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APPLICATIONS OF THE ENVIRONMENTAL SCANNING ELECTRON MICROSCOPE TO CONSERVATION SCIENCE

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Abstract

The environmental scanning electron microscope (E-SEM) provides electron imaging at relatively high sample pressure, with imaging and analysis capabilities comparable to those of traditional high vacuum SEM. Several case studies demonstrate the advantages and research potential of this new technology as applied to conservation science: 1) dynamic study of wetting and drying of consolidated and unconsolidated adobe samples; 2) semi-dynamic study of lead corrosion as a result of exposure to formaldehyde; 3) electron imaging of outgassing samples—parchment; 4) study of uncoated, non-conductive samples—swabs from Sistine Chapel cleaning; 5) X-ray analysis of uncoated insulators—gold and garnet jewelry. The environmental scanning electron microscope offers unique capabilities for dynamic experiments, imaging of outgassing samples and insulators, which may be applied to the study of deterioration mechanisms, material treatments, and ancient materials and technologies.

Key Words: Environmental Scanning Electron Microscope, Conservation Science, Dynamic Experiments, Dead Sea Scrolls, Adobe, Formaldehyde, Lead.

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Introduction

Conservation science is a multidisciplinary field, applying information from chemistry, material science, archaeology, art history and other areas to such problems as material degradation mechanisms, the testing of new preservation techniques and the study of ancient materials and technologies. This paper explores the application of a new technological development in scanning electron microscopy to conservation science. Scanning electron microscopy (SEM) has found a broad range of applications in the conservation field. Past examples of SEM studies in conservation include the analysis of pigments in paintings [6, 11], the examination of marble deterioration due to air pollution [7], and the analysis of ancient metal statues [13]. Some advantages cited most often when SEM is compared with light microscopy are: 1) high resolution, 2) exceptional depth of focus, and 3) compatibility with X-ray analytical methods [8]. However, it was clear from the beginning of SEM applications in different fields of science and technology that there are serious trade-offs for such superb performance.

The SEM is a high vacuum instrument, and samples intended for SEM studies must be stable at very low pressures. This requirement immediately excludes all wet, moist, or outgassing materials from being imaged untreated [8]. Additionally, high quality electron micrographs are generally attainable only from conductive or conductor-coated samples; otherwise, local surface charging would cause image distortion [10]. Sample preparation techniques such as drying, freezing, fracturing and surface coating were developed to meet the sample requirements of SEM [12]. Decreasing the energy of an electron beam is used in modern SEM instruments to study uncoated, non-conductive materials, because less charge buildup occurs at these low energies. However, a lower energy electron beam diminishes spatial resolution and significantly restricts X-ray spectrometry when chemical analysis is needed [8].

Several attempts have been made to increase, at least in a localized space, water or vapor pressure around

the sample to permit study of phenomena or features on the sample's surface which would be destroyed or perturbed by sample preparation procedures [14, 5]. These efforts were only partly successful because of low resolution and imaging limited to backscattered electrons. However, the principles necessary for the development of a higher resolution and more capable instrument were developed and refined over the past decade [2, 3, 4].

The possible range of SEM applications changed significantly with the commercial introduction of the Environmental Scanning Electron Microscope [Model ESEM-20, ElectroScan Corp., Wilmington, MA; 2]. A comparison of the E-SEM with conventional SEM operating conditions and performance illustrates some of the advantages of the E-SEM (Table 1). The electron beam column of the E-SEM requires a high vacuum, but the pressure in the sample chamber can be increased beyond 900 Pa (atmospheric pressure is ~101,300 Pa). At these pressures, wet samples remain hydrated during examination, and most liquids may be observed. The E-SEM maintains the pressure gradient from the sample chamber (200 Pa) to the electron gun compartment

(10^{-5} Pa) by dividing the electron column into a series of compartments with pressure-limiting apertures. Each aperture-limited chamber is pumped separately in order to maintain the vacuum differential (Figure 1).

Other changes in the design of the classic SEM instrument were required by the increase in working pressure. A higher brightness lanthanum hexaboride electron source is used to reduce the effects of beam scattering and to increase resolution to 5 nm. The Everhart-Thornley (ET) detector used for secondary electron imaging cannot be used in the E-SEM because of unwanted gas ionization from the high voltage bias on the detector. Instead of the Everhart-Thornley detector, the E-SEM uses a special gaseous detector called the Environmental Secondary Detector (ESD). This detector uses well-known gas ionization phenomena to detect signal electrons. Collisions between secondary electrons and neutral molecules result in a collision cascade, producing more electrons, which multiplies the secondary electron signal. In addition, the slow-moving positive ions which are formed in the collision process effectively neutralize surface charging on the sample. Therefore, a sample in the E-SEM does not need a

Table 1. Operating Conditions and Performance – Comparison of SEM and E-SEM

Operating conditions	Conventional SEM	Environmental SEM
Imaging modes:	Secondary Electrons (ET) Backscattered Electrons	Secondary Electrons (ESD) Backscattered Electrons
Working Distance:	6-40 mm	6-15 mm, resolution limited by beam scattering in gas
Accelerating voltage:	1-30 kV, normally 20 kV	1-30 kV, normally 20 kV
Vacuum Conditions:	10^{-5} to 10^{-3} Pa High vacuum	10^{-4} to 0.9 kPa Normally 10-250 Pa. Atmospheric pressure is 100 kPa. The imaging gas is usually water vapor, but air, helium, oxygen and nitrogen can also be used.
Magnification:	10 to 100,000 times	70 to 100,000 times
Resolution:	1.8 to 6.0 nm, usually 4.5 nm	7 or 5 nm
Sample Requirement:	Compatible with high vacuum Dry and conductive samples only	Any sample type (including liquids, solids, powders, and insulators) plus dynamic reactions.
Sample exchange time:	3-5 minutes	30-60 seconds
Approximate Cost:	\$65,000-250,000*	\$179,000-250,000*

*Depending on resolution and configuration

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conductive coating [2, 4].

To maintain the innate high resolution of an SEM, the ESD is coaxially mounted within the final lens in such a way that the distance between sample and lens can be kept as short as possible. This minimizes scattering of the electron beam by gas molecules in the sample chamber. Another advantage of the ESD is that it is insensitive to light. This lack of sensitivity allows study of red-hot or otherwise light-emitting samples which is not possible using a conventional SEM with an Everhart-Thornley detector. Laser or UV illumination may also be used while imaging.

Results and Discussion

Several experiments described below were designed to test the applicability of the E-SEM to problems in conservation science. All of the images were taken on an ElectroScan ESEM-20 electron microscope using a 15-25 keV electron beam, water vapor as the sample chamber gas, the ESD or rarely, the backscattered electron detector (BSE), as noted in the figures. Electron images were observed at TV scanning rates and recorded on a VCR. The dynamic sequences were photographed from a TV monitor displaying the videotape recording. Because of the limitations of the VHS medium, such photographs suffer a significant loss of resolution. Most of the micrographs shown here were recorded directly using the integrated Polaroid camera.

Dynamic Studies—Adobe wetting and drying

Consolidation of adobe structures is a very important problem in cultural heritage conservation. A number of important structures and monuments around the world, such as the California Missions and the Ramesseum in Egypt (Ramses I granary buildings) are built from adobe—a mixture of sand, clay, silt and often organic material shaped into bricks and dried in the sun. Adobe and structures built from it may deteriorate much more rapidly than other building materials [1]. They may endure for centuries, however, if properly maintained.

To study the capability of the E-SEM for dynamic experiments with wet samples, polymer-treated and untreated adobe samples were exposed to a wet-dry cycle *in situ* in the environmental microscope. The purpose of the E-SEM experiment was to study how the polymer treatment affects the wettability, water adsorption and swelling characteristics of the adobe. The samples were small chips of adobe from Fort Selden, New Mexico, where the Getty Conservation Institute has a testing station and an ongoing project in adobe consolidation in association with the State Museum of New Mexico. The samples were placed in a small cup on the temperature controlled stage of the microscope. With 100 Pa of water vapor pressure in the sample chamber, the temperature was gradually lowered from 20 to 5 °C until condensation formed on the adobe surface. After the samples were fully wetted, the temperature was raised back to 20 °C to dry the sample. All phases of the

wetting-drying cycle were observed by electron microscope using the conditions previously described. Still micrographs for this experiment were photographed from the TV screen using a 35 mm camera (Figure 2a-j and Figure 3a-j).

The first noticeable change observed during the wetting cycle on the untreated adobe sample was the darkening of the clay due to the adsorption of water (Figure 2b). The next change was the gradual expansion of the clay matrix, which forced apart individual sand grains (Figure 2c). The arrows in Figures 2b and 2c show the swelling of the clay matrix is approximately ~5 μm . The fully wetted adobe sample appeared very dark and almost featureless (Figure 2f). This phenomenon is due to the fact that the water layer on the sample surface had low emissivity of secondary electrons. Small clay and silt particles were observed floating in the surface water layer when the sample was completely wet (Figure 2f). With an increase of the stage temperature, the sample slowly dried (Figure 2g). The excess water evaporated first from the surface extrusions and flat surfaces (Figure 2h). During the drying process a visible shrinkage of the clay matrix between the sand grains, similar in magnitude to the swelling during wetting, was

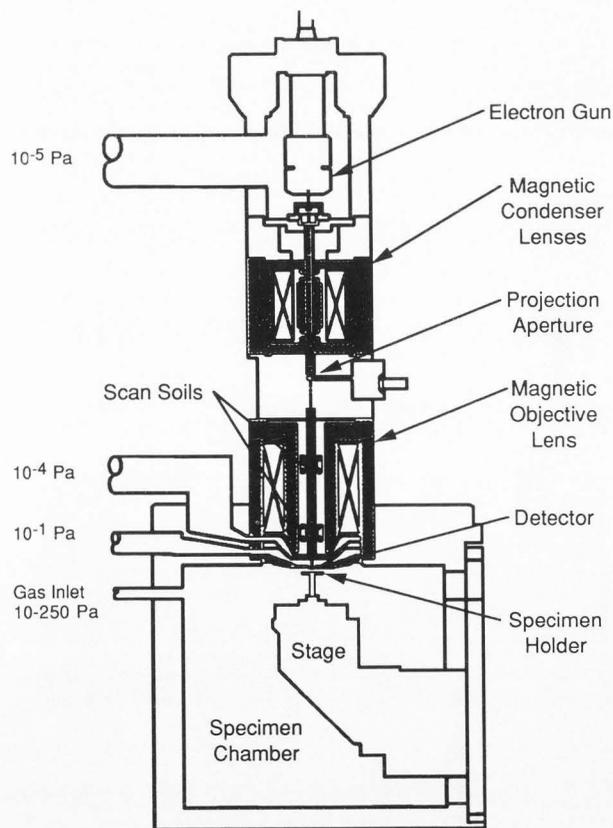


Figure 1. Environmental Scanning Electron Microscope

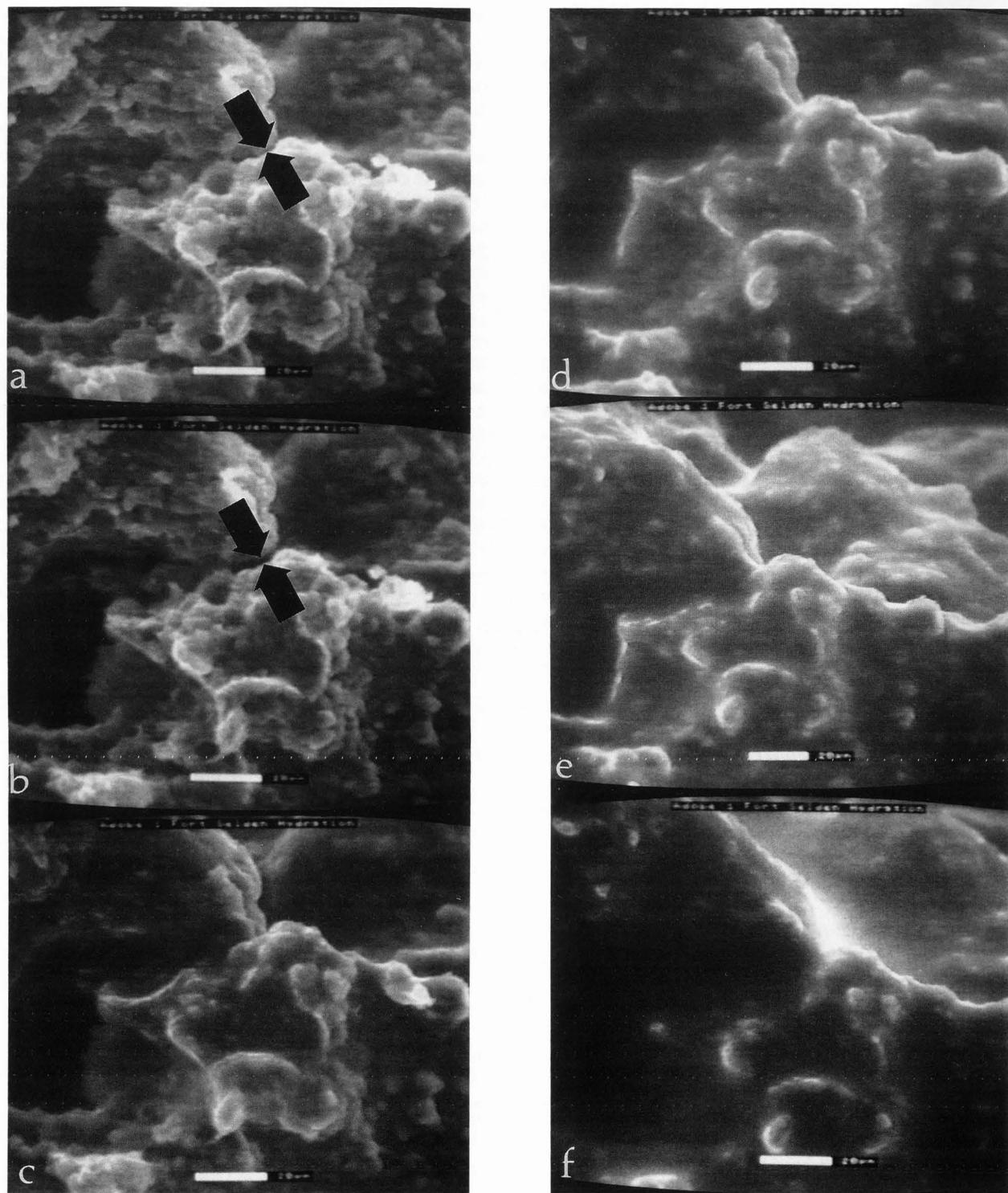


Figure 2a-f. Scanning electron micrographs from the environmental SEM illustrating the wetting (2a-f) of untreated Fort Selden adobe. Arrows in 2a and 2b indicate swelling of $\sim 5 \mu\text{m}$ due to moisture absorption. Note sample is covered with water in 2f. The white scale bar in each photo is $20 \mu\text{m}$.

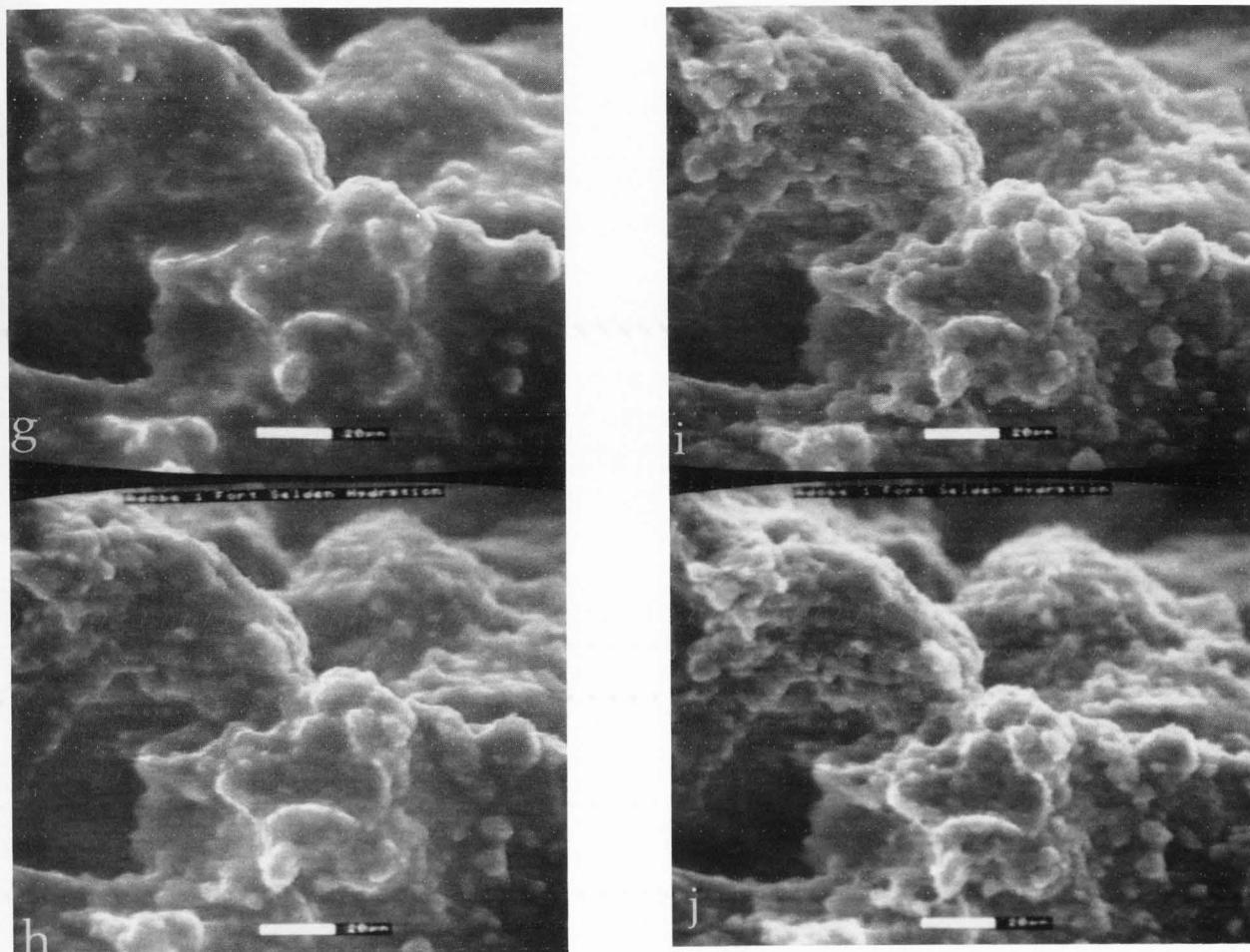


Figure 2g-j. Scanning electron micrographs from the environmental SEM illustrating the drying (2g-j) of untreated Fort Selden adobe. The white scale bar in each photo is 20 μm .

observed (Figure 2h-j).

The second adobe sample was treated by immersion in a solution of the isocyanurate trimer of hexamethylene diisocyanate (Mobay Corp. Desmodur N-3390) in a 1:1 methyl ethyl ketone/xylene solvent mixture. The polymer loading was 1 w/w%. This treatment has been shown to increase compressive strength, relative to untreated material, with minimal color change [1]. The polymer was seen in the micrographs adhering to quartz grains (Figure 3a). During the wetting procedure, the polymer-treated adobe sample did not darken evenly. Instead, localized water droplets were visible on the quartz particles (Figure 3b). No detectable swelling was observed during wetting of the polymer-treated sample, and no visible shrinking occurred during the drying sequence (Figure 3f-j). These results show that the polymer treatment apparently inhibits the adsorption of water on the clay surface. The mechanism for this effect is probably the occupation of adsorption sites by the polymer. The reduced

swelling of treated clay during the wetting and drying cycles is also a prerequisite for effective adobe consolidation.

Semi-dynamic studies – formaldehyde corrosion

Vapors of formaldehyde emitted from particle-board and other sources are known to result in the corrosion of lead objects in museum collections [9]. The E-SEM was used to study, semi-dynamically and without a conductive coating, the kinetics of corrosion products formation on a lead sample. A pure lead wire (5N, Alfa Products, Inc) was placed in a vial filled with formaldehyde vapors for 1, 5, 20, and 120 minutes. Corrosion product formation was monitored using the E-SEM (Figure 4a-f).

Exposure to formaldehyde vapors for one minute caused the formation of small anhedral crystals on the lead wire surface which were visible only at high magnification (2550x; Figure 4b). After 5 minutes of formaldehyde exposure, the wire surface was covered with small euhedral crystals 0.5 to 3 μm in size (Figure

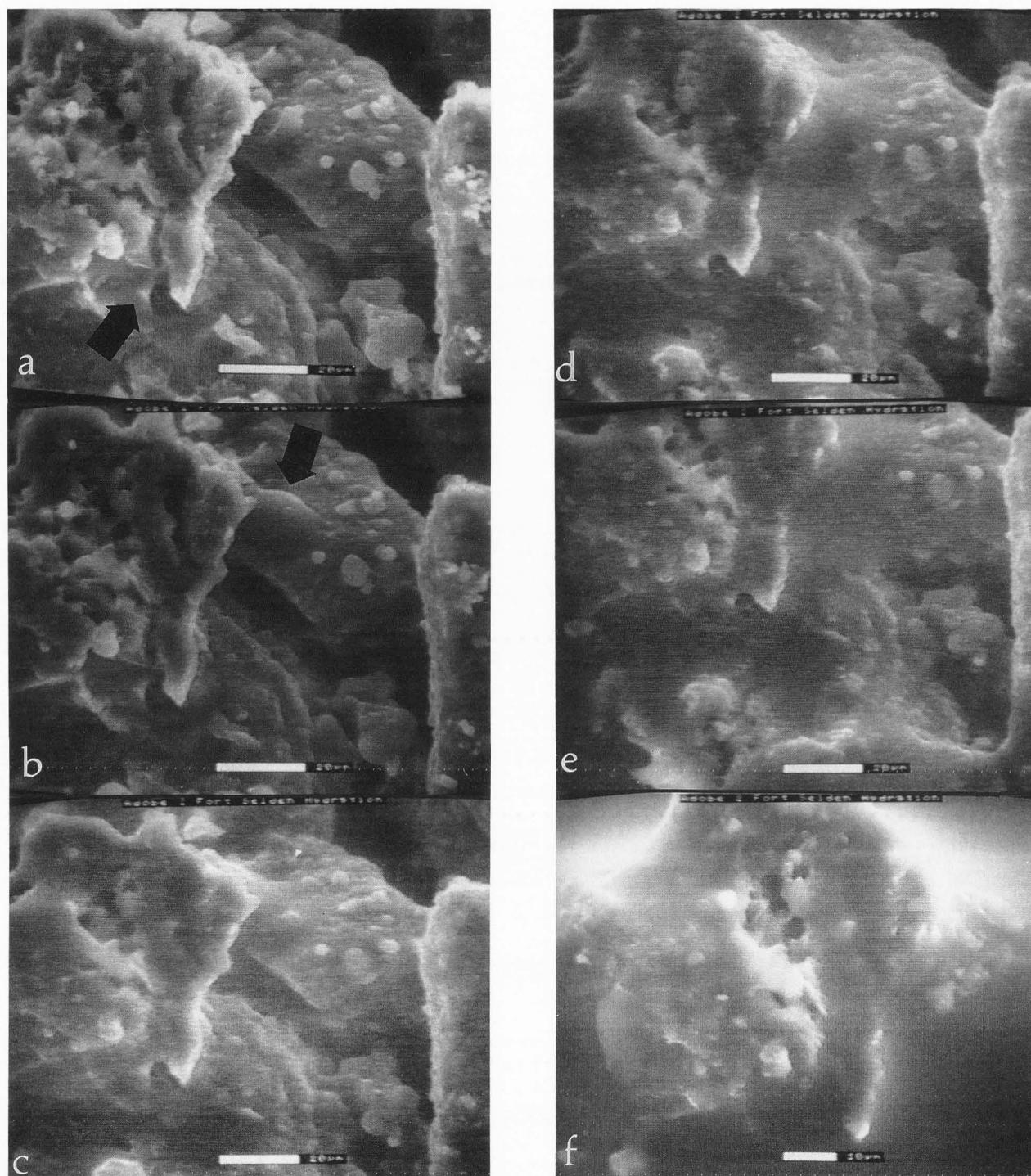


Figure 3a-f. Scanning electron micrographs illustrating the wetting (3a-f) of Fort Selden adobe treated with diisocyanate. Arrow in 3a indicates polymer adhering to quartz grain. Arrow in 3b indicates water droplet on quartz surface. The white scale bar in 3f-3i is 10 μm and 20 μm in 3a-e and 3j.

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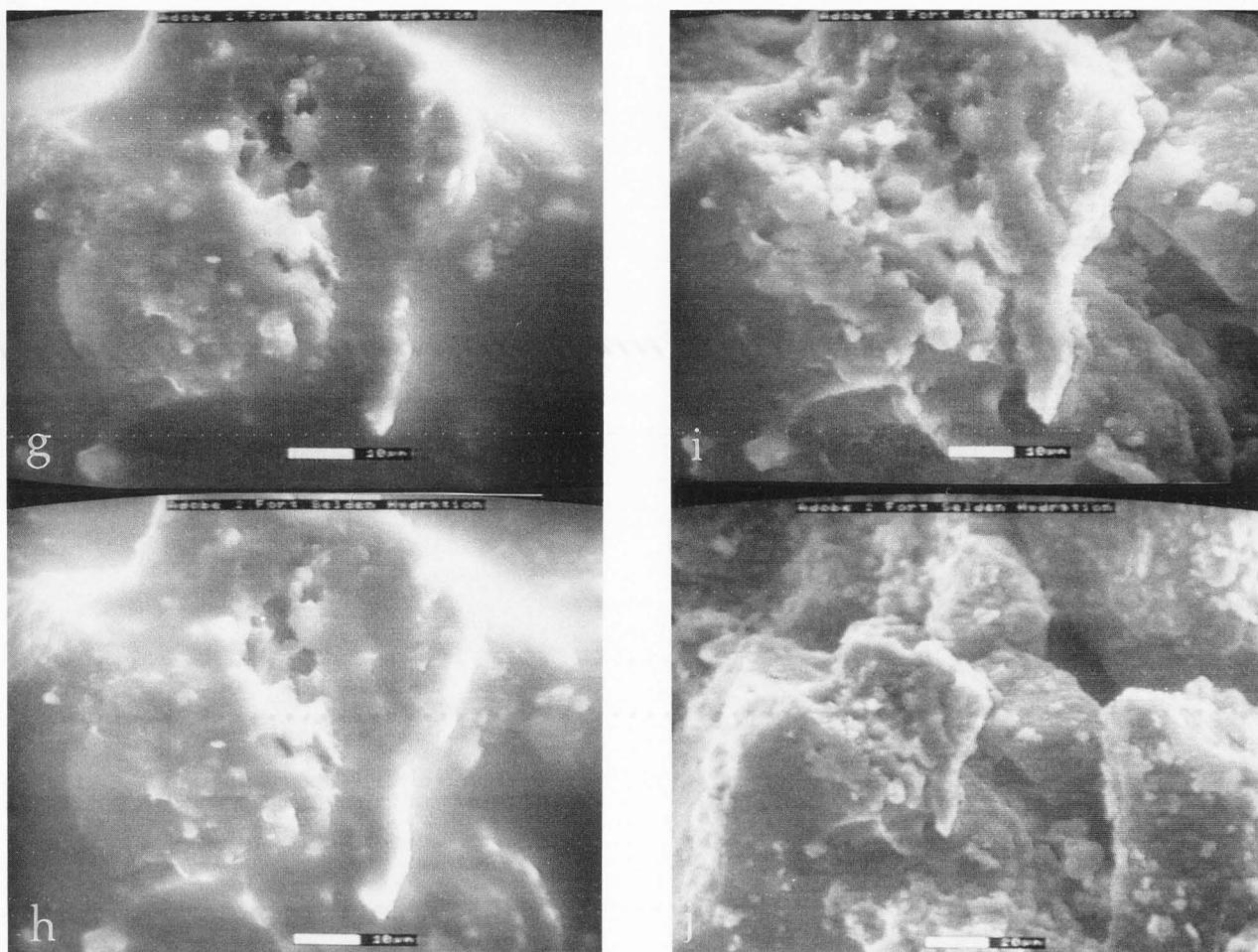


Figure 3g-j. Scanning electron micrographs illustrating the drying (3g-j) of Fort Selden adobe treated with diisocyanate. The white scale bar in 3f-3i is 10 μm and 20 μm in 3a-e and 3j.

4c). The crystals developed preferentially along cracks and elongation striations in the lead wire. After 20 minutes exposure time much of the lead wire surface was covered with oval shaped regions of larger euhedral crystals (2-7 μm). The crystals appear to radiate from small nucleation sites until an interlocking structure was developed (Figure 4d). After 120 minutes of exposure to formaldehyde vapors, a dense network of crystals had developed (Figure 4e-f). The experiment demonstrated the potential of the E-SEM for studies of art object corrosion by air pollutants. More advanced studies using a dynamical operation mode and *in situ* control of pollutant concentration are planned for the future.

Outgassing and organic samples

Samples that have a high moisture content generally require extensive sample preparation to prevent the outgassing of water vapor under high vacuum. Organic materials such as wood, tissue, and natural fibers are generally difficult to carbon coat because of their high surface area. The following sections illustrate the appli-

cation of the E-SEM to two samples that would normally require significant and careful sample preparation.

Dead Sea Scrolls. The degradation of collagen in parchment has been studied in order to determine the optimum conditions for the long term storage of ancient documents and manuscripts [15]. If stored in a relatively high humidity environment, the collagen in parchment may gradually denature and form gelatin [15]. Under such conditions, the parchment loses its fibrous structure and becomes soft and unstable.

Samples for conventional SEM examination must be carefully dried and gold coated before imaging. Outgassing water vapors can make observation and use of the conventional Everhart-Thornley detector difficult. The drying and coating process may also induce sample artifacts which could result in the incorrect interpretation of electron micrographs. With conventional low voltage SEM imaging, samples of uncoated organic materials with high surface areas may still have distortions from surface charging.

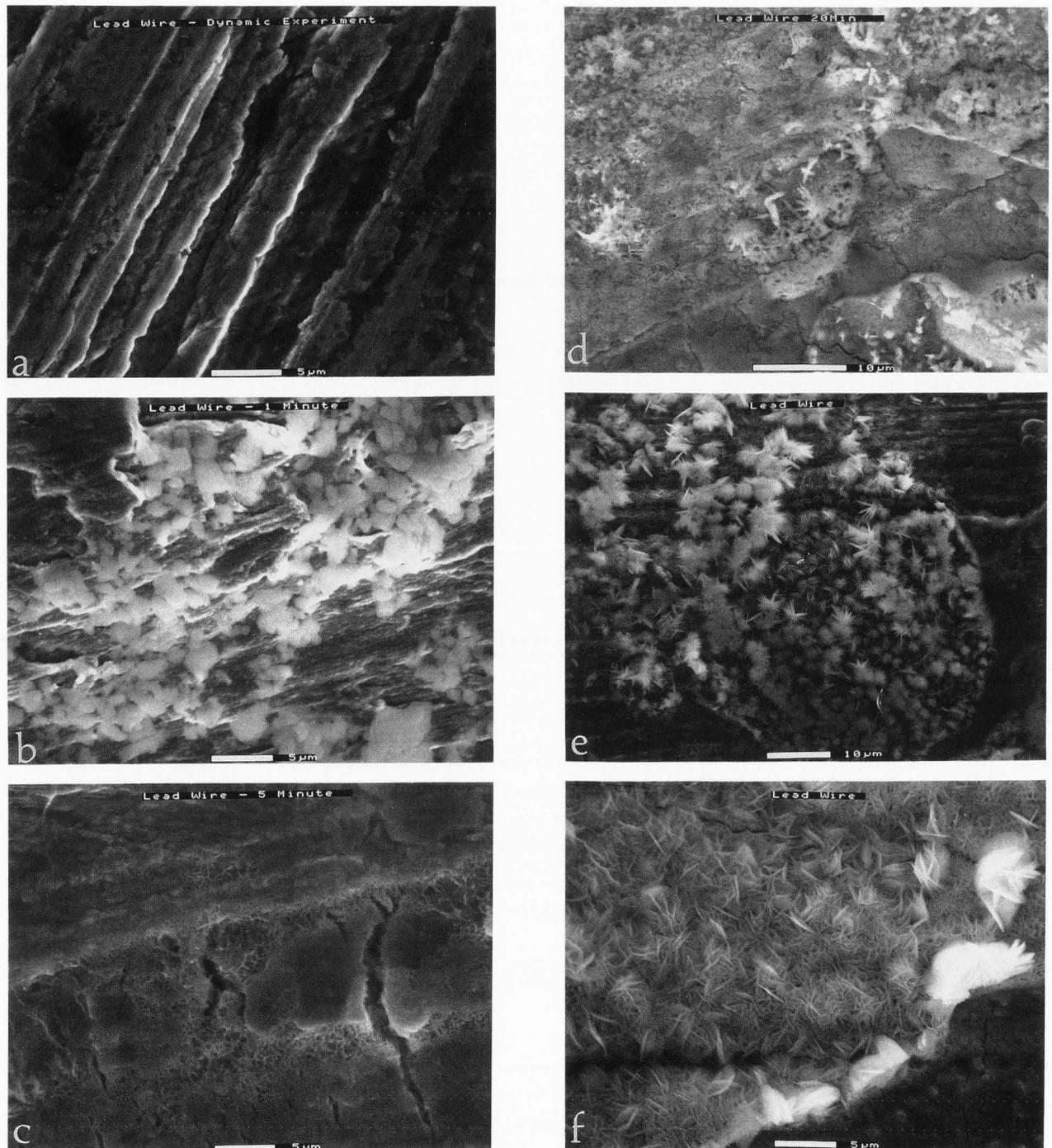


Figure 4a-f. Scanning electron micrographs of uncoated lead wire using the ESD. Scale bars are 5 μm for 4a, 4b, 4c and 4f and 10 μm for 4d and 4e. a) Surface of unexposed lead wire showing striations and dark areas of lead oxide. b) Surface of lead wire after 1 minute exposure to formaldehyde vapors (vapor from 37% aqueous formaldehyde solution). Note small anhedronal crystals. c) Surface of lead wire after 5 minutes exposure to formaldehyde. Note small euhedral crystals. d) Surface of lead wire after 20 minutes exposure to formaldehyde. Note larger euhedral crystals and radial growth pattern. e) Surface of lead wire after 120 minutes exposure to formaldehyde. Note well developed radial growth pattern. f) Close-up of lead wire after 120 minute exposure to formaldehyde vapors.

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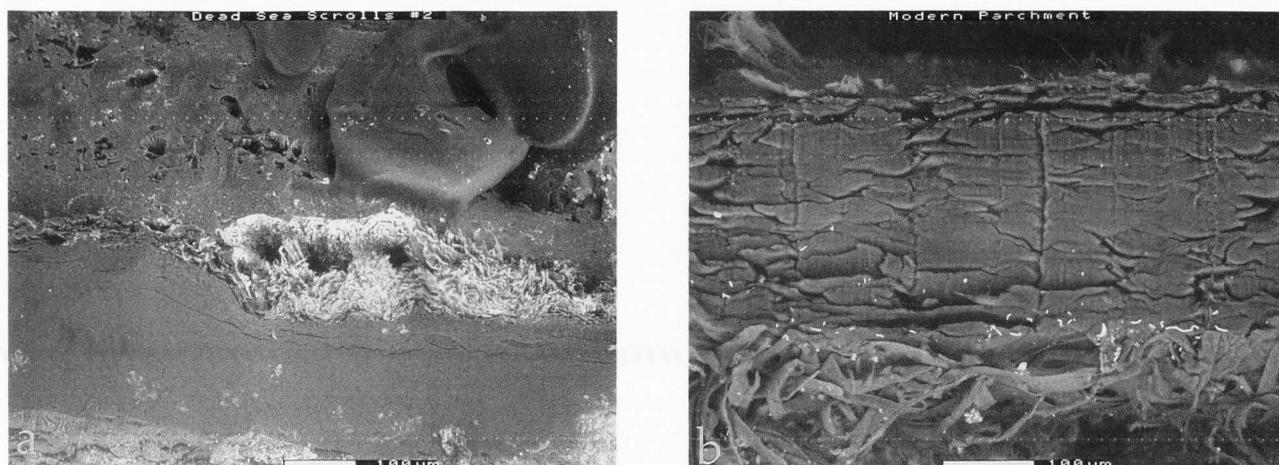


Figure 5. a) Top view of fragment from the Dead Sea Scrolls. Note structureless areas surrounding fibrous layering. b) Cross section of modern parchment showing well developed layered fibrous structure. Scale bar in each micrograph is 100 µm.

In this experiment, a fragment of the Dead Sea Scrolls was examined non-destructively (i.e., undried and uncoated) using the E-SEM. The resulting electron micrographs (Figure 5a,b) show no image distortion from surface charging. The relatively high partial pressure of water vapor (~100 Pa) in the microscope's sample chamber provided long term dimensional stability throughout the examination. Figure 5a shows a cross section of a fragment from the Dead Sea Scrolls. Layered fibrous structures are clearly visible as well as an almost structureless layer of material above and beneath the fibrous layer. These features are dramatically different from the features found in a cross section of modern parchment (Figure 5b). These observations help to define the physical changes that occur during the degradation of collagen. Additional experiments with parchment using a variety of conditions are planned, which will aid the conservation of these common organic materials.

Cotton swab. In conventional SEM studies, the necessity of coating a sample can interfere with the X-ray analysis for chemical composition. While gold/palladium sputtering is often used to coat SEM samples, the metal layer may obscure chemical differences between particles and interfere with X-ray peaks near those of gold or palladium. An alternate technique, coating with an evaporated layer of carbon, allows X-ray analysis, but does not allow as high resolution images, or as uniform a coating on complex, porous samples. Often this requires two samples being prepared—one for low resolution imaging and X-ray analysis, and one for high resolution imaging. Use of the E-SEM eliminates all of this sample preparation and allows high resolution imaging on difficult samples with simultaneous X-ray analysis.

Cotton swabs used in cleaning the Sistine Chapel were provided by Dr. Walter Persegati, the former Secretary and Treasurer of the Vatican Museums, for analysis of particles removed during the cleaning process. The swabs were dark grey-black in visible appearance, suggesting many soot particles. Of particular interest was if pigment particles (of much denser composition than soot) were also removed. An uncoated cotton swab was mounted on the E-SEM sample stage for electron imaging and X-ray analysis. Figure 6a shows electron micrographs of the cotton fibers. There are only a few dense particles in the cotton fiber swab. These include silicate dust, sodium, magnesium, calcium and chlorine-rich salt particles, and several iron and sulfur rich grains, which are most likely air pollution particles (Figure 6b). This application shows the usefulness of the E-SEM for more rapid and direct analysis of problematic samples, which are fairly common in conservation science.

EDS identification of uncoated semi-precious stone. The energy dispersive X-ray (EDS) analysis and electron microscope imaging of stones in ancient jewelry is hampered by SEM requirements to coat the surface of the electrically non-conductive stones. Carbon coating, which is needed for a successful EDS analysis, is difficult to remove without potential risk of damage to the art piece.

In this study, the surface morphology and chemical composition of an uncoated gold pendant with a dark red stone was imaged and analyzed using the E-SEM equipped with an EDS spectrometer (Kevex Corp., Delta 4 model with beryllium window). The cut of stone facets and polishing marks are clearly visible in Figure 7a. The X-ray spectrum (Figure 7b) and its qualitative interpretation identifies the stone as an almandine garnet ($\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$, with substitution of Mg and Ca

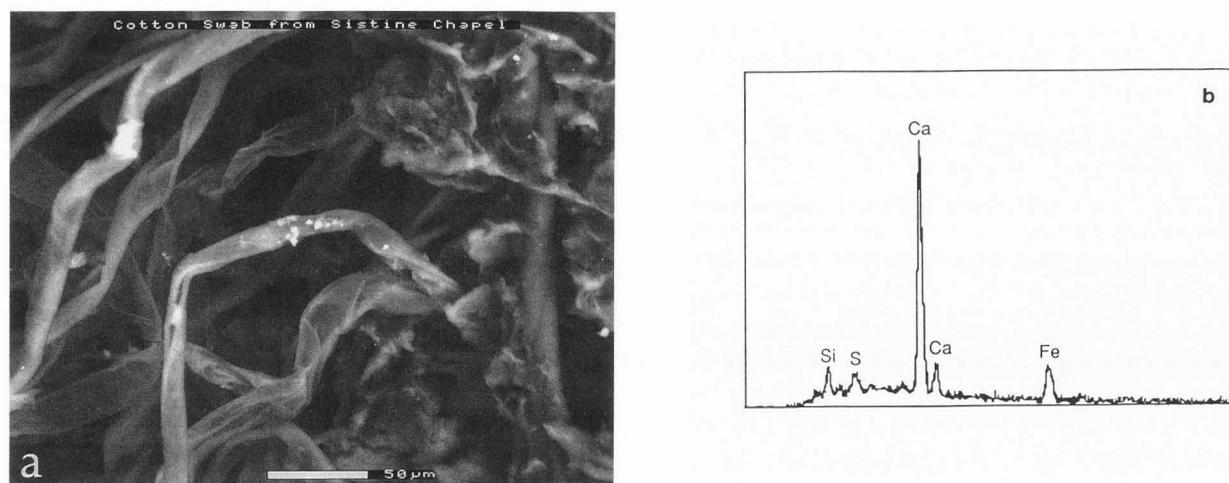


Figure 6. a) Backscattered electron micrograph of cotton swab from the cleaning of the Sistine Chapel. Note small bright particles (center) on the cotton fibers. Scale bar is 50 μm . b) Energy dispersive X-ray spectrum of a particle enriched in calcium, iron and sulfur (air pollution particle?).

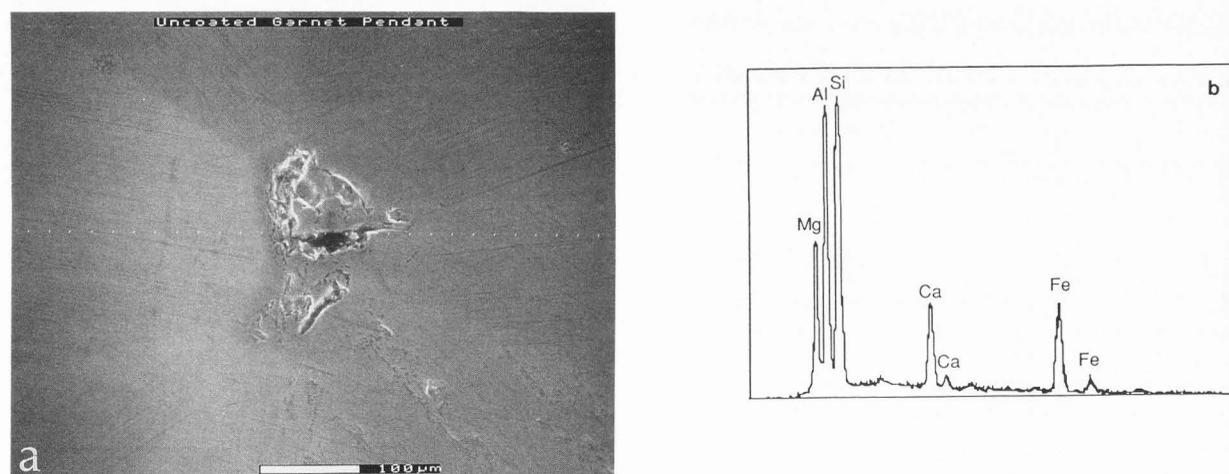


Figure 7. a) Scanning electron micrograph from the environmental SEM showing the intersection of facets on an uncoated stone. Note polishing marks. Scale bar is 100 μm . b) Energy dispersive X-ray spectrum indicating the garnet composition of the stone (Si, Fe, Al, Ca, Mg).

in the crystal lattice).

Conclusions

The Environmental Scanning Electron Microscope opens several new research areas to conservation science. The most important aspect is the ability of this instrument to dynamically image wet, moist or outgassing, non-conductive samples in a relatively high pressure environment without the need for complex sample preparation or sample coating. Using E-SEM, a conservation scientist can study

dynamic phenomena at high magnifications, such as corrosion, wet-dry cycles, solvent action, capillary action and infiltration, salt crystallization, melting and solidification cycles, freeze/thaw cycles, paint drying, crack formation and propagation, and topographical changes of polymers during curing. The development of accessories for the E-SEM sample chamber will bring cold and hot stages, *in situ* dynamic measurement, *in situ* aging, real-time image processing, sample micro-manipulation and physical testing. The sample chamber can be modified to incorporate temperature, humidity

and gas concentration control, and visible, ultraviolet or laser illumination. Now that light element EDS detectors are more common, the absence of any coating in the E-SEM allows the unhindered detection of carbon in samples. Naturally there are also some trade-offs. One difference in operating an E-SEM is that there are more variables to consider when optimizing the conditions for imaging than in normal SEM. The relation of gas pressure to working distance is very important for image optimization. Also, secondary electron emission in the E-SEM is not only a function of target material and its topography, but also of components absorbed on the target surface and of the environmental conditions in the sample chamber. Significant variation in secondary electron emission occurs from sample to sample because of the absence of a standard conductive coating. The bandwidth of the ESD is currently lower than a standard Everhart-Thornley detector. To avoid a decrease of spatial resolution from electron beam scattering on gas molecules, the working distance is limited to about 8-10 mm at 250 Pa. This limits imaging of samples which require a large depth of focus. Because of the short working distance and the diameter of the pressure limiting apertures, the current minimum magnification of the E-SEM is 100-200 times. This limitation can make locating different regions on the sample difficult. The spatial resolution achievable by the E-SEM (5 nm) is comparable to the resolution of an inexpensive SEM. The E-SEM can be used in the conventional SEM mode without the final differential apertures to obtain higher resolution by coating a sample and pumping down the sample chamber to a lower gas pressure. The backscattered electron detector or a conventional ET detector may be used at high vacuum. Thus, the E-SEM has all the capabilities of a traditional SEM in addition to its major strength, which is the ability to dynamically image samples in their natural state.

In conclusion, the introduction of the Environmental Scanning Electron Microscope represents a major breakthrough in SEM technology. Many research areas and experiments are now possible which could not have been attempted several years ago. A researcher has now two complementary tools to choose from to develop an optimal experimental strategy (SEM and E-SEM). The field of conservation and conservation science will profit greatly from the application of the E-SEM to the study of deterioration mechanisms, consolidation processes, and ancient materials and technologies.

Acknowledgments

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Discussion with Reviewers

M.E. Feather: Do you feel limited in sample size (especially thickness)?

Authors: We do not feel particularly limited by sample size. The E-SEM sample chamber is 30 cm in diameter and samples up to 10 cm thick can be accommodated with minor modifications to the stage. The heating and cooling stage is generally used for samples 1 cm³ or less in size.

M.E. Feather: How long have you had your E-SEM?

Authors: Our E-SEM was delivered on December 28, 1989.

M.E. Feather: Have you come across any samples that you have not been able to successfully image?

Authors: No, not yet.

M.E. Feather: Have you had a chance to look at the effect of cleaning solvents on paintings — i.e. before and after cleaning?

Authors: We have not had a chance to explore this subject.

M.E. Feather: Why did you record the dynamic sequences by still photographs of the video screen instead of using the built in Polaroid?

Authors: The dynamic changes in the adobe example take place over a few tens of seconds. This is not enough time to take several Polaroid micrographs. We plan to improve the quality of our dynamic micrographs by recording the video signal using a Super VHS recorder and digitally capturing images for electronic typesetting. ElectroScan may increase the bandwidth of the ESD detector system, which would lower the noise of the dynamic images.

R.J. Koestler: Examination of the micrographs of the untreated adobe before and after wetting of untreated adobe do not show any effects of hydration, is this to be expected?

Authors: We were uncertain what features to expect, since this type of experimentation and observation is new. Further experiments have shown that many small clay particles detach from larger grains during the hydration cycle.

R.J. Koestler: What kind of clays are typically found in the adobes you are studying? How much do they swell? What is the minimum amount of swelling you would

expect to see in the E-SEM? Did you see that with your adobe experiment?

Authors: There is allophane, kaolinite, illite, illite/smectite, and smectite in the adobes we are studying. The bulk swelling varies from 10-50%. In the E-SEM we are observing the clay/silt matrix expand (a "micro" view of swelling). The bulk swelling and the E-SEM swelling are generally in agreement.

R.J. Koestler: It should be noted that the use of EDS with the E-SEM is in its infancy and that there are significant details to be worked out before quantitative analysis are practical. For example, the loss in sensitivity, especially at the lower spectral ranges, needs to be understood for each gas or mixture of gases used. It is difficult enough for SEM-EDS results to quantitatively identify a stone as "almandine garnet" and far too premature to claim better results from a qualitative ESEM-EDS scan under very unique circumstances.

Authors: We agree that great deal of work needs to be done on the variable adsorption of X-rays by different gases and whether EDS can be quantized in the low vacuum environment. As a practical matter, however, using EDS qualitatively in the E-SEM to identify minerals is very similar to conventional qualitative SEM/EDS, and offers the additional advantages mentioned in the paper.