situ* operation for the AEXS is obtained through the use of a thin electron transmissive membrane to isolate the vacuum of the electron source from the ambient atmosphere, resulting in rapid spectrum acquisition, non-destructive evaluation of surfaces, and moderate-to-high variable spatial resolution in comparison to similar portable instruments. The applications of the instrument for NASA planetary exploration include determination of elemental abundance and identification of minerals suspect of past biological activities, through correlation of x-ray and optical luminescence data. The proof-of-principle for the instrument is being demonstrated through 1) simulation of observational capabilities for the instrument through spectra acquisition from samples of interest to geologists and exobiologists, 2) characterization of the effect of thin membranes on the properties of the excitation beam, and 3) assembly and characterization of a membrane-encapsulated prototype instrument. The observational capabilities for the instrument are simulated through acquisition of x-ray and luminescence spectra using the Scanning Electron Microscope (SEM), Cathodo-Luminescence (CL) spectrometer, and an environmental chamber that was constructed in our laboratory to simulate the effect of Mars planetary atmosphere. The effect of the membrane is determined by comparing the spectra acquired from metal and mineral samples with and without the membrane intersecting the excitation beam, and from samples in the

laboratory ambient and in the environmental chamber. The comparison isolates the effect of membrane and atmosphere interactions, which will determine performance limits for AEXS *in situ* operation. A breadboard vacuum-encapsulated stand-alone instrument requiring no vacuum apparatus support is being assembled in our laboratory.

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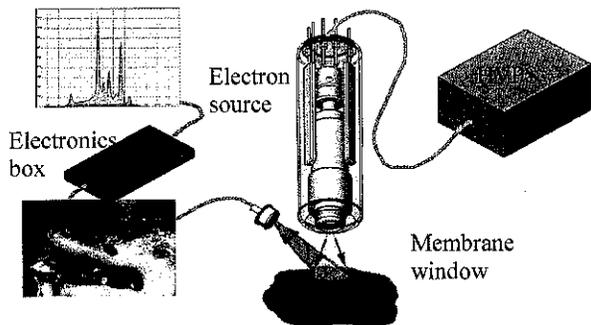
## 1. INTRODUCTION

This paper extends the work reported at the IEEE Aerospace conference in 2001 and 2003 where the concept and progress in the development of the so called Atmospheric Electron X-ray Spectrometer (AEXS) has been described.<sup>[1,2]</sup> The AEXS is a novel miniature instrument concept enabling rapid elemental analysis of samples on planetary surfaces *in situ* by energy dispersive analysis of x-ray fluorescence (XRF) spectra excited by a focused electron beam.<sup>[3-6]</sup> The viability of a vacuum-isolation membrane for the AEXS instrument has been demonstrated under the NASA's '98 PIDDP funding,<sup>[7]</sup> the investigation of the ability of the electron beam to excite and analyze both X-ray and electron-induced luminescence (Cathodo-Luminescence, CL) spectra has been funded by NASA's '02 ASTID program.<sup>[8]</sup> The development

<sup>1</sup> 0-7803-7651-X/03/\$17.00 © 2005 IEEE

<sup>2</sup> IEEE AC paper #493, Updated September 15, 2004

of a stand-alone, vacuum-isolated instrument accommodated on a rover has been funded by NASA's '04 MIDP program. [8] In this paper, we describe our progress in the development of the AEXS instrument, both hardware and analysis of the acquired data.



**Fig. 1.** The AEXS instrument concept. The AEXS consists of a miniature, vacuum-encapsulated electron source, a high-voltage power supply, and XRF detector. The high energy (>15 keV) electron beam is transmitted through an electron-transmissive vacuum-isolation membrane into the ambient atmosphere to strike the sample, exciting characteristic XRF spectra for elemental analysis of the irradiated spot. The spot area can be adjusted from sub-millimeter to several centimeter size by changing the membrane-sample working distance. In the flight prototype AEXS, the electron source and XRF detector will be integrated in a miniature instrument head. The head will be incorporated onto the rover arm, and the miniature power source and electronics placed inside the rover's warm box.

The enabling component for *in situ* operation of the AEXS is a thin electron-transmissive membrane that isolates the vacuum within the electron source from ambient atmosphere. The impinging electrons on external samples excite luminescence spectra that are analyzed to determine surface elemental composition, or in the case of CL, to identify unusual formations on surface that cathodoluminescence. The use of electron beam enables a new approach for *in situ* XRF measurements. In the past, XRF instruments have proved to be invaluable for determining the elemental makeup of the surface of a planetary body. To date, all *in situ* missions, including Surveyor, Viking 1, Viking 2, Mars Pathfinder, Mars Exploration Rovers (MER), and the Soviet Venera/Vega missions have carried some form of XRF instrument. These instruments have used radioactive sources to provide alpha particles<sup>[10]</sup> and x-rays for XRF excitation in planetary atmosphere, electron excitation was considered only within the context of a miniature Scanning Electron Microscopy (SEM) that would have required preparing and placing planetary samples into the SEM's vacuum.

Electron beam excited energy dispersive X-ray analysis is a widely accepted technique for determining the elemental surface composition, however it has not been previously used in ambient atmosphere due to the difficulty of generating and transmitting electron beams through the

atmosphere. Electron excitation using AEXS is similar to that used in SEM, with one significant advantage: Unlike in SEM, the membrane-encapsulation of the source vacuum obviates the need for sample to be drawn into the vacuum of the electron column. The electron probe requires no external pumping or sample manipulation. The spectra can be acquired from samples in their pristine state, since the electron-ionization of Martian atmosphere ensures a return current path<sup>[11]</sup> so that nonconductive samples do not need to be coated with conductive material to prevent charging effects.

The AEXS development has involved three parallel paths of the investigation: 1) Characterization of the effect of thin membranes on the properties of the excitation beam, 2) Assembly and characterization of a prototype electron source, and 3) Observation of samples of interest to planetary geologists and biologists using electron-induced excitation of XRF and other luminescent spectra in the SEM, Environmental Scanning Electron Microscope (ESEM), and CL spectrometer.

## 2. INSTRUMENT CONCEPT

Figure 1 shows the AEXS instrument concept. The AEXS consists of a high-energy (>10keV) electron gun encapsulated by an electron transmissive, vacuum-isolating membrane, an EDX detection and analyzer system, an optional CL detection system, and a high voltage power supply. The electron gun consists of an electron emitter and an electron optics that accelerates and focuses the electrons on the encapsulating membrane. The results of the simulation of the excitation process including the effect of electron interaction with the membrane and outside (Mars) atmosphere suggest that a 10  $\mu$ A beam transmitted through the membrane will resolve the electron-excited XRF spectra in less than 1 minute. Shown in the insets in Figure 1 are examples of information typical for the observational techniques facilitated by the instrument. In the upper left corner is an EDX spectrum that has been collected in our laboratory using a 10 keV proof-of-principle set-up. In the lower right corner is shown a CL image obtained for a tufa (calcium carbonate) sample colonized with a bacterial community. The image was obtained in a commercial CL spectrometer at George Washington University (GWU).<sup>[12]</sup> Differences in the color in the image have arisen from differing mineralogy in the sample. The correlation of the CL and EDX spectra facilitate obtaining characteristic signatures for samples of interest to exobiologists.

The most significant concern associated with using the encapsulation membrane is that it degrades the spatial resolution and energy coherence of the electron beam. Although the spatial resolution of the AEXS will never be as good as the nm-sized spots of laboratory scale SEMs, it is still significantly better than any of the state-of-the-art *in situ* XRF instruments. Whereas the spatial resolution for the Alpha-Particle X-ray Spectrometer (APXS) on Mars Exploration Rover (MER) mission is on the order of several

cm, the surface area irradiated by the AEXS beam can be varied from several cm to less than 1 mm by varying the “working” distance between the instrument membrane and target. In fact, the spatial dispersion for the electron beam enables two different modes, a large spot-size (cm-scale) “survey”, and a high-resolution (sub-mm scale) observation. The focusing properties of the electron beam are controlled by electron optics within the electron source. The electrons that are transmitted through the membrane interact with both the membrane and outside atmosphere leading to beam divergence that depends on membrane composition and thickness, atmosphere pressure, and electron energy. This beam spreading can in turn be used to vary the size of the irradiated spot on the sample by simply varying the distance between the membrane and the sample. By positioning the instrument head between several millimeters to several centimeters away from the target, the spot size can be varied from several hundreds of microns to several centimeters in the Mars atmosphere.<sup>[13]</sup> Using a relatively large working distance (10 cm-scale on Mars) the size of the irradiated spot can be cm-scale, making it possible to use the AEXS instrument for *surface reconnaissance*. When an area appears interesting, the instrument head could be brought close to the surface for a more detailed inspection and surface maps acquired during instrument head stepping. *Rapid spectrum acquisition* is needed to use the high-resolution capability for the electron beam. Rapid acquisition is enabled due to the combination of a large flux and high excitation efficiency using an electron beam. Electron-induced excitation is a one-step process, leading to spectra acquisition times less than 1 minute for a 10 $\mu$ A beam (as compared to about 1 hours for APXS). Such short times will also result in *low energy consumption* per

spectrum and thus enable multiple readings assessing sample heterogeneity.

The penetration depth for the electrons into subsurface is on the order of several micrometers. *Short penetration depth* ( $\mu$ m-scale) will allow surface coatings and weathering rinds on rocks to be studied with minimal mixing effects from deeper material. Measurements of unaltered surfaces will require prompt sampling of freshly cored or broken rocks, activities that are planned in several future Mars sampling missions.

The main attributes of the AEXS include:

- *In situ* characterization of samples with no sample preparation and no-contact operation with no vacuum pump support, enabled by the use of a thin, microfabricated electron-transmissive membrane for vacuum-isolation of the electron source.
- *Rapid spectrum acquisition* achieved by high conversion efficiency from the electrons to XRF radiation. The short acquisition times (< 1 min) result in corresponding low energy consumption (<100 J predicted per spectrum).
- Variable spatial resolution ( $mm^2$ – $cm^2$  scale for the irradiated spot on Mars surface), enabled by electron focusing optics and by changing (from about one millimeter to several cm) the working distance.
- An *observational strategy* consisting of rapid screening of mineral surfaces at several spatial scales to locate areas for detailed time and power consuming analysis techniques, enabled by rapid spectra acquisition.

A comparison of the AEXS with the APXS and an X-ray excitation based XRF instrument, is shown in Table 1.

**Table 1.** Comparison of salient features of portable x-ray instruments of interest to planetary scientists. While the AEXS is comparable in mass (approximately 1 kg, not shown in the table) with the other instruments, it offers two potential advantages: short spectrum acquisition time and improved spatial resolution. A consequence of the short spectrum acquisition time is that the energy expended by the instrument per acquired spectrum is less than for the other techniques.

Property	Electron-induced excitation	XRF/XRD (proposed)	APXS (flight) <sup>[14]</sup>
Excitation particles	Electrons	x-ray photons	$\alpha$ -particles
Particle rate	$6 \times 10^{13}$ /s (10 $\mu$ A)	Primary current: 0.3mA; X-ray photons: $2 \times 10^{12}$ /s	$2 \times 10^9$ /s (50mCi)
Power	5 W (peak)	13 W	0.34 W
X-ray photons/second	$> 2 \times 10^4$	$10^2$ to $10^3$	$\sim 1$
Spectrum acquisition time <sup>(2)</sup>	<b>&lt; 1 minute</b>	5 minutes	$\sim 1$ hour
Energy per acquired spectrum	<b>50 J</b>	5,000 J	1,000 J
Spatial resolution	Controlled: $mm^2$ – $cm^2$ by focusing and varying the working distance	$\sim 4 cm^2$ (at 2 cm working distance)	$\sim 20 cm^2$

### 3. BREADBOARD INSTRUMENT DEVELOPMENT

The approach to demonstrating a proof of concept of the AEXS has been through 1) Demonstrating viability of micro-fabricated membranes, and 2) assembling and

operating AEXS setups with increasingly integrated functional components and supporting equipment.

#### 3.1. Membrane Viability

The membrane properties were investigated in detail at the project beginning due to its critical role in the encapsulated instrument. A series of experiments determined that our designed membranes have high electron transmission, yet are capable of isolating high vacuum, are able to withstand differential pressure in excess of one atmosphere, survive vibrational shocks of a magnitude to be expected during a planetary mission. Typical membranes were 200 nm thick films of Silicon Nitride (SiN) grown using low pressure chemical vapor deposition under non-stoichiometric, silane rich conditions to produce a low tensile stress, pinhole free film on both sides of a 400  $\mu\text{m}$  thick silicon wafer. The membranes are microfabricated within a Si support frame. The window openings (1.5 mm x 1.5 mm) are defined by standard photolithography and reactive ion (RIE) and wet chemical etching. Figure 2 shows the membranes in the support frame. Using a vacuum chamber, we have successfully demonstrated vacuum sealing and robustness capability for the membranes. The electron transmissivity was demonstrated in SEM with the membrane intercepting the electron beam.

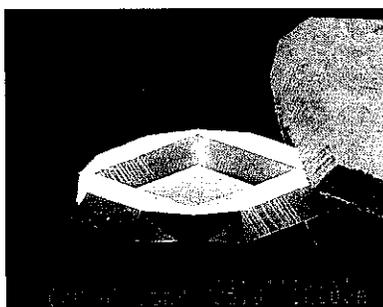


Fig. 2. SEM of a SiN membrane etched into a silicon frame.

The properties of the transmitted electrons through the membrane and atmosphere are modified due to electron interaction with the molecules of the traversed medium. To determine the effect of the transmission on the excited spectra, characterization studies were performed that consisted from 1) Electron beam

spreading modeling and measurements, and 2) Comparison of the excited x-ray spectra in vacuum without and with the intervening membrane. The effect of the transmission was simulated using a Monte Carlo code for transmission through multiple layers and measured in SEM. To gain a understanding of the membrane's electron transmission properties and its ability to vary the spatial resolution of the measurement by changing the working distance, we have performed experimental and theoretical studies with emphasis on determining 1) The fraction of the transmitted electrons, 2) beam spreading, and 3) loss of the electron energy.

Electrons suffer both elastic and inelastic collisions as they travel through a matter. Elastic collisions are essentially Rutherford scattering events and are responsible for beam divergence while inelastic collisions due to XRF generation decrease electron energy, leading to a loss of energy coherence. Monte Carlo simulations<sup>[13]</sup> were first performed using conventional formulas<sup>[15]</sup> for the interaction of high-energy charged particles with matter. These formulas were later modified based on low energy electron-beam

lithography results.<sup>[16]</sup> Fig. 3 shows the predicted spatial resolution (irradiated spot size) for electron transmission through a 200-nm-thick SiN membrane using both formulas. The spot sizes are shown as a function of the beam energy and the working distance and are compared with experimentally obtained values. Experimental measurements were conducted in two ways: 1) By moving a "knife-edge" across the transmitted beam and measuring the beam current impinging on a collector below, and 2) By acquiring XRF spectra from a moving Si wafer sample whose surface was half-covered with a Ti layer. Both experiments were performed in an SEM with the membrane inserted into the beam path, above the knife-edge or the Si-Ti wafer, with similar results obtained for both cases. Note that the experimental data are between the spot sizes predicted by the original and modified formulae. The validated model gives us confidence to data gives us confidence to predicts AEXS spatial resolution under Martian operating conditions. For example, at a working distance of 10 cm, the predicted spot size is on the order of 1 cm for 20kV electrons.

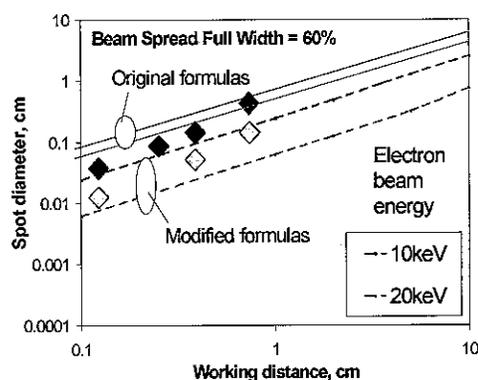


Fig. 3. Predicted spatial resolution using the original<sup>[21]</sup> and corrected<sup>[22]</sup> scattering formulas for a an electron beam transmitted through a 200 nm thick SiN membrane. The diamonds are experimentally obtained data in vacuum ( $\diamond = 20\text{keV}$ ,  $\blacklozenge = 10\text{keV}$ ). Note that the irradiated spot size increases nearly linearly with the working distance, and that the experimental values fall within the curves predicted using the original and corrected model.

To generate quantitative composition maps, a geologist will need to correlate the traversed distance with the number of the excitation particles. We have modeled the angular-energy distribution of the dispersed electrons for an original thin pencil beam. The particle energy peaks at the beam center, corresponding to least interaction with the membrane. Thus, should a smaller irradiated spot size become desirable, a magnetic lens can be designed to perform efficient post-membrane focusing.

To determine the membrane effect on the spectral count, we have collected x-rays without and with the intervening membrane for several targets. Figure 4 shows the spectra for feldspar in SEM. Note that the spectrum with the membrane present shows an increased peak at Si energy

line. Similar observations were made for other targets, suggesting that the increase in the Si counts is associated with the Si in the SiN membrane. The peak height will depend on mutual geometry of the membrane, target and detector; the peak count will be minimized when no x-rays with the membrane origin reach the detector entrance aperture.

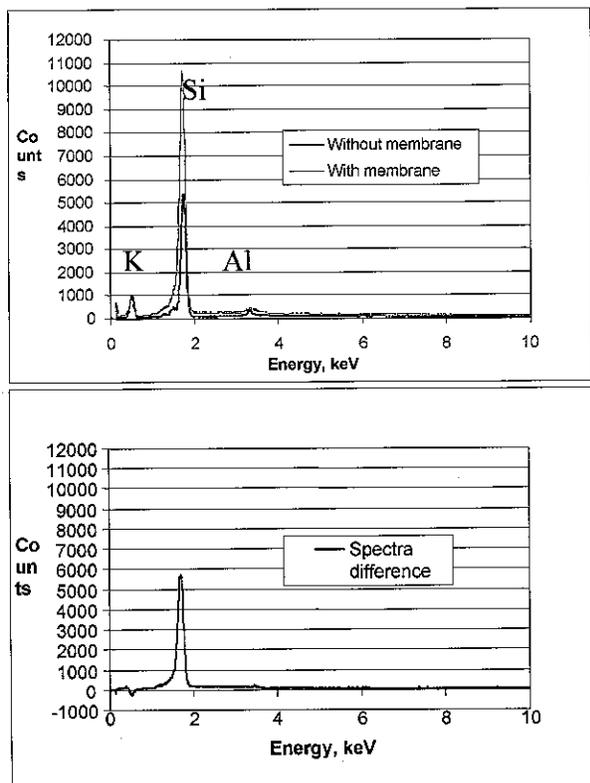


Figure 4. Feldspar spectra taken within SEM: (a) without/with the intercepting membrane (b) spectra difference.

### 3.2. Proof-of-principle experiments using a 10 keV electron source

The next step in the AEXS development consisted of assembling and operating a setup that consisted of a vacuum chamber (approximately  $10^{-6}$  Torr), a miniature 10 keV electron gun (manufactured by Loxel Imaging Systems Inc.) incorporated into it, and a SiN/Si window that was attached to a stainless steel flange (using Epotech type H20E silver epoxy) and integrated into the chamber window through which the electron beam was transmitted into the outside atmosphere. Using this initial setup, the robustness and vacuum sealing capability for SiN membranes has been demonstrated.<sup>[6]</sup>

Fig. 5 shows a setup that has been subsequently constructed as the next step towards the construction of a portable instrument. The setup consists of an encapsulated 10 keV gun, supported by a high vacuum pump, operating in the ambient atmosphere. To encapsulate the gun, the critical process consisted of hermetically joining dissimilar materials. The gun employs lead-glass (Type L-29)

envelope around its components as is common for many TV tubes or CRT's. The coefficient of thermal expansion (CTE) of Si is on the order of 3ppm whereas for the L-29 glass it is 80-90ppm, requiring a graded seal glass tubing to be inserted between the gun and the membrane. We manufactured a glass tubing transition region where approximately 10 thin rings of different glass types with progressively smaller CTEs are glass-blown together. The graded seal allowed us to transition from the L-29 glass to Pyrex whose CTE is near 3ppm. Pyrex has been also selected due to its ability to anodically bond to silicon. Fig. 5 shows the gun transition region joined to the Pyrex-T, and encapsulated with an anodically bonded Si chip. Anodic bonding processes are well established for making hermetic bonds between pyrex and silicon<sup>[17]</sup> since the Coefficients of Thermal Expansion, CTEs, are well matched at approximately 3

ppm. Anodic bonding requires complete flatness of both surfaces and no particles in the bonding area. In Fig. 5, the encapsulated gun is shown mounted to a vacuum processing station in order to process the tube and exhaust the residual gases from the vacuum envelope.

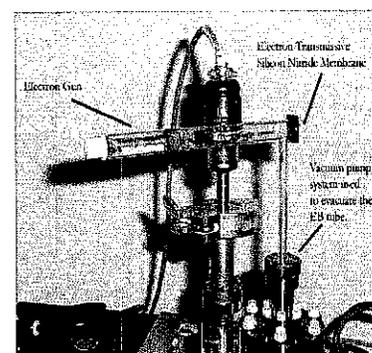


Fig. 5. The vacuum in the electron column in the encapsulated 10 keV gun is supported by a vacuum pump.

In the setup, the XRF spectra are acquired using a Si PIN diode detector Peltier cooled to 255K, a shaping amplifier, a multi channel analyzer (MCA) to count and sort the pulses into the proper energies, and a computer attached via RS-232 to acquire and analyze the data. The setup was used to acquire XRF spectra from metal and mineral samples in an Earth atmosphere ambient that were compared with XRF spectra obtained in a laboratory SEM using both the built-in, liquid nitrogen cooled, high resolution XRF detector as well as the Amptek XRF detector. The spectra comparison is shown in Fig. 6. The SEM spectra were acquired with and without the presence of an intervening membrane above the sample. The XRF yield depends on a number of factors, including the electron beam energy, beam current, chemistry and pressure of the outside atmosphere, and the relative positions and orientations of the electron source, the target and the detector. Qualitatively, for irradiated spot sizes of about 1 mm and XRF acquisition times of about 100 sec, there is excellent agreement between all the spectral sets shown. We found that we were able to detect trace elements with a relative abundance of a few percent within a matrix. Note that Figs. 6a and 6b exhibit X-ray transition lines at the same locations (as they should) in all cases. Line-width broadening is observed in Fig. 6b due to the poorer resolution of the Amptek detector, increased background due to the increased scattering of the electrons by the

intervening membrane and the outside (760 Torr) atmosphere. Si lines observed in the presence of the membrane are generated by electron interaction with the membrane and the membrane (Si) rim. The peaks are better resolved in the SEM due to the greater sensitivity of a liquid nitrogen (77K) cooled x-ray detector. For the Peltier cooling, the best obtainable x-ray peak width is approximately 250 eV.

The setup was also used to obtain spectra for several standard alloys and minerals, and JSC-1 sample. In our setup, the particular spectrum shown was obtained for a Mars composition simulated sample JSC-1. The x-ray detector was a silicon *p* type-intrinsic-*n* type (PIN) photodiode based system manufactured by Amptek Inc. and used on the Mars Pathfinder APXS<sup>[10]</sup> instrument. The elemental composition was determined by analyzing the excited XRF using the EDX analyzer system.

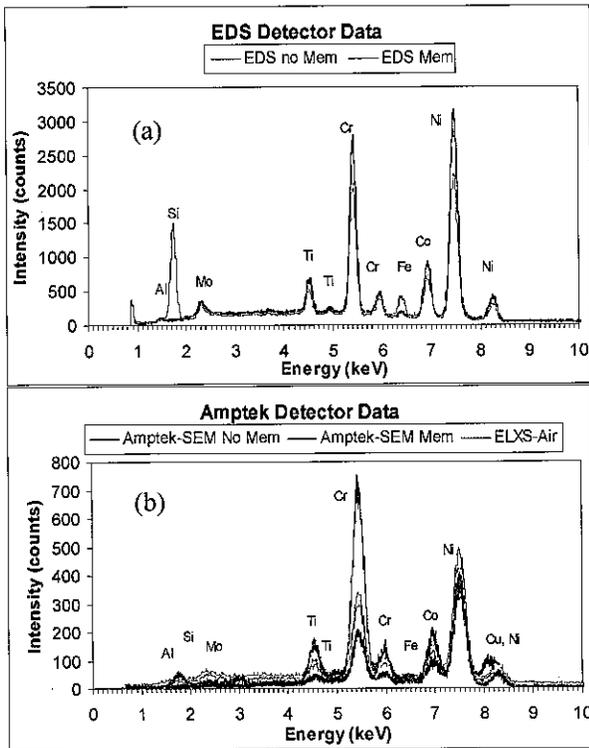


Fig. 6. X-ray spectra obtained from a Waspaloy (about 59%Cr, 19% Ni, 12% Co, 4% Mo, 3%Ti) standard. (a) in SEM without and with the intervening membrane using EDS detector, (b) in SEM and the AEXS setup (Fig 5) using the Amptek detector and 10 kV electron gun. All peaks occur at their correct locations, Si peaks occur due to electron-membrane window interaction, and lines in (b) are broadened due to the poorer resolution of the detector.

### 3.3. Development of a stand-alone 20 keV AEXS source

The electron gun that has been selected as our “baseline” for the development of a portable, stand-alone instrument without the support of a vacuum pump is a Thomas Electronics<sup>[18]</sup> electron gun (#70-1368-A) rated for operation

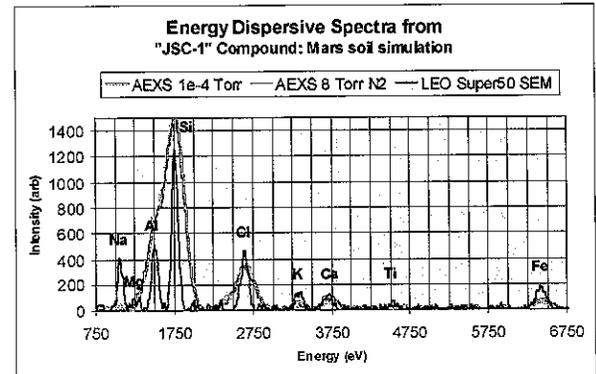
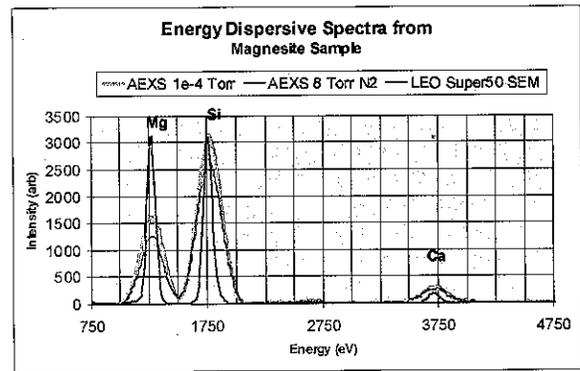


Figure 7. EDX spectra comparison taken for samples in SEM and in the AEXS environmental chamber using the encapsulated 10keV electron gun. (a) Magnetite, (b) JSC-1 sample.

at up to 20kV, and used in medical imaging systems. Similar to the 10 keV gun, the Thomas Electronics gun consists of a thermionic emitter and electrostatic optics assembled within an evacuated tube to focus and accelerate the electrons. The use of more energetic electrons results in reduced beam divergence (smaller spot size on the target), increased beam transmission, and the ability excite the higher energy, characteristic XRF from heavier elements. In

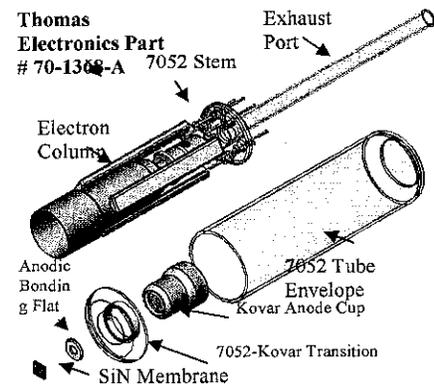


Fig. 8. Exploded view of the 20 keV gun. The mount is supplied on a 7052 boro-silicate glass stem containing an evacuation port, is vacuum sealed by (i) glass blowing a glass envelope, (ii) anodic bonding of the membrane-bearing Silicon chip to the Pyrex/Kovar exit aperture assembly, and (iii) laser-welding the assembly to the Kovar/7052 transition.

addition, the gun lends itself to a more robust vacuum-encapsulation process. In a departure from the 10 keV design, the membrane is used to seal a supporting "envelope" structure within which the electron gun is placed. The sealing for the 10keV gun was complicated by the fact that the large mismatch in CTE between the lead-glass envelope and Si required a CTE-graded glass transition region from L-29 glass to pyrex. For the 20keV gun, instead of resorting to CTE transition region, an "envelope" encapsulation approach is used. (Figure 8) The gun is procured mounted on a 7052 glass stem, a 7052 glass envelope is constructed for the stem/tube subassembly and subsequently joined to a commercially available 7052 glass to Kovar transition containing an evacuation port. In a separate process, the membrane chip is anodically bonded to a machined and polished Kovar disc (the inset in Figure 9). The encapsulation process is completed by making the final Kovar/Kovar bond using laser welding. Following encapsulation assembly, the electron source is evacuated, vacuum processed (bake out and vacuum cleaning) and the evacuation port "pinched-off" by flame sealing the exhaust tubing at the Pyrex T, and the active getters are flashed and activated to create the stand-alone vacuum encapsulated electron source (Figure 9).

Another advantage of using 20 keV electrons is that the membrane thickness can be increased, resulting in a more robust electron source. In addition, we have been successful in applying a novel, JPL-pioneered micro-fabrication process to define circular opening for the thin membrane in the Si-frame. It has been our experience that stress in the membrane tends to concentrate in corner regions of rectangular openings, degrading reproducibility of the bonding results of the anodic process and membrane robustness. The combination of increased membrane thickness and circular opening has resulted in membrane-windows with greatly increased robustness. A "circular opening" membrane is shown in Figure 8, and an encapsulated gun in Figure 9.

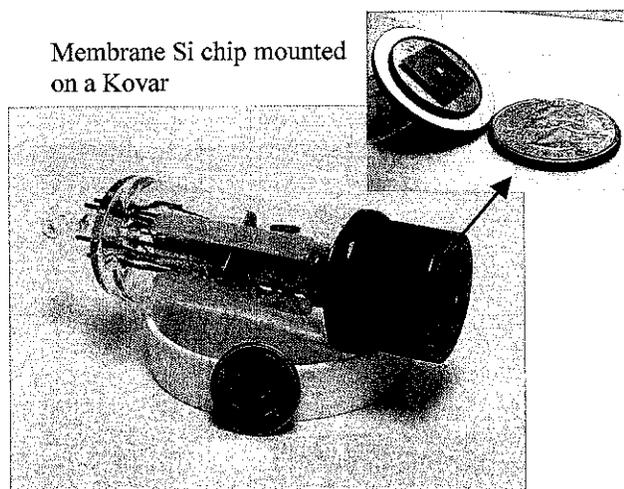


Figure 9. Vacuum-Isolated Thomas Electronics 20keV Electron gun

The spectral fidelity depends strongly on mutual position of the detector, target and the gun. To isolate the effect of the membrane presence from that of the atmosphere on the spectra, an environmental chamber to house the 20 keV encapsulated gun and samples within a controlled atmosphere has been assembled. The chamber (Figure 10) has the ability to control the pressure and atmospheric content of the sample atmosphere. It is capable of holding high vacuum levels ( $2 \times 10^{-6}$  Torr) or regulating to a set pressure (simulating Martian atmosphere) The results of our modeling effort indicate that the spectra will be affected by the 7 Torr much less than by the Earth atmosphere.

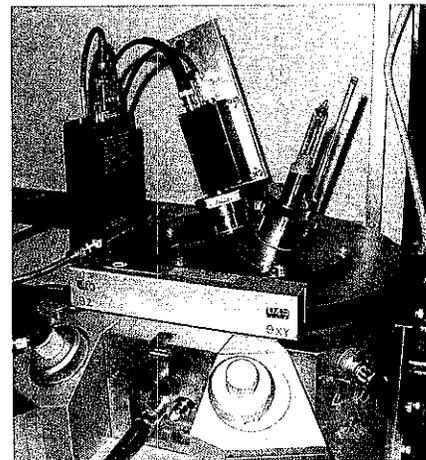


Figure 10. Environmental Chamber integrated with the Electron gun and Amptek detector.

#### 4. CORRELATION OF EDX AND CL SPECTRA

Parallel to the electron gun development, SEM and CL measurements were performed on samples of biogenic origin to determine the ability of electron-induced excitation measurements to determine regions on samples that were modified by biogenic activities.

Figure 11 is a photo of a silica mineral sample from Mojave, California, National Reserve.<sup>[19]</sup> The sample is characterized by three distinct regions, an unaltered rock (white region), an area stained with iron oxide (red area), and an area affected by biological activity (green area). Figures 12, 13 and 14 summarize the results of SEM and CL measurements in the various regions. The figures show SEM and CL images, EDX spectra, the results of quantitative elemental composition analysis, and CL spectra. Figure 12 shows the above in the white (unaltered host rock) region, Figure 13 in the red (iron oxide stained) region, and Fig. 13 in the green (biologically altered) region. The data were collected in the LEO SEM in the Reliability group at JPL with the field emission electron gun, 20keV

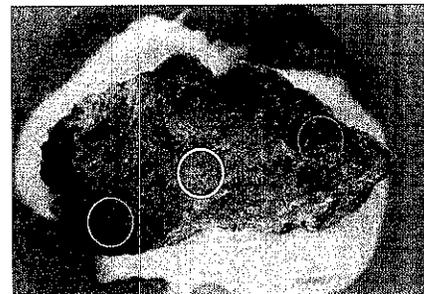


Fig. 11. Silica sample from Mojave National Reserve

acceleration voltage, 25 degree takeoff angle, 100 sec spectra acquisition time, using a backscattered electron detector for the SEM image, EDS dispersive X-ray spectrometer for the XRF spectra, and CL spectrometer for CL images and spectra. In Figures 12-14, the differences in the elemental abundance and CL spectra in the various regions are clearly seen.

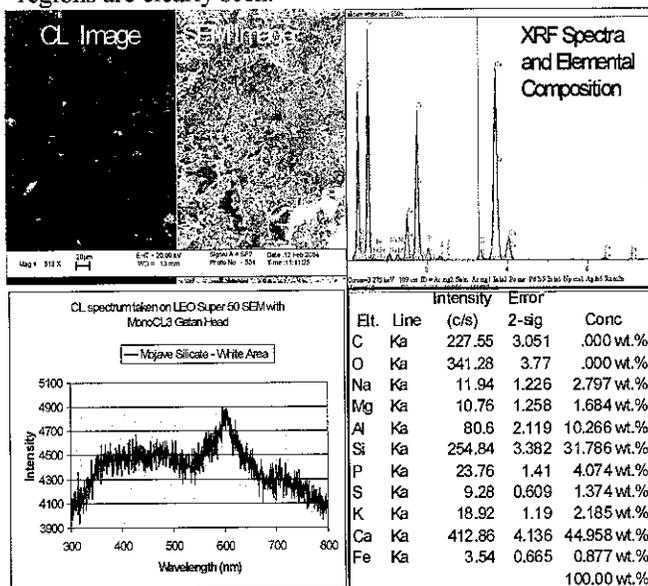


Figure 12. Mojave Silica sample, white (unaltered rock) area: CL and SEM images, XRF spectrum and the results of the elemental analysis, and CL spectrum.

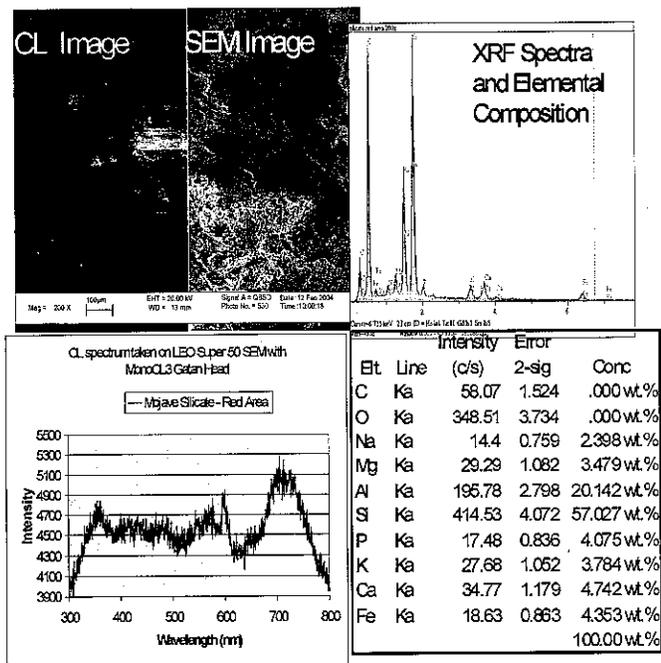


Figure 13. Mojave Silica sample, red (stained with iron oxide) area: CL and SEM images, XRF spectrum and the results of the elemental analysis, and CL spectrum.

The examination of the sample in Fig 11 showed that the presence of the microbial community within the host rock was accompanied by changes in texture and appearance. In non-colonized regions, the crystal shape of the constituent mineral grains was generally more smooth than in the regions that were colonized by microorganisms, where the mineral grains looked "corroded" with numerous pits, crumbled surfaces, and jagged, indistinct edges. The green region also enclosed small mineral precipitates, presumably formed as a result of microbial activity; either indirect physicochemical weathering due to microbe-induced chemical changes in the microenvironment and/or nascent precipitates formed biogenically.

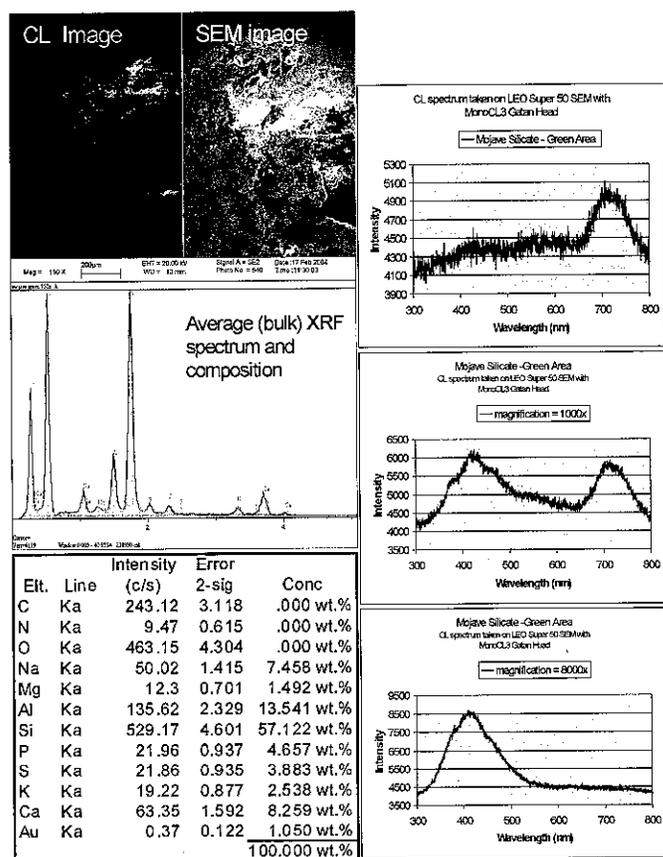


Figure 14. Mojave Silica sample, green (microorganism-containing) region: CL and SEM images, XRF spectrum and the results of the elemental analysis, and CL spectra from three different bright spots on the sample surface. The variation of the CL spectrum across the green area is in correspondence with the area textural variability.

The textural differences were accompanied by differences in elemental composition and CL spectra. The SEM-EDS analyses showed that there were significant differences in elemental composition between the microfossil-containing region and host rock, both in terms of different bulk-averaged composition over the individual areas, and large variability in the spatial distribution of the elemental

composition and CL spectra when acquired at high magnification from small spots at several different locations in the microorganism-containing region. In general, the regions colonized by microorganisms had a different suite of elements than the host rock, and exhibited more significant variations than the host rock. The EDS results in Figures 12 and 13 are presented in counts/sec (line intensity) and in element concentration in the matrix (weight %). Thus it represents a percentage, in terms of the number of atoms present for all the elements measured. Note that the red area exhibited elevated levels of Al and Fe, as expected, and the green area exhibited a significantly elevated level of Na, while the unaltered background host region simply contained Si, Al and Ca. In Figure 13, the EDS results shown refer to a representative bulk (ie. averaged over a relatively large area) composition (as elemental composition of smaller spots exhibited significant variations). The differences in the elemental composition were, in general, accompanied by differences in the CL spectra. Figure 13 shows CL spectra obtained at three different locations in the green area. The locations were selected as the locations at which the CL image exhibited bright spots (the CL image of the green area is seen to the left of the SEM image in Figure 13). The fact that the CL spectra exhibit large variations within the microfossil-containing region, is consistent with heterogeneous segregation of elements and morphologic structures.

It should be noted that the green area was unmistakably microbial. Therefore we are confident that our results show real differences between the mineral and microorganism-containing regions on the sample. No beam damage was seen to occur to the specimen, which would indicate that the beam might be penetrating through or destroying the sample.

## 5. CONCLUSIONS

In summary we have embarked on an effort to develop an electron-based instrument for observation of planetary surfaces in situ. In situ observation in planetary atmospheres is enabled through using a thin electron-transmissive membrane for vacuum-isolation of the electron source. The electrons accelerated in the electron column to 10keV-20keV, are focused and transmitted through the membrane on samples in ambient atmosphere where they excite characteristic XRF and other (eg., CL) luminescence from the irradiated spots. The proof-of-principle experiments performed in our laboratory to date include 1) simulation of measurements in SEM to determine the spatial resolution and performance limits for the proposed instrument, 2) acquisition of spatially resolved XRF spectra of samples in air by using a breadboard setup, and 3) verification of the utility of correlated EDS and CL measurements for characterization of samples of interest to planetary geologists and exobiologists using standard laboratory equipment. In addition, as the next step towards the construction of a portable electron source, we are

proceeding to encapsulate a commercially available electron gun and evacuate it using our laboratory station to fabricate a standalone 20 keV electron probe requiring no external vacuum support.

Using a 10 keV electron beam and a 2 mm working distance in one atmosphere, we have obtained x-ray spectra from pure metal and JSC-1 samples using 10 keV beam, with the analysis time as short as 100 seconds. We have determined that the irradiated spot size by the transmitted electrons through the SiN membrane is on the order of several hundreds micrometers to several millimeters, depending on the electron beam energy and the working distance between the membrane and target. In Mars atmosphere (approximately 7 Torr) a 20 keV beam has been predicted<sup>3</sup> to resolve areas as small as 100  $\mu\text{m}$  at 2 mm working distances, thus offering the potential for a compact instrument for performing rapid in-situ surface analysis at medium spatial resolution. Additionally, examination of CL images and spectra shows that a correlation with XRF spectra exists, suggesting that by collecting both spectra, an additional insight into the nature of interesting formations on target surfaces could be obtained.

At the present time, CL images and EDS and CL spectra are being collected from other samples using the 20 kV source. We expect this new analysis tool to find its place among other ambient pressure surface analysis systems. The potential for miniaturization and the spatial resolution of the encapsulated electron beam-based instrument fills the gap between non-portable, high resolution laboratory instruments and portable, low resolution in situ instruments such as the APXS used in the 1997 Mars Pathfinder mission.

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