

## Environmental Microscopy in Stone Conservation

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**Summary:** The natural weathering of stone is accelerated by the combined effects of acid rain, salt crystallization, and the freeze-thaw cycles of water. Since weathering will take place until the system reaches chemical equilibrium, we can mitigate the loss to historic stone monuments and structures by treatments of the stone that retard hydrolysis and impart mechanical strength. While macroscopic studies of stone weathering have been performed addressing the causes, the reactions, and the kinetics involved, the mechanisms of weathering, and the chemical remediation of stone need to be better understood at a microscopic level. Our approach uses environmental scanning electron microscopy where samples can be imaged in their wet, natural state, thus facilitating the in situ study of the weathering processes. The environment in the microscope is set up to simulate the conditions of degradation by introducing corrosive liquids and gases and varying the temperature, pressure, and water content in the environmental chamber of the microscope. In this study, we observed specimens of limestone, treated calcite, and sandstone. We have characterized the morphology, structure, and chemical constituents of the samples for comparison at a later stage when protective coatings will be applied. In situ leaching tests were performed on limestone samples to study the mechanisms of degradation. Granular disintegration due to leaching of the binding material between the grains was seen. We have also observed, in situ, the changes in the structure of sodium sulfate, used in salt crystallization tests, during hydration and dehydration cycles; it changed from that of dense grains to hydrated mesoporous granules with the generation of new surface area.

**Key words:** environmental microscopy, stone preservation, weathering protection.

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Supported by the Laboratory Directed Research and Development Program at Sandia National Laboratories. Sandia National Laboratories is a U. S. Department of Energy facility supported by DOE Contract Number DE-AC04-94AL85000.

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### Introduction: Weathering of Stone

All over the world, we see stone structures such as buildings, monuments, sculptures, and temples that constitute cultural, historical, archaeological, religious, and even scientific treasures of our time (Freemantle 1996). It is of interest that the same factors that affect historic, architectural, and monument sites affect biodiversity and the environment in general; they are development, population growth, tourism, illegal traffic, air pollution, war, neglect, and sometimes poor conservation techniques (Holloway 1995). Stone weathering follows the law of stability of rocks and minerals in that the stone will remain stable in its native environment of formation, and when it is removed from this environment it will change or adapt to attain a stable state. The weathering of this stone exposed to the environment is accelerated by the synergistic effects of acid rain, salt crystallization, freeze-thaw cycles, and other stress factors (Amoroso and Fassina 1983, Keller 1977, Winkler 1977). Water is responsible for most of the damage in stone by its hydration, hydrolysis, and dissolution of rock. Water enters the system by gravity, osmotic pressure, capillary forces, and siphoning. Subsurface water in stone pores can be "locked" up and, because of freezing, can exert pressures as high as 2100 atm at  $-22^{\circ}\text{C}$  (Winkler 1973). Clay minerals also can swell by hydration and exert internal forces.

Water with carbon dioxide dissolved in it can solvate carbonate rock more readily. The pH of most rain water ranges between 4 and 7 and averages 5 to 5.5. The first few seconds of wetting of stone from water that contains dissolved gases such as oxides of sulfur, nitrogen, and carbon is seen to be the critical stage during which most of the weathering takes place (Keller 1977). In addition, the gases are responsible for the incremental effect where the pH is reduced by another unit or two (Baedecker and Reddy 1993). The reaction rates of simulated acid rain leaching of stone was found to be ten times higher. This can be understood from a mass transfer viewpoint in that the film of water on the surface, that can potentially offer both diffusional and convectional barriers to transport, is least effective in the beginning stages of wetting. After a certain time, the film stabilizes and takes up ions that reduce the chemical potential difference between the stone and the body of water. Another reason for the torrential flood of dissolved ions in the first few seconds of wetting is due to the relatively higher acidity, and leaching of the loosely held cal-

cium carbonate that had recrystallized or precipitated from the thin film discussed above.

The kinetics of calcium carbonate dissolution are fairly well established (Reeder 1983, Stumm and Morgan 1996). However, the reactions cannot be classified as first order reactions since the kinetics differ depending on the degree of nonequilibrium. Surface reactions dominate at conditions close to equilibrium, whereas diffusion of ions or transport processes govern systems that are far from equilibrium. Other factors such as salt crystallization in the pores can bring about massive pressures when the salts hydrate and dehydrate from one mineral form to another. Salts are found in stone and can also be formed as products in the leaching reactions.

### Environmental Scanning Electron Microscopy

Microscopic examination of stone surfaces reveals the history and state of the material. The environment to which the stone is exposed leaves an indelible mark on the surface in the form of fractures, large cracks, deposits of airborne materials, salt crystals, modified porosity, and so forth (Amoroso and Fassina 1983, Winkler 1973). This study is further aided by electron microscopy coupled with energy-dispersive x-ray analysis by which qualitative and semiquantitative information can be obtained about a specific mineral or deposit on the stone. Studying the stone surface and deposits can lead to a better understanding of the degradation mechanisms and show ways to prevent weathering.

This process is better examined using environmental scanning electron microscopy (ESEM) where samples can be imaged in their wet, natural state (Danilatos *et al.* 1989, Goldstein *et al.* 1992). The environment in the microscope facilitates the simulation of the stone weathering process. This environment is very important because an understanding of the interaction, transport, permeability, and physical-chemical action of liquids is crucial to an effort to characterize, clean, and treat stone surfaces. The action of corrosive fluids can be studied by introducing acidic solutions and observing the leaching phenomena. Another factor in the weathering of carbonate rocks is the crystallization of salts such as gypsum and sodium sulfate; salt solutions can be introduced into the microscope using a microsyringe and can be allowed to crystallize either by elevating temperature or lowering pressure to mimic the process of salt crystallization. The temperature of the sample can be varied to simulate freeze-thaw conditions that are also a major factor in stone degradation.

Another factor that is being studied is the hydrophobicity of the stone surface which is revealed as small spherical droplets of water compared with a hydrophilic surface where the water molecules adsorb onto the surface as layers without forming droplets. Using the micromanipulator attachment, secondary bonds between the stone surface and contaminants can be studied by observing how electrostatic and Van der Waals forces influence the adhesion of foreign particles onto the stone surface. In addition to nondestructive examination of large specimens of historical significance and stone sur-

faces, the effect of cleaning agents and protective coatings on these materials can be best studied using this wet environment. This technique of environmental microscopy has been used previously in conservation science to study the wettability, water absorption, and swelling characteristics of adobe clays that were treated with a diisocyanate polymer (Doehne and Stulik 1990). Their studies showed that the treatment rendered the surface hydrophobic, as seen by the distinct droplets of water, compared with uniform condensation of a water film on an untreated clay surface. In another pioneering effort by the same group, sodium sulfate was exposed to hydration/dehydration and dissolution/recrystallization cycles (Doehne 1994). Highly porous submicrometer-sized particles of sodium sulfate decahydrate implicated in stone degradation resulted from the hydration cycling. Fracture surfaces of sandstone revealed pores containing sodium sulfate decahydrate which can potentially form "crystal wedges."

### Microscope/Microreactor Environment in the Environmental Scanning Electron Microscope

The low-vacuum scanning electron microscope (SEM), called an environmental SEM (or simply ESEM) (Danilatos *et al.* 1989), is being used in our stone conservation research (ESEM Model E-3, Electroscan Corp., Wilmington, Mass.). The ESEM contains a series of differentially pumped chambers separated by pressure-limiting apertures, so that the specimen chamber can be kept at high pressure (13–2600 Pa or 0.1–20 torr). Descriptions of two variations of this device are available in the literature; the ESEM (Danilatos 1988) and a wet-SEM (Buchanan 1983). An imaging gas that serves to amplify the signal by its ionization is present in the ESEM chamber. The cations produced neutralize the electrical charge on the specimens, enabling observers to study materials in their natural states without coating and drying. The diversity and uniqueness of samples and experiments conducted in the following research efforts highlight the advantageous features of ESEM that we utilize in stone conservation. Researchers have observed insulators undergoing dynamic fracture (Bolon *et al.* 1989), concrete hydration (Lange *et al.* 1990), ancient ivory fragments (Koestler *et al.* 1990), and materials undergoing phase changes (Bolon and Robertson 1990). The ESEM has been used for wool fiber research, determining the shape of dry and wet *Bacillus apiarius* spores and watching the growth of live specimens (Danilatos 1988). Other scientists have looked at hydrated lung tissue and the release of plant spores when the humidity changes (Pope and Scheetz 1990). More relevant investigations to our research on stone surface preservation have been conducted with the ESEM by studying the wettability, water sorption, and swelling characteristics of adobe clays (Doehne and Stulik 1990); salt crystallization on sandstone (Doehne 1994); metal surface degradation due to biocorrosion (Ross *et al.* 1994); and the unique stress-strain properties of aerogels formed at ambient pressure (Prakash *et al.* 1995). Many historical structures are discovered underground, and at some time in their history they may

have been exposed to groundwater. When water permeates cementitious materials or stone, the cement can corrode or dissolve. Ramsay *et al.* (1987) studied how cement forms colloids in solution. Our research with this instrument in the area of stone conservation is expected to have a significant impact on the understanding of the underlying chemical and physical processes involved in stone degradation and conservation.

### Stone Surface Investigations

There have been many efforts to preserve stone using materials such as epoxies, polyesters, acrylics, silicones, alkoxysilanes, and other organic/inorganic polymers (Amoroso and Fassina 1983, Sleater 1977, Winkler 1973, Wheeler *et al.* 1992a). However, weakness of the chemical bond between the stone and the protective treatment, oxidative degradation of organic treatments, thermal decomposition, incompatibility of materials, ultraviolet degradation, subsurface weathering, and poor penetration are some of the demerits that offer challenges to future stone conservation research (Sleater 1977; Wheeler *et al.* 1992a,b; Winkler 1973). Our approach to stone conservation is to develop a mineral-specific treatment that will retard any further chemical or physical weathering by first rendering the surface passive toward hydrolysis and second by strengthening or consolidating the already weathered structure (Cygan *et al.* 1995; Rao *et al.* 1995a,b). The passivant molecule will bind to the calcite surface and also act as a coupling layer to the consolidant which provides strength to the weathered stone. The coupling is achieved by a polymerizable "tail" on the passivant to enable sol-gel condensation reactions. In our stone conservation work, we first characterized an array of stone samples. We examined Monks Park limestone obtained from Bath, England; single crystal calcite from Chihuahua, Mexico; and sandstone from Tuba City, Arizona. Next, we weathered an untreated limestone sample by injecting a dilute sulfuric acid solution (simulated acid rain, pH~4.5) on the stone surface and observed the changes that took place. A calcite sample, representative of the mineral in limestone, was passivated with a silicon modified ethylenediaminetetraacetic acid (EDTA) molecule and then exposed to deionized water in the environmental chamber. Another limestone sample was subjected to salt crystallization by sodium sulfate.

### Experimental Methods

The samples were dusted to remove loose debris and were placed in the ESEM with no further treatment prior to observation and energy-dispersive x-ray (EDX) analysis. The salt was placed in its anhydrous form on the limestone surface in the voids of the oocyte shells and was allowed to hydrate and dehydrate by varying the vapor pressure of water in the chamber. The microscope was operated at an accelerating voltage of 10–25 keV with a lanthanum hexaboride electron emitter. Limestone samples were imaged at 20 keV to obtain a strong electron signal, and coated calcite was imaged at 10 keV to

obtain x-ray information about the surface coating. The optimum gas pressure in the environmental chamber is chosen by cycling through from an evacuated state to a saturated state. The minimum gas pressure that can effectively neutralize the surface charge and amplify the electron signal is chosen as the operating pressure. Water vapor, the standard imaging gas, was chosen for its simplicity and compatibility with the planned leaching experiments. The distance between the sample and the detector is minimized until the image quality degrades which corresponds to about 6 mm for our experiments in the presence of water vapor. The microscope is equipped with a microinjector for injecting fluids and a micromanipulator for probing samples. The signal is detected by an environmental secondary electron detector. The images were acquired digitally using Electroscan's Image Acquisition and Archiving Software and processed using Adobe Photoshop to yield the micrographs. X-ray spectra are obtained by tilting the sample stage by 45° and focusing the electron beam on the area of interest in spot mode.

### Results and Discussion

The untreated limestone is filled with coccolithic structures and appears amorphous on the surface but, upon closer inspection, reveals polycrystalline phases of calcite (Figs. 1, 2). Large voids amidst clusters of fine grained calcite in the limestone are seen. The remnants of marine creatures such as oocytes are seen to be either empty or filled with salt deposits (Figs. 3). The bright areas in the images are due to contrast enhancement in the postprocessing stage and not due to charging of the sample. The sandstone samples have large macropores in between the quartz particles (Fig. 4). The dense particles were not bound tightly to each other when probed by the micromanipulator, and this suggests that granular disintegration is an important mechanism of degradation for this sandstone.

When dilute sulfuric acid was injected onto the concave surface of the limestone sample (Fig. 5) and allowed to react for 30 s, we observed large particles that were dislodged from the surface by dissolution of the binding material as seen in Figure 6. The dislodged grains enveloped by the acid layer moved with the retreating drying front of the acid.

The hydrophilic nature of the surface is also seen by the apparent stretching of the liquid layer. The leaching resulted in significant etching of a calcite layer many micrometers thick as seen by comparing Figures 5 and 7.

The leaching is consistent with observations made in parallel experiments using an atomic force microscope (Rao *et al.* 1995a,b). Dissolution of submicrometer-sized calcite crystals is seen along with deposition of calcium sulfate (Figs. 8 and 9). Sulfur peaks shown on EDX confirm the presence of the white precipitate calcium sulfate. Calcium sulfate is more soluble than calcite and can adversely affect the durability of the stone by promoting granular disintegration.

The calcite crystal was treated with a silicon-modified EDTA passivant that has two functions: one is to bind to the

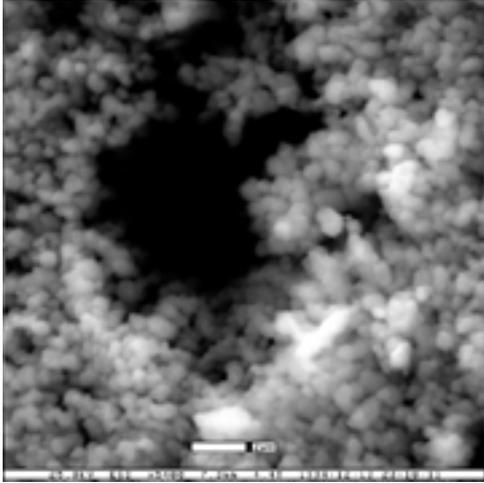


FIG. 1 Limestone showing porosity (white scale bar = 2  $\mu\text{m}$ ).

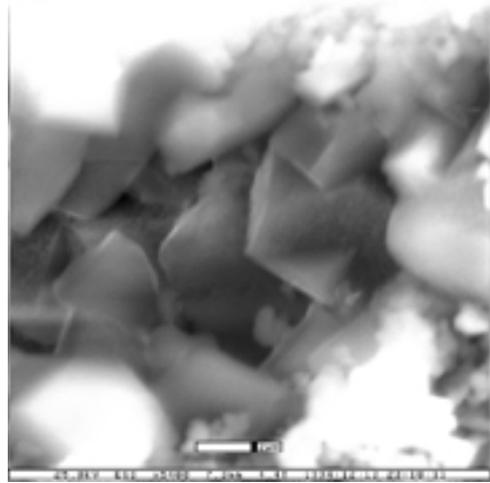


FIG. 2 Polycrystalline interior of limestone (scale bar = 2  $\mu\text{m}$ ).

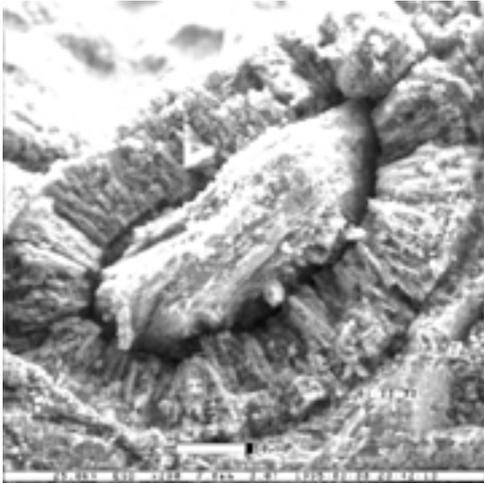


FIG. 3 Natural oocyte and salt deposits within fossilized shell in limestone (scale bar = 50  $\mu\text{m}$ ).

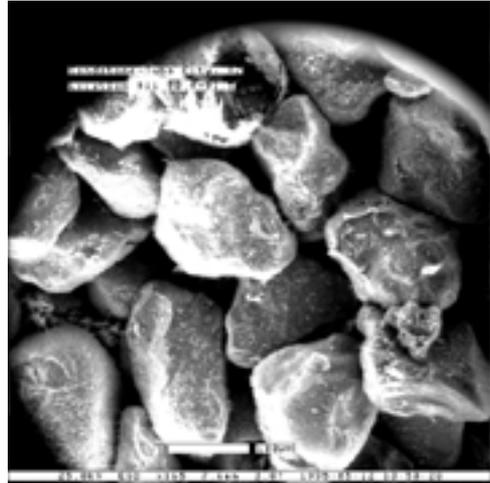


FIG. 4 Large macropores in sandstone from Tuba City, Ariz. (scale bar = 100  $\mu\text{m}$ ).

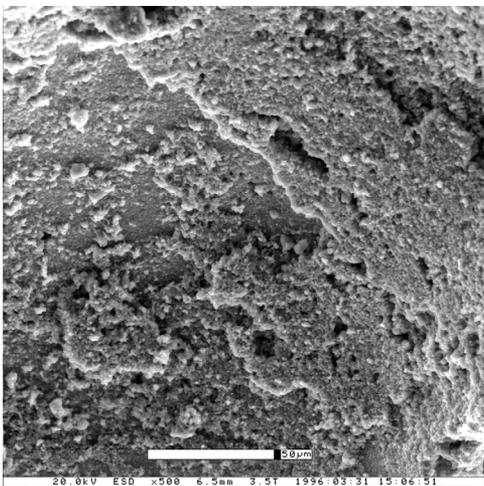


FIG. 5 Concave surface of coccolith fossil on limestone prior to leaching. Dil.  $\text{H}_2\text{SO}_4$  was then injected to leach surface (scale bar = 50  $\mu\text{m}$ ).

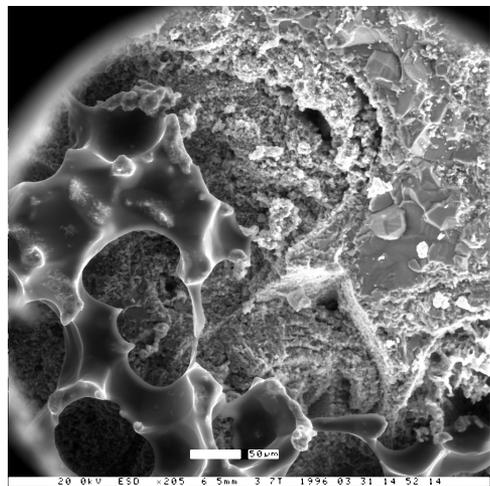


FIG. 6 Thin film of dilute acid on limestone surface (left side of image). Note the weakly bonded grains that are being washed away. Leach time  $\sim 30$  s (scale bar = 50  $\mu\text{m}$ ).

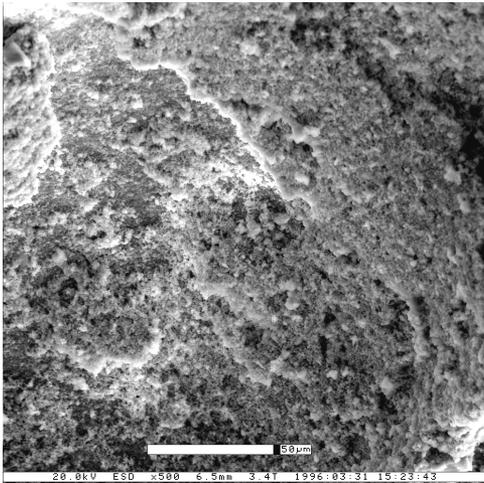


FIG. 7 Comparison of fresh and leached surface shows that a 30 s exposure to simulated acid rain does significant damage to limestone by etching away the calcite grains (scale bar= 50 μm).

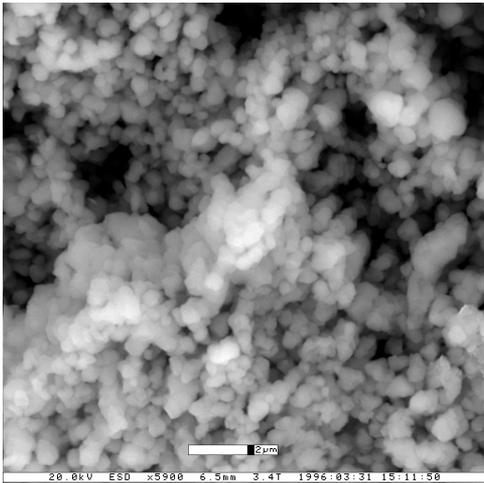


FIG. 8 Close-up view of limestone prior to leaching (scale bar= 2 μm).

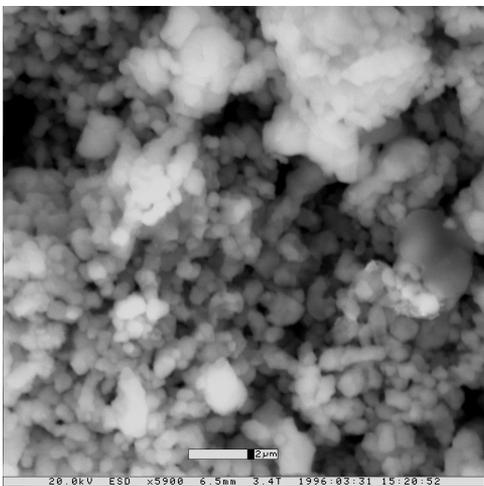


FIG. 9 The surface after leaching shows signs of dissolution and reprecipitation. Deposits of calcium sulfate are also seen in the top of image (scale bar= 2 μm).

calcite and the other is to offer a polymerizable alkoxy silane “tail” for subsequent sol-gel reactions to consolidate the stone. We noticed from Figure 10 that agglomeration of passivant is taking place at two scales: a micrometer scale and the other much smaller as evidenced by the small dots in the image. This agglomeration may be due to the presence of moisture on the surface that enhances condensation reactions between the silicon groups present in the passivant. The identity of the passivant was established by the silicon peak as seen in Figure 11. The chloride peak is from the salt present in the passivant solution.

The source of the copper peak was unknown. When deionized water was injected on the coated calcite, we noticed that the agglomerates were washed away (Fig. 12), suggesting that this form of the passivant molecule is ineffective in preventing hydrolytic attack. One way to circumvent this problem is

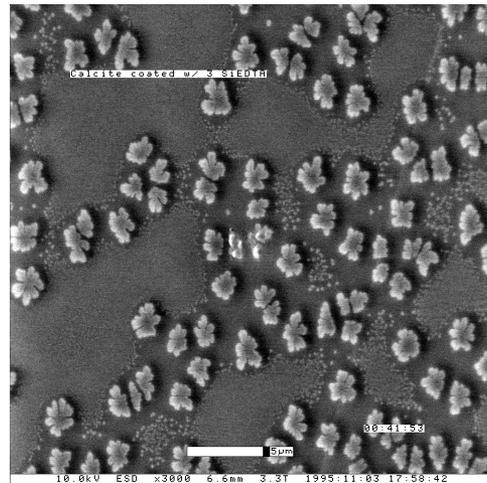


FIG. 10 Calcite coated with a sol-gel-based passivant shows a nonuniform coating. Aggregates formed due to condensation reactions from the moisture on surface (scale bar= 5 μm ).

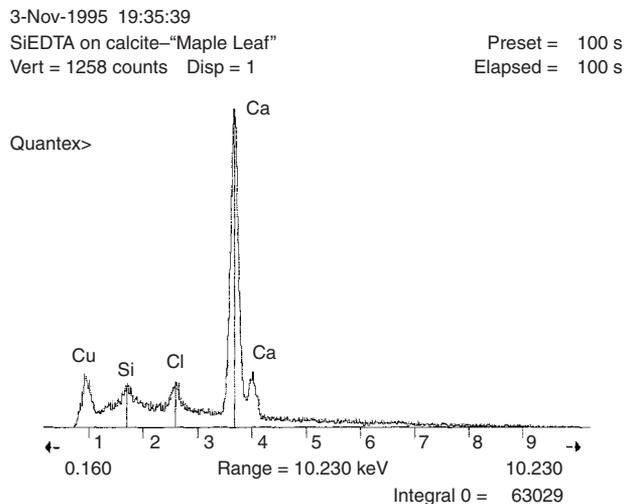


FIG. 11 EDX spectrum confirmed that aggregates were due to passivant condensation. Passivant molecule contains silicon which is seen.

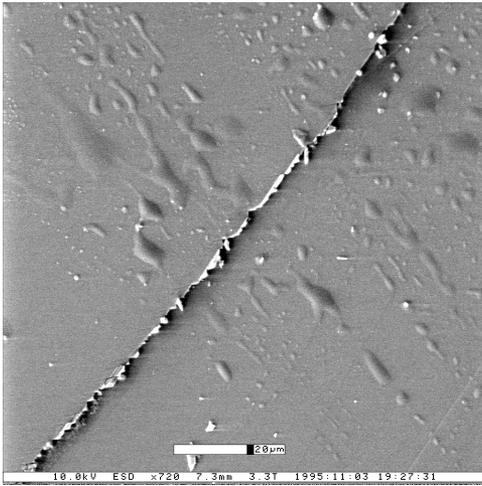


FIG. 12 When passivated calcite was exposed to deionized water, agglomerated passivant was washed away. The dark line is a step edge typically seen in calcite cleaved along the {104} plane.

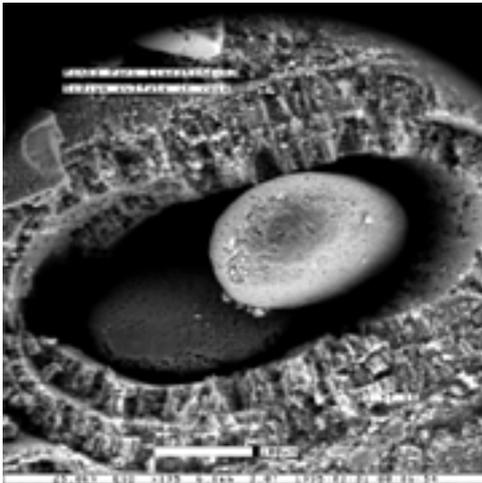


FIG. 13 Sodium sulfate grain placed in oocyte for salt crystallization experiments (scale bar = 100 µm).

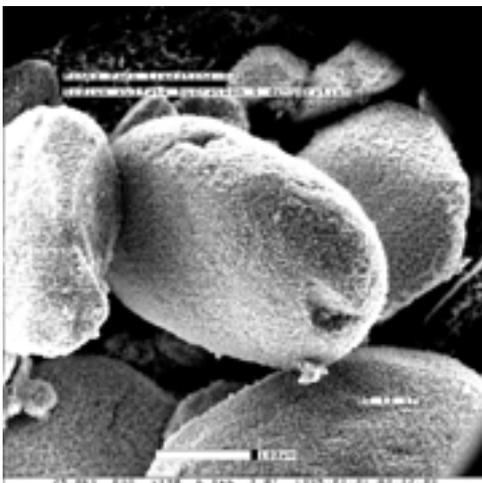


FIG. 14 Adjacent sodium sulfate granules after dissolution and recrystallization reveal new surface area generated (scale bar = 100 µm).

to ensure that, prior to passivation, there is no moisture on the surface by drying it or by washing it away with a solvent, although this may be hard to accomplish in the field. Another technique to enhance the surface reaction while suppressing the sol-gel reaction is to reduce the number of reactive functional groups in the “tail” of the passivant.

The surface of anhydrous sodium sulfate salt introduced onto the limestone was smooth in surface texture and structurally dense, as seen in Figure 13; no discernible features were seen at high magnification. After cycling between hydration and dehydration a few times, mesoporosity is generated as seen in the adjacent salt granules of Figures 14 and 15, which corresponds to the formation of a decahydrate of the salt (Doehne 1994). The transition from a dense material to that of a porous material is seen as new surface features that are visible at high magnifications (Fig. 15). The relative change in volume of the salt between hydration and dehydration cycles can induce large internal stresses in the stone.

In addition, the creation of surface area further destabilizes the stone because of the additional sorption and reaction sites generated. It was not possible to observe the recrystallization and subsequent destructive effects of the salt inside the pores of the limestone because of the large volume of limestone present which absorbed the dissolved liquid far away from the surface. Modifications are being made to the liquid/vapor injection systems to facilitate such an observation.

## Conclusions

We have observed the surface morphology of limestone, calcite, and sandstone. Environmental microscopy allowed us to simulate the effect of acid rain on limestone which showed significant etching of the calcite present. Large grains were dislodged from the surface by dissolution of the binding material. Passivated calcite showed a nonuniform coating that was easily attacked by deionized water suggesting a modification

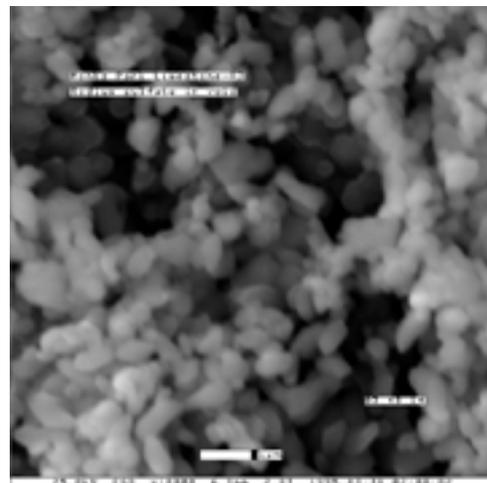


FIG. 15 Magnified view of the surface of sodium sulfate nodules reveals mesoporosity (scale bar = 1 µm).

of the passivant. Salt crystallization experiments demonstrated the structural and phase changes that accompany hydration and dehydration cycles. Observation of treated limestone under the same simulated acid rain conditions will provide insights into the leach resistance of the material. We plan to observe the calcite and limestone treatment process in the environmental chamber. We anticipate better topographical and atomic number contrast by examining these inhomogeneous materials by using a newly acquired backscatter detector. It is imperative that the mechanisms of degradation and effects of conservation are understood both at the microscopic and macroscopic levels. By examining the specimens during degradation as simulated in the ESEM and by studying them before, during, and after treatment with preservatives, we can better control the weathering and thereby conserve stone and other structural materials.

### Acknowledgments

The authors are grateful to Dr. George Wheeler, Metropolitan Museum of Art, for excellent collaborative input and for providing limestone samples. They are also grateful to the Getty Conservation Institute for collaborating in this research effort, especially Dr. Eric Doehne who gave helpful advice and guidance in environmental microscopy techniques.

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