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Scanning Electron Microscopy in Conservation: The Abydos Reliefs

The Abydos Reliefs, the bas-relief sculptures from the small temple of Ramesses I at Abydos in the collection of the Metropolitan Museum, New York, have had an eventful history. The temple, built around 1310 B.C., was buried in shifting sand and soil and was subjected to periodic wetting and drying by the Nile's flooding waters.

A village was later built above the area, and the temple was fortuitously found by the villagers during the digging of a water well in A.D. 1910. The excavation that followed was carried out by the villagers themselves with little concern for proper archaeological procedures. A detailed description of the temple, its reliefs, and their history up to the time they were donated to the Metropolitan Museum, is given by Winlock.[1,2]

The Museum received the reliefs in 1911-12. Since then their story has not been much happier. The problems associated with their rapid deterioration due to high salt content and unsuccessful previous treatments were described in more detail in previous reports.[3,4] The reliefs were removed from exhibition in 1966.

Instrumentation

In the present study the scanning electron microscope (SEM) was used to examine the condition of the limestone, to assess the degree of penetration of the consolidant and the effectiveness of the cleaning method, and to compare the microstructure of the treated and untreated samples.

The use of SEMs in the conservation of works of art has not been fully exploited. A wide understanding of the operation of the instrument, its strengths, and its weaknesses is essential for its maximum utilization.

The SEM is basically a "reflecting" microscope (fig. 1) employing a fine beam of electrons instead of light photons. Electrons are emitted from a heated filament and are driven by a high voltage variable from one to fifty kV, through electromagnetic lenses that focus the electrons to a beam of the order of 2nm in width. The final electromagnetic lens carries coils employed to drive the focused beam in a scanning raster of x-y form. The specimen is normally attached to a special holder, called a stub, which provides a stable conducting platform for the specimen. The stub is placed in a stage that has mechanical or electrical feedthrough controls that allow for movement of the specimen while it is under vacuum.

The signal from the interaction of the electron beam with the specimen surface results from the generation of secondary electrons that reach an electron multiplier detector that generates a visible signal on a cathode ray tube (CRT). The displayed signal follows the point by point tracing of the scanning raster by the electron beam.

The number of secondary electrons collected at each point—a function of the surface topography, specimen tilt, and other factors—determines the point by point contrast on the visual CRT. Thus an image of the specimen is generated on the CRT. The image may also be recorded on film or videotape, or stored in a computer for further processing. More detailed information on the operation of the SEM may be obtained from a variety of sources, such as Goldstein et al.[5] or Heinrich.[6]

Other useful signals are x rays, cathodoluminescence, backscattered electrons, auger electrons, transmitted electrons, and specimen current. To collect each signal requires different detectors and different specimen preparation procedures.

Specimen Preparation

Specimens to be viewed in the SEM generally require some special preparation depending on the type of signal desired and the nature of the specimen: whether it is a conducting material, whether it contains moisture, whether it can withstand a vacuum.

For the samples examined in this study it was found that fractured surfaces did not provide enough information, so another method for specimen preparation was developed following Lewin's suggestion.[7] In this procedure the specimen was sawed and the surface was polished and then lightly etched with 1M HCl. All samples were sputter coated with 10nm of gold.

Examination of the Abydos Reliefs Stone

Before any treatments were attempted, the cause of the deterioration and the condition of the stone itself had to be established. The deterioration could be attributed to the high concentration of such soluble salts as halite, soda-niter, and magnesium chlorides, sulfates and nitrates, present in the stone. The highly hygroscopic magnesium salts—which have a tendency to deliquesce—draw in sufficient quantities of water to dissolve other soluble salts. When the relative humidity changes, these salts, in turn, can recrystallize, producing the mechanical disruption of the stone matrix.[8]

The paraffin wax and tung oil treatments that the reliefs received during the years 1911-13 produced a thin, leatherlike layer of "consolidated" stone, which was broken up and lifted off the rest of the stone when salts crystallized under it. Figure 2 shows a general view of the surface of the stone with the "skin" peeling off. Details of the edge of the skin, showing halite and gypsum crystals, are shown at higher magnification in figures 3, 4 and 5.

Laboratory Testing of the Consolidant

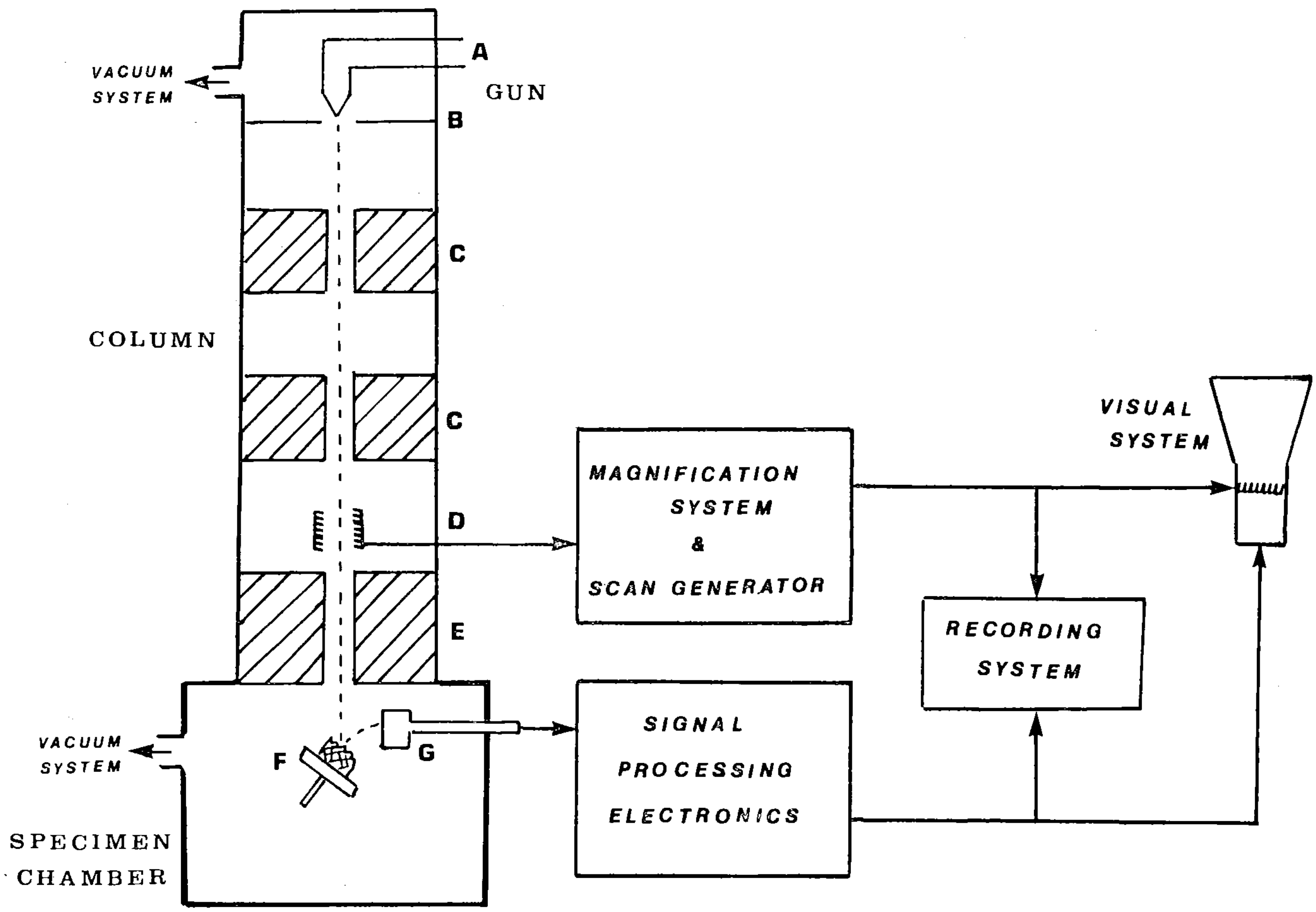
Possible consolidants were first tested on a marly limestone from Dendera similar in texture and composition to the Abydos stone. Paraffin wax and tung oil were applied to this limestone following the procedures of 1911-13. The treated stone was then artificially aged to produce conditions similar to those of the stone from the reliefs.[8] After testing of some consolidants, methyl trimethoxy silane (Dow Corning Z-6070 or T-4- 0149) was chosen.

The first specimens were prepared from fractured surfaces of the treated stone. Figure 6 shows the microstructure of the Egyptian limestone treated with paraffin wax and tung oil and after being consolidated with the silane. The consolidant is not readily visible in this picture. To find a better means of observing the consolidant and assessing the degree of consolidation the etching technique previously described was used. Figure 7 shows the appearance of the consolidant matrix that is left behind after the etching has removed the exposed calcareous part. Notice that this matrix is homogeneous indicating the solubilization of the wax and oil mixture by the silane.

Testing of the Cleaning Procedure

Since the reliefs had been treated with paraffin wax and tung oil, a procedure that, as noted by Pliny the Elder,[9] considerably darkens the light-colored surface of stone, cleaning was necessary. Usually this is undertaken before any consolidation is carried out. In the special case of the Abydos Reliefs the surface was so delicate that it

Fig. 1. Diagrammatic representation of a scanning electron microscope. (a) filament; (b) anode; (c) condenser lens; (d) scanning coils; (e) final lens; (f) specimen holder and specimen; (g) detector.



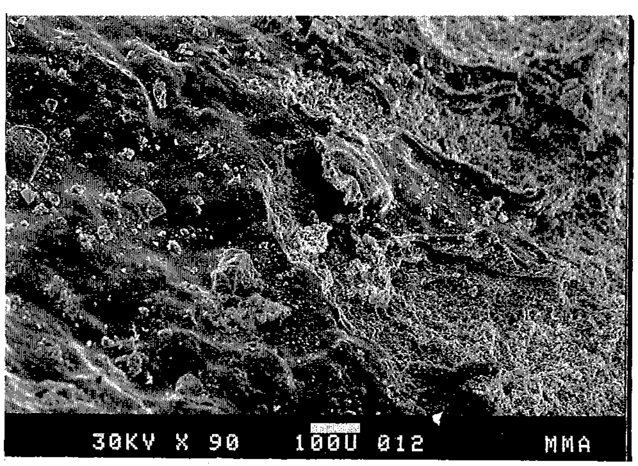


Fig. 2. Leatherlike layer of "consolidated" stone produced by paraffin wax and tung oil treatments. Layer lifts off from the rest of the stone as salts crystallize under it.

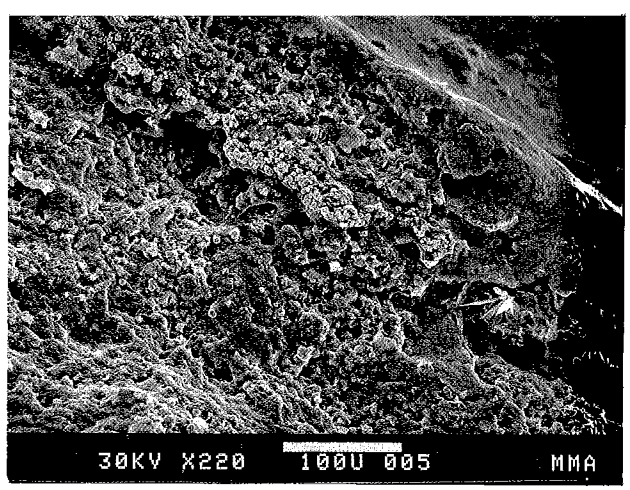


Fig. 3. Edge of leatherlike layer showing the separation from the underlying stone.

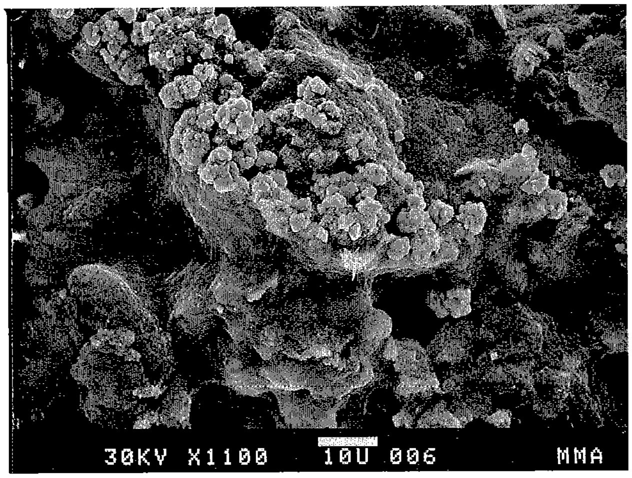


Fig. 4. Detail of edge at higher magnification showing crystals that are responsible for lifting of layer.

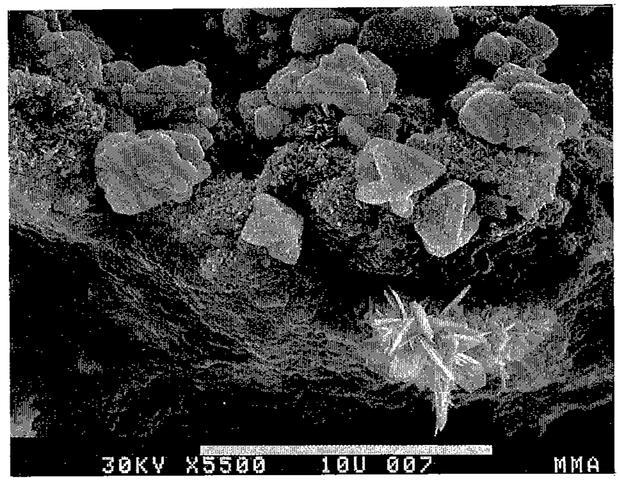


Fig. 5. Detail of edge showing masses of halite crystals and rosettes of gypsum crystals.

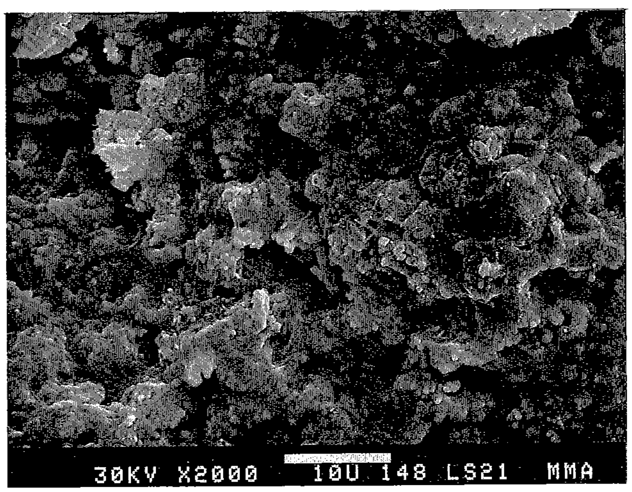


Fig. 6. Microstructure of Egyptian limestone treated with paraffin wax and tung oil and consolidated with methyl trimethoxy silane. The consolidant is not readily visible.

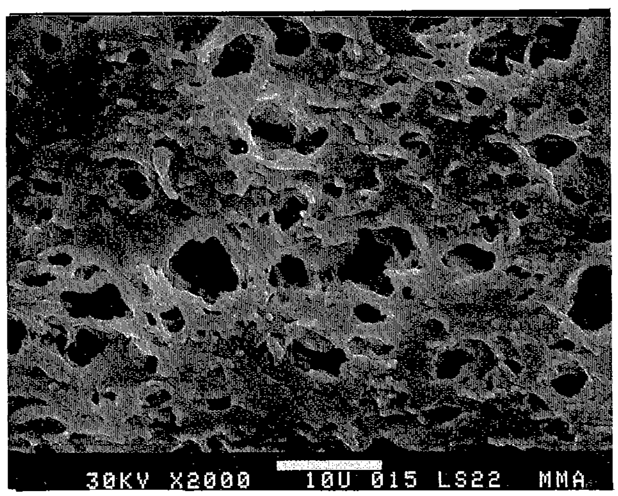


Fig. 7. Consolidant matrix left behind after specimen was treated by the polishing and etching technique. White rounded protrusions are produced by the solidification of the wax-oil mixture.

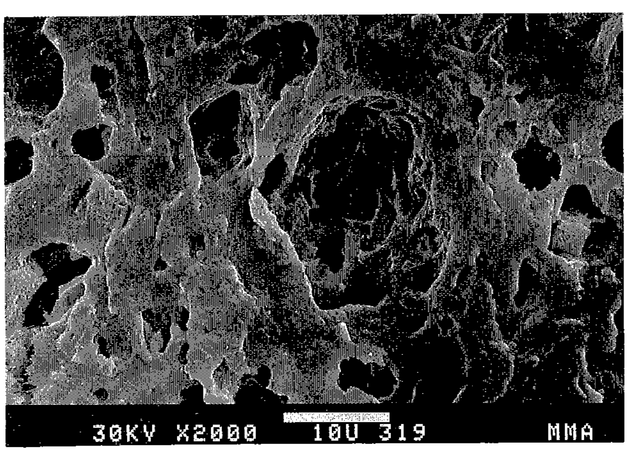


Fig. 8. Appearance of the consolidant matrix after application of one poultice (PERC in attapulgite). Notice the diminution of the number of white protrusions.

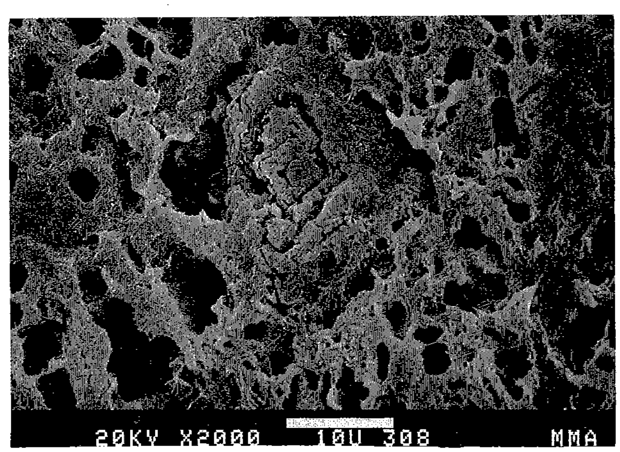


Fig. 9. Appearance of the consolidant matrix after application of two successive poultices. Practically no wax-oil mixture is left behind.

was considered necessary to consolidate first and clean after the curing of the consolidant. A more detailed description of the decision-making process is given elsewhere.[10]

Laboratory tests were carried out to ascertain the feasibility of cleaning after consolidation had taken place. Samples for these tests were also examined under SEM. Figure 8 shows the appearance of the Egyptian limestone sample after the application of one poultice (perchloroethylene in attapulgite). Figure 9 shows the appearance after the application of a second poultice. Both specimens were prepared using the polishing and etching technique.

Testing on the Reliefs

Samples from the sides of the reliefs were used for laboratory testing. Figure 10 is a fractured surface of one of these specimens. Figure 11 shows another fractured surface after consolidation with silane. Again the consolidant is not too evident. Figures 12 and 13 are micrographs of samples prepared by the polishing and etching technique. The matrix of the consolidant is clearly visible. It can also be noticed that the silane forms a homogeneous matrix with the wax-oil mixture from the previous treatments.

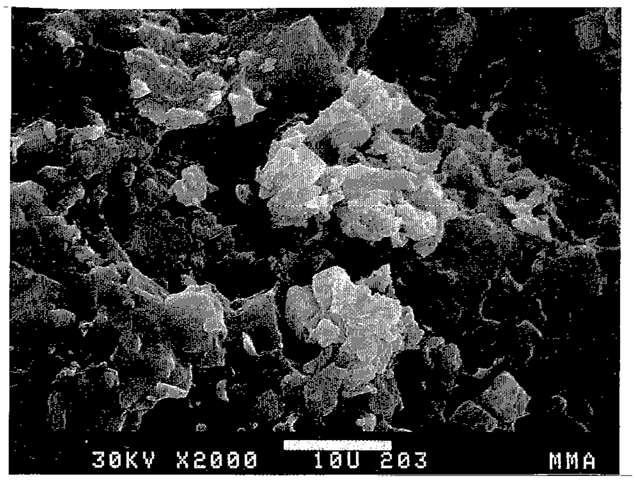


Fig. 10. Fractured surface of a flake from the Abydos Reliefs.

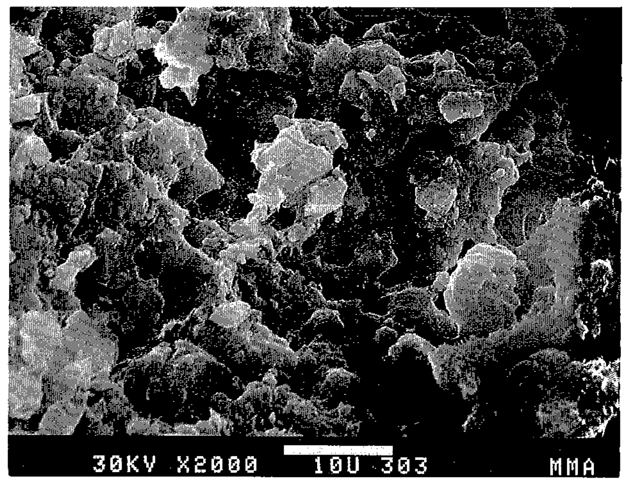


Fig. 11. Fractured surface of another flake from the Abydos Reliefs after consolidation with methyl trimethoxy silane. The consolidant is not clearly visible.

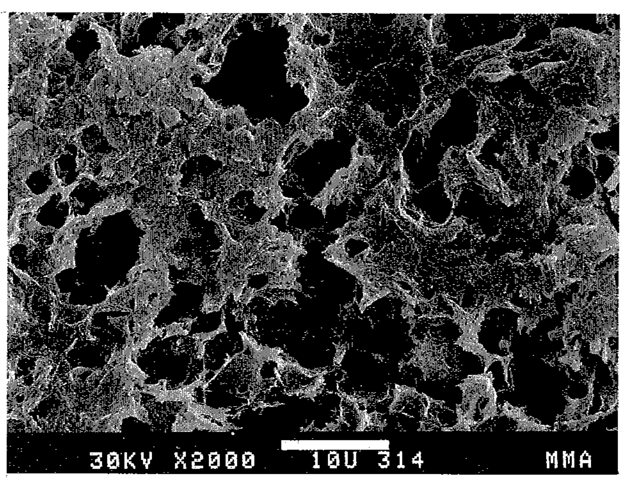


Fig. 12. Polished and etched specimen of the Abydos Reliefs. The hydrophobic nature of the wax-oil mixture in the stone shapes the residue.

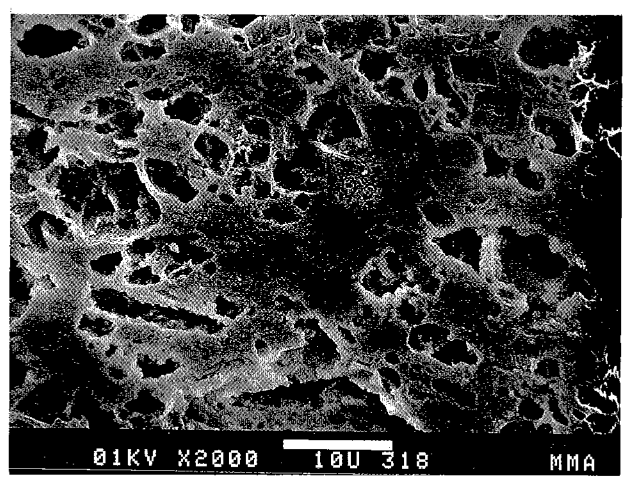


Fig. 13. Polished and etched specimen of the Abydos Reliefs after consolidation with silane. The consolidant forms a homogeneous matrix with the existing wax-oil mixture.

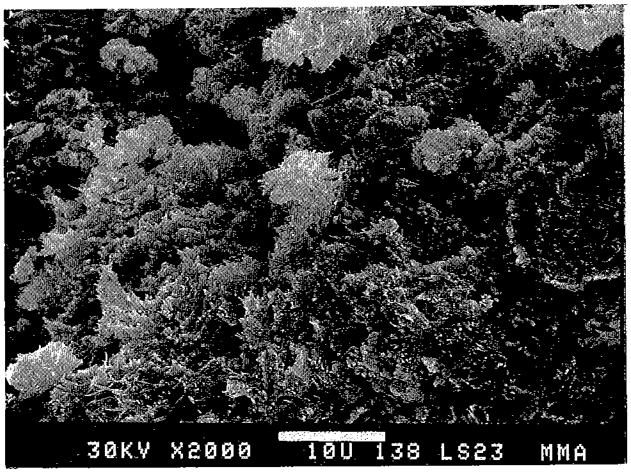


Fig. 14. Fractured surface of Egyptian limestone after treatment with wax-oil mixture, silane, and one poultice application. The micrograph is from an area near the edge of the specimen which is richer in oil. The white rounded protrusions and needle-like formations are due to the wax-oil mixture that solidified after being partially mobilized by the solvent (PERC).

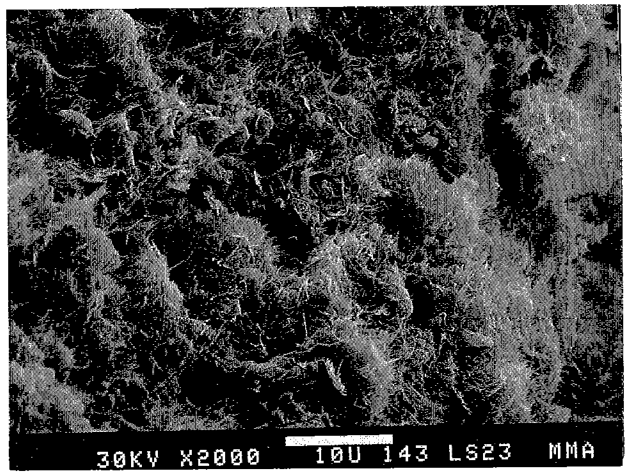


Fig. 15. Micrograph of the same sample but towards the interior of the specimen. The thin white needles are mainly paraffin wax that crystallized after the evaporation of the solvent that mobilized it.

Discussion

Through scanning electron microscopic examination of the microstructure of the samples it is possible to visualize the consolidating action of a particular compound and to deduce the mechanisms involved during cleaning procedures. The microstructure of fractured surfaces does not by itself provide all the information and can in some cases be misleading (compare figs. 10 and 11). The use of the polishing and etching technique permits a better assessment of the consolidating action of the silane (figs. 9 and 13).

The consolidant forms a mesh that holds the particles of the stone together. Methyl trimethoxy silane also forms a uniform "solution" with the wax and oil in the reliefs (figs. 6 and 13). This feature was important in the choice of the consolidant because the poor condition of the reliefs made it necessary to consolidate the stone without removing the previous treatments. That cleaning after consolidation can take place is shown in the series of micrographs (figs. 7-9) in which the decreased concentration of wax in the matrix of the consolidant is clearly evident.

The mechanism through which the wax is removed during poulticing is easier to deduce from the examination of fractured surfaces (figs. 14 and 15) than from polished and etched surfaces. Figure 14 corresponds to an area toward the edge of the specimen that is richer in tung oil. This component did not penetrate as readily into the stone as did the silane or even the molten paraffin. Figure 15 corresponds to an area towards the center of the sample. The fibrous-looking crystals are the paraffin wax that crystallized after the evaporation of the solvent (PERC) that mobilized it. The difference in morphology in the crystals from these two micrographs is due to the different composition of the wax-oil mixture. It would appear that the tung oil is also mobilized along with the wax. The poulticing technique is therefore a series of wax dissolution-crystallization steps, with each step drawing the wax and any oil that can be mobilized further out from the stone.

To achieve a thorough understanding of stone, or any sample, by SEM examination, special specimen preparation techniques may have to be developed. No one technique can provide all the necessary information. The different specimen preparation techniques selected should be used to provide complementary information and to ensure that accurate interpretaion of the images is derived.

Acknowledgments

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