

volume. Subsequently, drying cracks evolved at the grain boundaries of the hydrated crystals and the total volume of the salt mass is reduced. At the end of the drying process the microscopic picture shows several nano cracks penetrating the salt matrix and enormously increasing the inner surface.

Similar effects could be observed during wetting the samples not only by treatment with liquid water (or salt solution) but rather by changing the relative air humidity around the sample. The measured deformations on the surface after exceeding the deliquescence humidities of the particular hydrate phases of magnesium sulfate could be comprehended microscopically. That way, increasing the humidity above 85% RH, we observed the formation of solution films on the surface of the samples leading to a complete de-correlation of the laser speckle pattern. Below this limit of relative humidity micro deformations were detectable not disturbed by de-correlations. These deformation measurements were used to define the best sampling moment for detailed microscopic analyses.

Low relative humidities effected in migration processes in side of the samples yet, leading to exciting early deformations. In most cases these effect came along with a compaction with salts of the pore space close to the surface. So the measured deformation amount is not only a pure surface effect but in all probability is influenced by this compaction up to about 1 mm depth.

It has been recognized that the pore space directly at the surface between the glass grains is filled with salt differently. In some cases, it was possible to identify different hydration phases on the basis of the backscattered electron signal. However, the main question at what time and under which conditions this surface compaction takes place is not yet answered satisfactorily.

The high damage potential of soluble salts migration processes only effected by the humidity conditions has been underestimated in the past. So far the view was advanced that salt loaded indoor masonries need a constant relative humidity on a medium level to avoid damage dynamics. Our results show that salt migration processes accompanied with a damage potential by compacting the surface start at much lower humidities (depending on the salt) as believed up to now.

This is of great importance in particular to protect valuable cultural heritage buildings and indoor surfaces (e.g. historical wall paintings).

3D- μ CT in the analysis of sculpture

A. BADDE,¹ B. ILLERHAUS²

¹Staatliche Museen zu Berlin (SMB), Berlin, Germany. ²Bundesanstalt für Materialforschung und -prüfung, (BAM), Berlin, Germany

The Alte Nationalgalerie, SMB and the BAM tested the accomplishment of the 3D- μ CT—a new flat panel detector CT system at the BAM with extended energy range, with high voltage X-ray tubes (330 and 225 kV), with micrometer focal spot size and micro-meter resolution and enlarged object size (up to 70 cm diameter)—for examining plaster statues.

The high spatial and density resolution of the tomograph enable detailed insights into the individual work processes of the investigated cast plaster statues. While initiated in support of the conservation process, CT analysis has assisted in revealing relative chronologies within the series of the cast works of art, thus serving as a valuable tool in the art-historical appraisal of the oeuvres.

Image-processing systems visualize the voids and cracks within and the cuts through the original cast works. Internal structures, armoring, sculptural reworking as well as restorative interventions are virtually reconstructed.

The authors are currently employing the 3D- μ CT systems at the BAM into the detection of defects in Carrara marble sculpture. Micro-cracks, fractures and material flaws are visualized at spatial resolution of 10 μ m. Ultrasound tomography measurement data is verified by analyzing correlations in the results obtained from the complementary application of these two NDT-methods of diagnosis.

Scanning microscopy techniques in the study of salt damage affecting cultural heritage

E. RUIZ-AGUDO,¹ C.V. PUTNIS,²
C. RODRÍGUEZ-NAVARRO¹

¹Department of Mineralogía y Petrología, Universidad de Granada, Granada, Spain. ²Institut für Mineralogie, Universität Münster, Münster, Germany

Stone deterioration is due to a number of physical, chemical, and biological weathering mechanisms. In particular, the physical damage caused by soluble salts, i.e., the so-called “salt weathering”, is primarily due to the mechanical pressure exerted by salt crystals when they grow in a confined space (pore).^{1,2} This pressure easily exceeds rupture modulus of most ornamental materials, leading to their crumbling and

disintegration.³ Salts have also been related to chemical rock decay due to enhanced mineral dissolution.¹ Unfortunately, research on methods to mitigate salt damage has not kept up with advances in understanding of the mechanism of damage.² As a result, most existing conservation methods have been only partially successful.

Recently, the use of crystallization inhibitors (additives) has been proposed as a new means to halt and/or mitigate salt damage.^{2,4,5} However, very little is known about the effects of organic additives on the crystallization of highly soluble salts. Even less is known on the effects of these compounds on mineral dissolution induced by salt solutions. Dynamic information acquired at the nano- to micrometer scale using scanning microscopy techniques is critical to our understanding of both the interactions between organic compounds and highly soluble salts, and the interactions among salts, additives and stone support (e.g., effects of additives on chemical weathering).

In this work environmental scanning electron microscopy (ESEM) and atomic force microscopy (AFM) are used to study *in situ*, at high magnification, the effects of organic additives (phosphonates, carboxylates, and polyacrylates) on the crystallization of magnesium sulfate, a highly damaging salt, as well as on the salt-induced dissolution of calcite surfaces. Calcite was selected because this mineral is the main constituent of limestones and marbles, extensively used in the architectural and sculptural heritage.

Habit and size distribution of sulfate crystals, and real-time changes taking place during crystallization or hydration/dehydration events in the presence or

absence of additives, were studied using an ESEM coupled with Peltier and heating stages. Important changes in epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) morphology, from equilibrium-shaped bulky forms to acicular-shaped crystals were observed (Figure 1) when crystallization occurred without and with additives, respectively. The rate of volume shrinkage and crack density development during epsomite thermal dehydration were reduced in the case of additive-doped crystals. These results indicate a strong interaction between magnesium sulfate and some of the additives that act as nucleation inhibitors and habit modifiers.

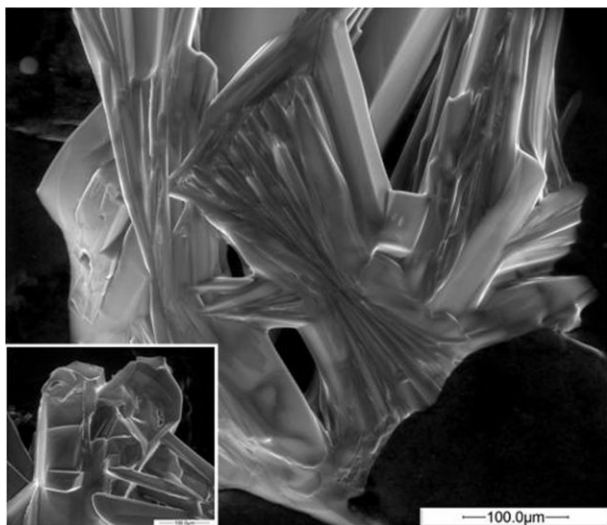


Fig 1. Photomicrographs of epsomite crystals directly precipitated in the ESEM chamber from: a) saturated MgSO_4 solution (inset) and b) saturated MgSO_4 solution + 0.01 M diethylenetriaminepentakis-(methylphosphonic acid) (pH 8).

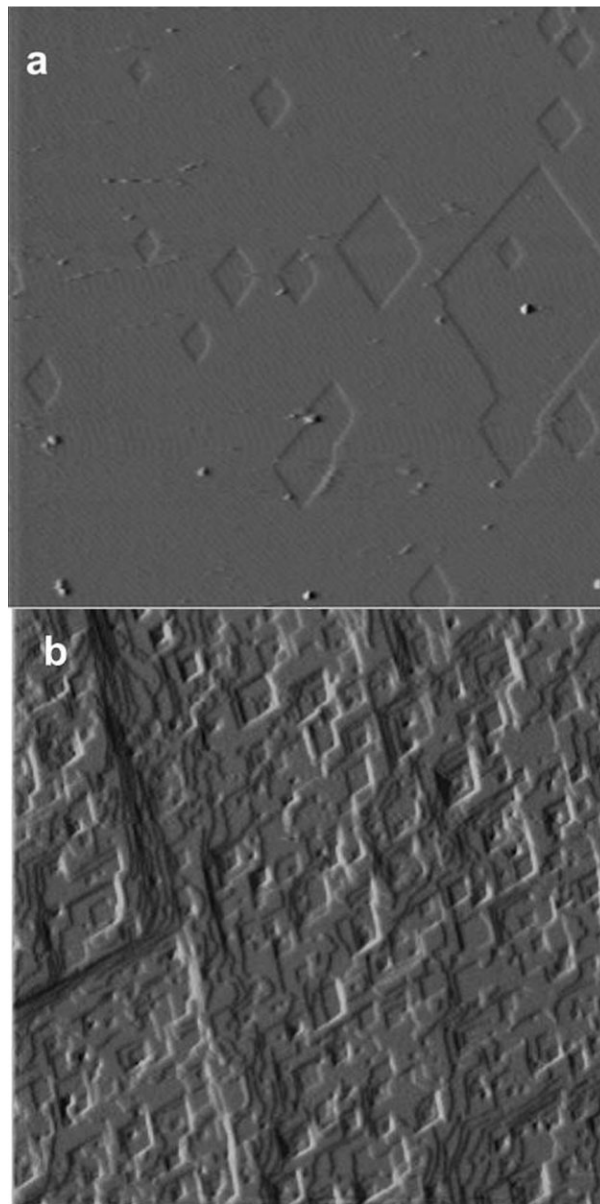


Fig 2. AFM deflection images of calcite dissolution in the presence of: a) water and b) 1M MgSO_4 solution (the side of each photomicrograph is 5 μm).

AFM experiments were conducted in a fluid cell using calcite cleavage surfaces in contact with solutions of MgSO_4 in the presence and in the absence of different additives. MgSO_4 increases calcite dissolution rate as well as the density and depth of etch pits (Figure 2). AFM deflection images of calcite dissolution in the presence of: a) water and b) 1 M MgSO_4 solution (the side of each photomicrograph is 5 μm). This confirms that magnesium sulfate induces chemical weathering. In the presence of additives, the dissolution rate was reduced. This research strives to contribute to the establishment of a scientific basis that may help in the development of a new conservation methodology based on the use of organic additives for preventing salt damage affecting ornamental stone.

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Focused Ion Beam Microscopy

Membrane folding by He^+ ion implantation using a focused ion beam

W.J. ARORA,¹ S. SUIBRANDIJ,² L. STERN,²
H.I. SMITH,¹ G. BARBASTATHIS¹

¹Massachusetts Institute of Technology, Cambridge, MA, USA. ²ALIS Corporation, Peabody, MA, USA

We used ALIS Corporation's He^+ focused ion beam microscope to implant He^+ ions into selected areas of 150nm-thick free-standing silicon nitride membranes. High dose ion implantation ($>10^{17}$ ions/cm²) caused the membranes to fold based on the area implanted and the dose given (Figure 1). Varying the ion energy caused the membranes to fold either up or down (Figure 2). The radius of the folds is approximately

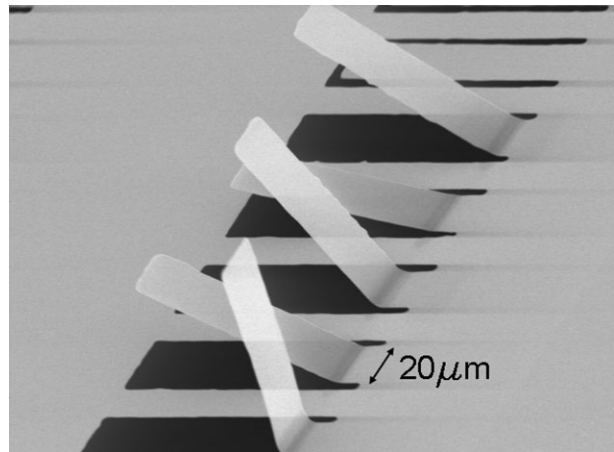


Fig 1. A set of 150 nm-thick silicon nitride cantilevers implanted with He^+ ions at 30 keV. The implanted areas are rectangular, near the base of the cantilevers. The length of the area is a constant 25 μm while the width varies. The ion dose also varies. From top to bottom, these values are: 1 μm , 2.5×10^{17} ions/cm²; 1 μm , 7.5×10^{17} ions/cm²; 2 μm , 2.5×10^{17} ions/cm²; 4 μm , 2.5×10^{17} ions/cm².

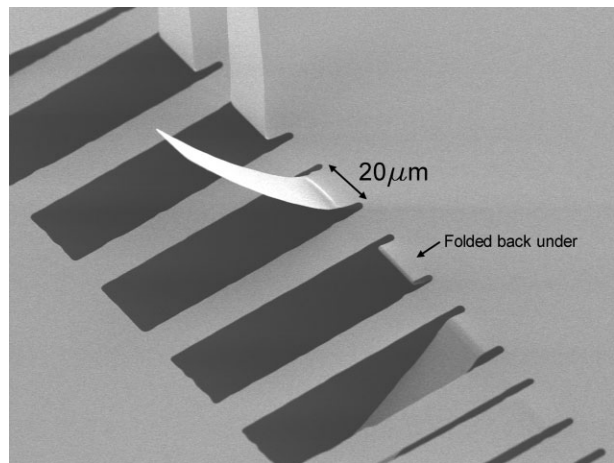


Fig 2. A set of 150 nm-thick silicon nitride cantilevers in which the ion dose and implant area was fixed at 2.5×10^{17} ions/cm² and $20 \times 4 \mu\text{m}$ while the acceleration voltage varied. From top to bottom, the acceleration voltages were: 22.5, 18.5, 14.5, 10.5, 6.5 and 2.5 kV.

1–2 μm . In most cases, the implantation did not visibly damage the membrane.

We modeled the implantation using SRIM¹ and theorize that the implantation creates a compressive stress proportional to the implanted ion concentration. Since the ion concentration varies through the thickness, a bending moment is created in the membrane. Higher dose implants create more stress and fold the membrane to larger angles (Figure 1). Changing the ion energy changes the projected range of the implantation. Ions implanted near the bottom of the membrane fold