Clays and Clay Minerals, Vol. 46, No. 4, 414–422, 1998.

THE ROLE OF SEPIOLITE-PALYGORSKITE IN THE DECAY OF ANCIENT EGYPTIAN LIMESTONE SCULPTURES

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Abstract—An ancient Egyptian limestone sculpture was found to be undergoing major structural decay when stored in a museum environment. Mineralogical and petrographic analysis of the limestone showed a high proportion of clay (≥10% by weight) that was concentrated along bedding planes. The clay fraction consisted mostly of sepiolite (>90%) and palygorskite (<10%). Minor quantities (≤1%) of soluble salts (NaCl and $NaNO_3$) were also found. Wetting/drying with distilled water and relative humidity cycling resulted in the same delamination cracking damage as that observed in the museum environment. Thermomechanical analyses (TMA) confirmed that the damage was due to expansion (>4.5%) parallel to bedding planes when the limestone was immersed in water. The expansion due to swelling of the clays was directly observed at high magnification in an environmental scanning electron microscope (ESEM) when wetting/drying cycles were performed. X-ray diffraction (XRD) analysis showed that crystalline swelling of sepiolite occurred. This was determined by a shift of *(110)* reflection (from 12.07 to 12.20 Å) and a decrease of *(060)* reflection (4.47 Å, to 4.44 and 4.41 Å), when in contact with ethylene glycol (EG) and dimethyl sulfoxide (DMSO), respectively. Swelling also occurred due to hydration of the clay surfaces and to electrostatic forces between clay particles, which, it was assumed, was promoted by the presence of Na counterions in water solution. Possible treatments for the conservation of these artistic objects are proposed and discussed.

Key Words—Clays, Egyptian Sculptures, ESEM, Limestone Decay, Polygorskite, Sepiolite, Swelling.

INTRODUCTION

Damage produced by cyclic swelling and shrinking of clays commonly found as minor components in ornamental and building stone is a major problem in the conservation of cultural heritage (Dunn and Hudec 1966; Caner and Seeley 1978; McGreevy and Smith 1984; Wendler et al. 1991; Martin-Patino et al. 1993; Kuhnel et al. 1994; Ruiz et al. 1995; Brattli and Broch 1995).

We studied one type of clay-containing Egyptian limestone stela from Naga el-Deir (Abydos/Thebes region) which exhibits an ongoing problem of deterioration that is evidenced by continuous delamination of the surface. The stela was acquired from archeological investigations carried out in a cemetery in Naga el-Deir early in the 20th century. It has been noted that this Egyptian sculpture, as well as many others carved from the same limestone (Thebes-Abydos limestone) and stored in different museums (Metropolitan Museum of Art, New York; British Museum, London; Phoebe Hearst Museum of Anthropology, Berkeley), develop the same pattern and degree of decay, even though they were not fully exposed to an outdoor environment (Charola et al. 1982; Bradley and Middleton 1988; Rodriguez-Navarro et al. 1996). In fact, during the time these limestone sculptures were stored in the museum environment, they experienced a complete loss of the carved surface relief, while being subjected only to the relative humidity and temperature changes that occurred in the storage areas. According to previous studies carried out on Thebes-Abydos limestone sculptures (Oddy et al. 1976; Helms 1977; Charola et al. 1982; Hanna 1984; Bradley and Middleton 1988; Middleton and Bradley 1989; Miller 1992), it was thought that most of the observed damage was due to cyclic crystallization of small quantities of salt (sodium chloride and sodium nitrate). In fact, such sculptures had been treated and desalinated by aqueous poulticing, but the decay process was not arrested, as evidenced by major loss of surface stone after storage for a period of years. Bradley and Middleton (1988), studying various types of Egyptian limestone sculptures in the collection of the British Museum that exhibit similar deterioration, pointed out that the mineralogy, and especially the clay content, should play a role in the susceptibility of this stone to decay.

In a previous work (Rodriguez-Navarro et al. 1996) some preliminary results on the analysis of the decay mechanism of this material were presented. In this paper, new analyses demonstrate that the original hypothesis, that is, the swelling of the clay minerals in this limestone, is the principal mechanism responsible for the observed damage.

The aim of this work is to identify and characterize the clay within this stone and demonstrate its role as the main contributor for its decay. In this paper we present and discuss data showing that normally nonexpandable clays (sepiolite and palygorskite) can promote significant damage due to swelling (osmotic swelling), a process that has been extensively reported in the case of expansive clays (smectites), but not in the case of sepiolite and palygorskite.

MATERIALS AND METHODS

Samples from an Egyptian limestone stela dated to the II to IV Dynasty (2720–2150 BC) from the Phoebe Hearst Museum (Berkeley, California) were studied by means of optical microscopy, XRD, ESEM and transmission electron microscopy (TEM) with energy dispersive spectrometry (EDS) microanalysis.

The clay fraction was extracted using the following experimental protocol: 50 g of crushed limestone were treated with 1 *M* acetic acid and the acid-insoluble residue was washed repeatedly with distilled water. The silt (2–20 μm particle size) and clay (<2 μm particle size) fractions were separated by centrifugation. Oriented clay aggregates (air-dried, EG- and DMSO-solvated, and after heating to 550 °C) were prepared. XRD analysis of the oriented clay aggregates was performed with a Philips PW-1710 diffractometer, equipped with a graphite monochromator and automatic slit, using Cu*K*α radiation. Silicon powder was used as an internal standard. The clay content was calculated from the weight of the clay fraction following drying at 90 °C for 24 h. The clay fraction morphology and chemical composition were studied by means of TEM with coupled EDS (TEM-EDS, Philips model CM20).

The high magnification study of the *in situ* dynamics of clay swelling was performed using an environmental scanning electron microscope (ESEM, ElectroScan, Model E-3) by treating limestone samples (2 × 4 × 4 mm) with distilled water (using a syringe) after they were placed in the ESEM chamber at low vacuum (2 torr). Additionally, repeated condensation-evaporation cycles were performed by increasing (up to 5.5 torr) and reducing (to 2.0 torr) the ESEM chamber pressure while maintaining the sample at constant temperature (1.5 °C) using a cooling stage (Messier and Vitale 1993). The expansion of the pure clay (extracted from the acid-insoluble residue and air-dried for 48 h) when in contact with water (following condensation of water in the ESEM chamber) was also observed by means of the ESEM. The same experiment was performed after adding a 1% by weight NaCl solution to the pure clay (1 cc of saline solution was added to 1 g of pure clay), following drying at room temperature and before introducing the sample into the ESEM chamber. Numerous still and video images were recorded before, during and after water treatment.

To observe stone damage due to contact with water, wetting/drying cycles were performed by immersing 5 samples (2 × 3 × 4 cm) in distilled water for 4 h, then drying for 20 h in an oven at 90 °C. Most of the samples collapsed after the first cycle, but some withstood 3 cycles.

In order to reproduce the damage mechanism of the limestone under conditions similar to those in the museum environment, 4 Egyptian limestone blocks (2 × 3 × 5 cm) were placed in a chamber where they were submitted to cyclic relative humidity changes (RH ranging from 40% up to 90%; each cycle lasting 8 h; total number of cycles 100). Damage was evaluated by weighing the material that fell off of the stone surfaces. Total weight loss was expressed as a percentage of the original weight of the samples.

Total expansion due to water absorption of the stone was estimated using TMA. Four limestone samples (5 × 5 × 5 mm) were tested. Each sample was placed in the TMA sample holder with the bedding planes parallel to the bottom and was allowed to equilibrate in the laboratory environment (30 °C and 55% RH) for 2 h. Then, distilled water was added and the isothermal linear expansion of the sample was recorded using a Mettler TA300 TMA instrument. When maximum expansion was reached, the sample was dried and contraction of the sample was recorded. Two wetting/drying cycles were performed for each sample and the results were averaged.

The stone compressive strength (for both dry and wet samples) was evaluated using an Instron Model 4201. Ten samples were cut (20 × 20 × 40 mm) and tested after drying in an oven at 80 °C overnight. Half of the samples were tested after immersion for 30 min in distilled water.

RESULTS

Geological Provenance of the Egyptian Limestone

The Egyptian limestone studied belongs to the upper member of the early Eocene Thebes formation (Amer et al. 1970; Said 1962; Said 1990) and was quarried at Naga el-Deir (Abydos/Thebes region, Egypt). This member is made up mostly of marly, cryptolaminated and laminated limestone, with rare shelly limestone beds, and horizons of flints and silicified concretions. Its thickness varies from 98 to 120 m. This member was extensively quarried in ancient Egyptian times for building and sculptural purposes. In fact, this material was easy to carve and was reported to be durable under the arid conditions of the upper Egypt (Rutherford 1988). Many tombs in the Valley of the Kings, as well as in the Valley of the Queens, were cut following the bedding and fractures of this limestone formation. However, Rutherford (1988) reported considerable damage to the tomb structures due to flooding of the Nile River and subsequent expansion of the stone when in contact with water. These floods were reported to be responsible for the limestone salt uptake (Charola et al. 1982).

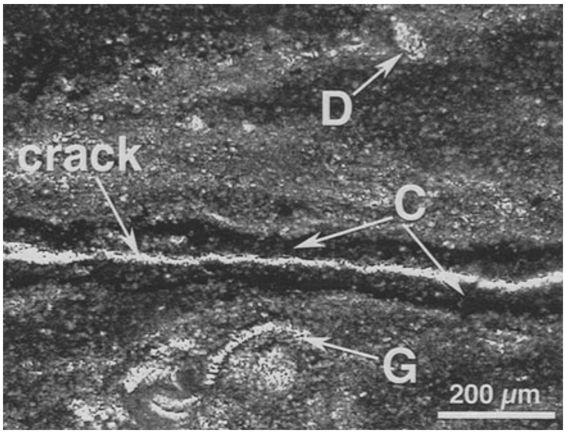

Figure 1. Optical micrograph of the Egyptian micritic limestone. Bedding planes are evident due to crack development where clays (C) are concentrated. Dolomite (D) rhombohedra and *globigerina* bioclasts (G) are visible in the limestone matrix.

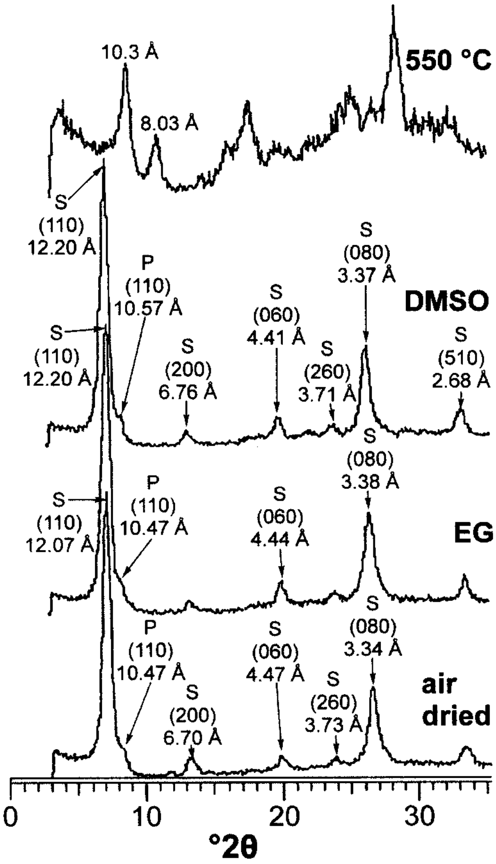

Figure 2. XRD patterns of air-dried, EG-solvated, DMSO-solvated (DMSO) and after heating to 550 °C oriented aggregates of <2 μm fraction of Egyptian limestone acid-insoluble residue showing principal peaks of sepiolite (S) and palygorskite (P) (Cu*K*α radiation, λ = 1.5405 Å).

Optical Microscopy Analysis

Optical microscopy of the Phoebe Hearst Egyptian limestone stela samples revealed this stone to be micritic limestone, containing mostly micritic calcite with a small amount of dispersed bioclasts (mostly foraminifera). A few dolomite rhombohedra were also seen dispersed within the matrix. Bedding planes appear clearly marked by parallel fractures and bands of dark color, probably due to the high concentration of clays and iron oxides deposited along these planes (Figure 1). No evidence for post-diagenetical dissolution and or stylolitization during compaction was observed, indicating that the concentration of the clay minerals along the bedding planes was sindepositional.

XRD Analysis

Powder XRD analyses of the bulk samples showed that calcite was the major phase (70%), with dolomite (<20%), clay minerals (<10%) and quartz (<5%) as minor phases. Also, minor amounts of halite and soda niter (<1% by weight) were detected. The acid-insoluble fraction of the limestone was 15.9% by weight. The insoluble fraction comprises mostly clay with small amounts of quartz. The silt (6.3% by weight) and clay (3.5% by weight) fractions were separated by centrifugation. XRD analysis of the silt fraction indicated the presence of clay with traces of quartz. Oriented aggregates of the clay fraction were prepared and analyzed by means of XRD. Figure 2 shows the results of the XRD analyses of the oriented aggregates. An intense peak appears at 12.07 Å, which changes to 12.20 Å after treatment with either EG or with DMSO, and disappears after heating to 550 °C, shifting to a broad peak at 10.30 Å. This peak was assigned to the (*110*) reflection of sepiolite. The sepiolite peak at 3.34 Å (*080*) shifts, after glycolation, to 3.38 Å, and the (*060*) peak at 4.47 Å shifts to 4.44 Å. A minor peak at 10.47 Å, corresponding to the palygorskite (*110*) reflection, shifts to 10.57 Å after DMSO solvation, and collapses after heating to 550 °C. Sepiolite and palygorskite are present at concentrations of >90% and <10%, respectively (as deduced from semiquantitative XRD analysis).

TEM-EDS Analysis

TEM-EDS analysis of the clay fraction confirmed the presence of sepiolite and palygorskite in all samples studied. A representative structural formula for the sepiolite based on the Brauner-Preisinger model (Brauner and Preisinger 1956) calculated from TEM-EDS analyses (Table 1), is:

$$(Si_{11.73}Al_{0.27})(Mg_{7.84}Al_{0.04}Fe_{0.09})O_{30}(OH)_4(OH_2)_4\text{-}$$

$$(Ca_{0.09}K_{0.03})\cdot(H_2O)_8$$

The average SiO_2/MgO ratio (2.40 ± 0.08), falls close to the theoretical 2.23, indicating little substitution of

Table 1. Representative element composition of sepiolite and palygorskite fibers from the Naga el-Deir stela, determined using TEM-EDS microanalysis. Data in wt%.

Analysis†	Mg	Al	Si	K	Ca	Fe	Na
Sepiolite #1	35.284	1.236	60.742	0.306	1.269	1.163	nd
Sepiolite #2	34.742	1.345	60.619	0.871	1.279	1.144	nd
Sepiolite #3	36.562	0.902	58.238	0.430	1.554	2.313	nd
Sepiolite #4	33.019	0.817	63.822	0.208	0.994	1.140	nd
Sepiolite #5	34.927	0.195	61.758	0.219	1.564	1.337	nd
Sepiolite #6	35.439	1.548	61.249	0.184	0.688	0.892	nd
Palygorskite #1	17.435	11.655	57.076	4.156	0.595	7.849	1.236
Palygorskite #2	17.775	10.588	57.414	4.710	2.035	6.279	1.988

† Microanalyses performed on different crystals in 2 samples; nd = not determined.

Si and Mg on both the tetrahedral and octahedral sheets. Also, the Al substitution in the tetrahedral sheet, as well as the Mg/Al ratio in the octahedral sheet, fall within the compositional ranges reported by Jones and Galan (1988) for typical sepiolites.

Due to the small amount of palygorskite in the Egyptian limestone, only a few EDS analyses were successful in characterizing the composition of this clay. This means that the palygorskite compositional data presented (Table 1) may not be representative. A structural formula for the palygorskite is:

$$(Si_{7.44}Al_{0.56})(Mg_{2.63}Al_{1.02}Fe_{0.51})O_{20}(OH)_2(OH_2)_4\text{-}$$
$$(Ca_{0.05}Na_{0.20}K_{0.39})\cdot(H_2O)_4$$

The composition of the palygorskite in the Egyptian limestone is very similar to that found by Wiersma (1970) in a desert environment (Jordan Valley, Israel). On the other hand, the palygorskite composition does not approach that of the model formula for the half-unit cell: $Si_8Mg_5O_{20}(OH)_2(OH_2)_4{\cdot}4H_2O$. In fact, the octahedral cation population is close to 4.0 (4.16). As pointed out by Weaver (1989), this is a common feature for most palygorskites.

In short, the composition of sepiolite and palygorskite in the Egyptian limestone stela is consistent with previous data for fibrous clays (Jones and Galan 1988; Weaver 1989).

Decay Tests

Immersion of the samples in distilled water resulted in fissure development parallel to the bedding planes and complete disintegration of the stone within a few hours. Relative humidity cycling in an environmental chamber led to almost complete destruction of the stone blocks, due to spalling and exfoliation of the surface skin and fracture development along the bedding planes. After 84 cycles, the average weight loss of the samples was 7.17%. After 100 cycles, complete destruction of 1 of the blocks was observed.

In Situ, High Magnification ESEM Dynamic Studies

The damage process described above was observed at high magnification by means of an ESEM. The ESEM results showed that cyclic wetting and drying of the limestone samples produce swelling and shrinking of the clays, processes that promote the development and broadening of fractures parallel to the bedding planes (Figures 3a and 3b). Also, this decay process affects the internal microtexture of the fibrous clays within the stone. The sepiolite and palygorskite fibers appear oriented perpendicularly to the bedding planes after fracture development due to cyclic wetting/drying in the ESEM chamber (Figures 3c and 3d). The ESEM studies demonstrated that, when wetted, the clay minerals accumulated along bedding planes within the stone expand and produce tensile stresses perpendicular to the bedding planes, leading to fissure development, which can be followed by stone delamination.

It was seen by means of ESEM that, when in contact with water, the fibrous clays alone (extracted from the acid-insoluble residue) also expand and contract (Figure 4). This expansion was strongly enhanced in the presence of NaCl (added as a 1% by weight solution to the clay before performing the ESEM experiment) as is shown in Figure 4 (d–f). The cyclic swelling/shrinking of the fibrous clay due to condensation/evaporation in the ESEM drastically transformed the clay structure from partially oriented to disoriented, as can by seen in Figure 5. Disorientation of the sepiolite and palygorskite fibers was only observed in the samples of clay (alone) where NaCl solution was added.

TMA and Compression Tests

Figure 6a shows the results of the TMA. When immersed in distilled water (30 °C) for less than 1 h, the stone swelled about 3% in the direction perpendicular to the bedding planes. When the first wetting/drying cycle was completed, a 0.3% permanent mechanical deformation was noted. A second wetting/drying cycle produced a faster and greater expansion of the sample (up to 4.5%), indicating that the structural damage created in the first wetting/drying cycle enhances the damage produced in the following ones.

Compression tests show that a large strength reduction was achieved when tested samples were wet. The

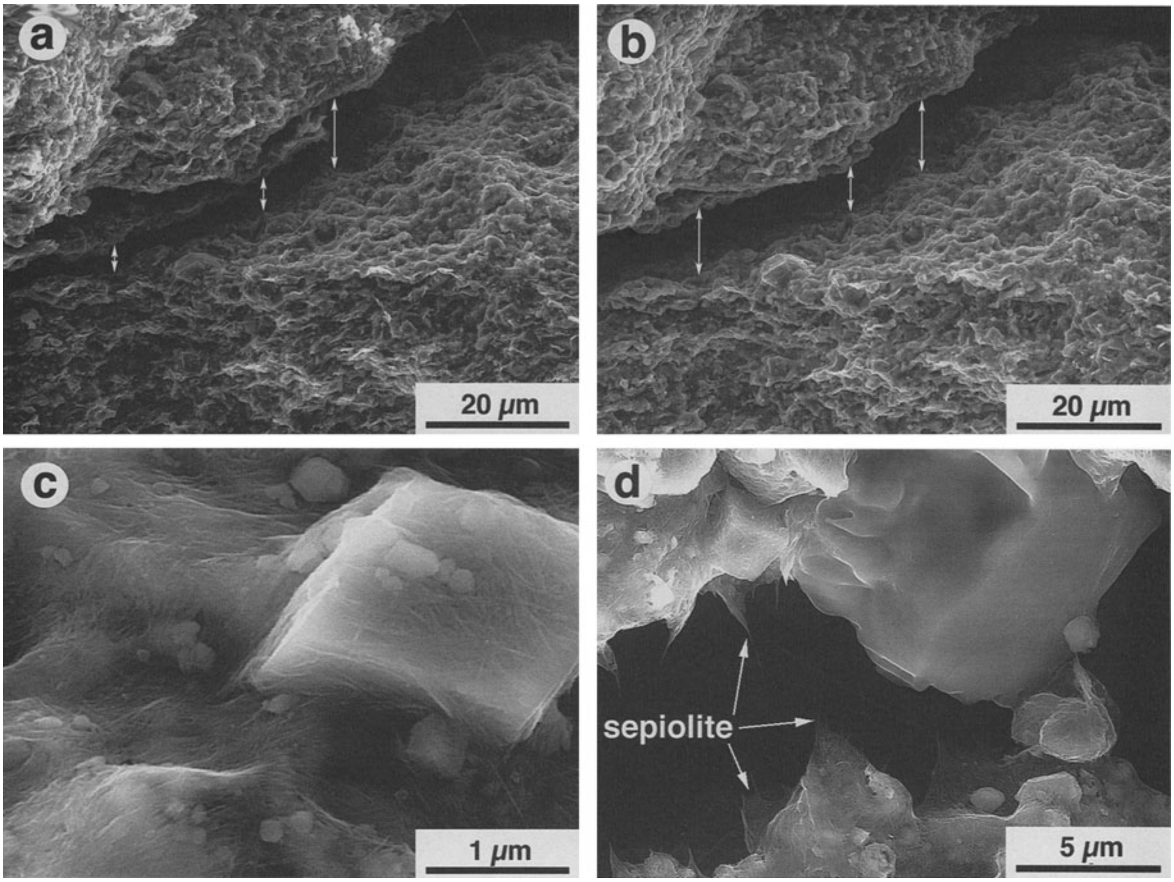

Figure 3. ESEM micrographs of the process of crack development in the Egyptian limestone stela. Before (a) and after (b) a condensation/evaporation cycle. Clay distribution in a pore (covering a calcite grain), and along a crack after 1 condensation/evaporation cycle (c and d, respectively).

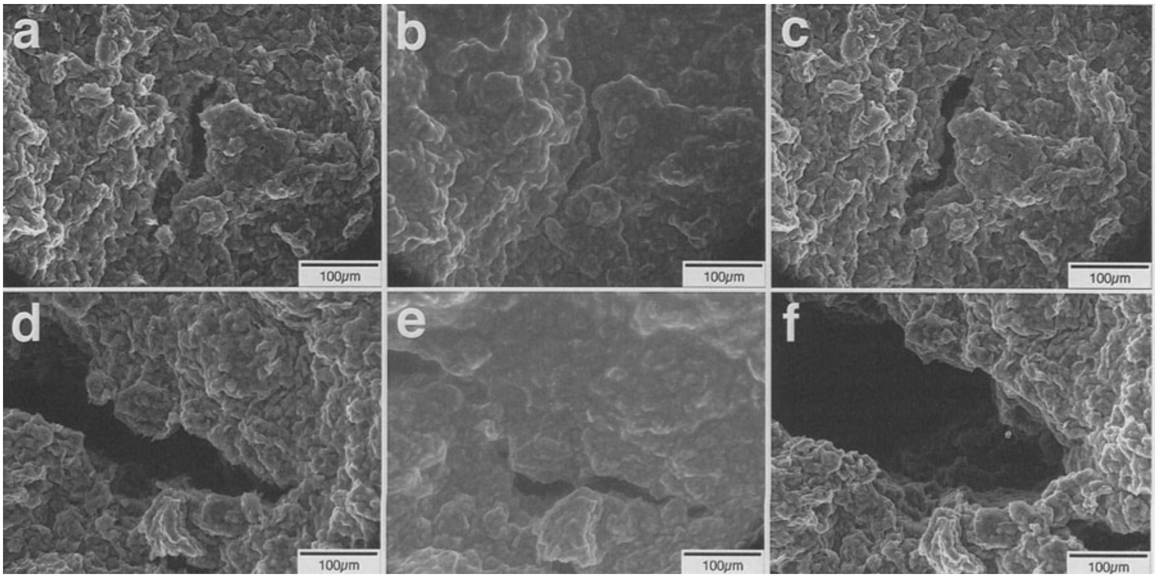

Figure 4. ESEM sequential micrographs of swelling and shrinking process of the clay fraction alone, without (a–c) and with NaCl (d–f). Before (a), during (b) and after (c) a condensation/evaporation cycle without NaCl; and before (d), during (e) and after (f) a condensation/evaporation cycle in the presence of NaCl.

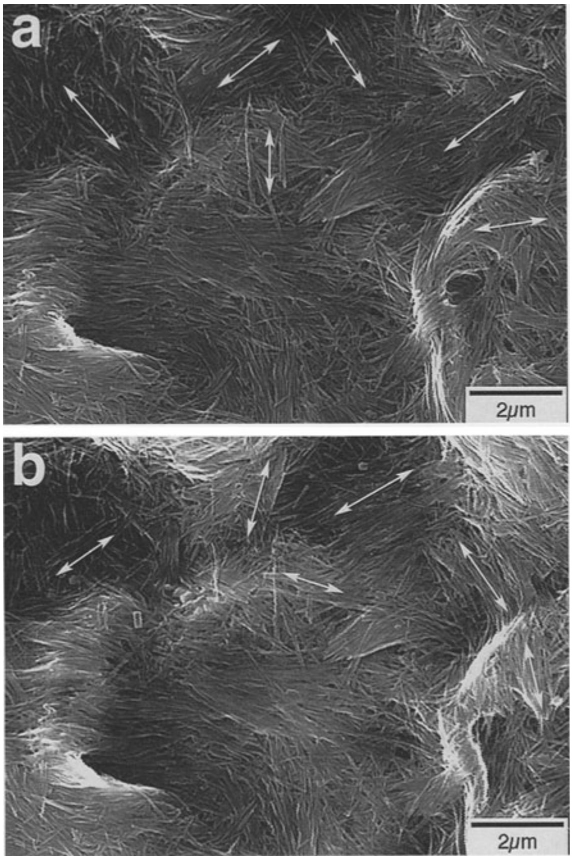

Figure 5. Detail of the microstructure in a sepiolite (plus palygorskite) sample (clay alone) before (a) and after (b) a wetting/drying cycle in the presence of NaCl. Arrows indicate orientation of the clay fibers.

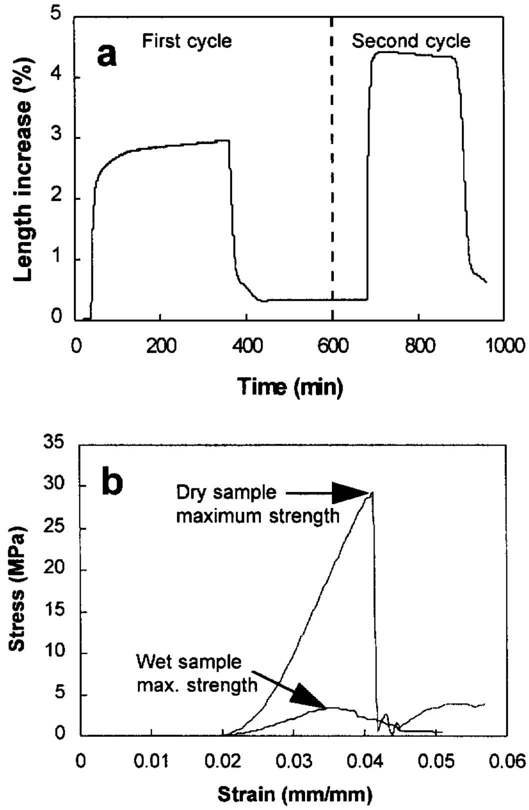

Figure 6. a) Results of the TMA of Egyptian limestone (2 wetting/drying cycles); and b) strain versus stress graph for the Egyptian limestone (both dry and wet samples).

average dry compressive strength was 29 MPa. The wet strength was 3.5 MPa. Figure 6b shows the strain/stress curves for both dry and wet Egyptian limestone samples.

DISCUSSION

The experimental results lead us to consider that the presence of clays is the main factor that is responsible for the damage observed in the limestone materials studied. This damage mechanism involves the fixation of water molecules to the fibrous clay surface and results in eventual swelling. In general, swelling of clays is a well-known phenomenon in smectites and vermiculites as well as in mixed-layer clays (Norrish 1954; MacEwan and Wilson 1980), where these minerals undergo both intraparticle (crystalline) swelling and interparticle (osmotic) swelling (van Olphen 1977; van Olphen 1987; Laird 1996). However, Low (1987) reported that clay swelling can take place at the clay-water interface as a result of hydration forces due to the adsorption of ordered water molecules on the clay surface, even in nonexpandable clays. Yatsu (1988) reported that the latter mechanism strongly contributes to the decay of many nonswelling clay-rich rocks (illite- and kaolinite-rich shales, tuffs and mudstones) submitted to wetting/drying cycles.

Crystalline (intraparticle) swelling resulting in a volume change of fibrous clays in the presence of polar organic liquids (EG, for example) has been reported previously by Watts (1976) and Jeffers and Reynolds (1987) in the case of palygorskite, and by Fleischer (1972), Guven and Carney (1979) and Jones and Galan (1988) for sepiolite. Results from XRD analyses confirmed that sepiolite in the Egyptian limestone studied here swells (crystalline swelling) to a certain extent (~1% unit cell expansion) when in contact with EG and DMSO. However, this limited swelling does not explain the enormous expansion of this stone (as well as the clay fraction alone) when submitted to wetting. It can be hypothesized that, in this case, the hydration pressures generated by the adsorption of water molecules on the clays' external surface (Low 1987) will result in swelling of the clays within the stone. Additionally, in the presence of an electrolyte, an electrical double layer can be created at the clay-solution interface (van Olphen 1977), resulting in swelling due to electrostatic repulsion forces between nearby fibrous clay particles (Shidharan and Satyamurty 1996).

Sepiolite and palygorskite can adsorb water and cations on their external surfaces (Prost 1976; Newman 1987). The hydration of the fibrous clay surface will result in an initial swelling. However, the presence of NaCl and $NaNO_3$ within the stone offers a supply of Na ions to the solution formed when water (as vapor or as liquid phase) enters the pore system of the limestone. The Na ions can act as counterions and, once they are hydrated, can contribute to the swelling of single fibrous sepiolite and palygorskite crystals (crystalline swelling). Then, once the hydration of the clay surface is completed, an electrical double layer will be formed, resulting in interparticle swelling due to electrostatic repulsion forces between nearby sepiolite (and palygorskite) particles. This can create sufficient swelling pressure to damage the layered structure of the stone. With regard to the effects of soluble salt in clay swelling and the resulting damage to ornamental stone, Chatterji et al. (1979) reported that the formation of Na-clay (smectite) by an ion-exchange process suffered after the stones were placed in a building and exposed to NaCl or Na_2SO_4. This process promoted the splitting and breakdown of clay-rich limestones (especially those where the clays were concentrated along the bedding planes). Additionally, McGreevy and Smith (1984) observed that the presence of sodium salts (sulfates and chlorides) within layered smectite-rich limestones resulted in significant damage to the stone upon wetting.

The ESEM dynamic analyses confirmed our working hypothesis regarding the role of sepiolite and palygorskite as a decay factor, since it was observed that addition of water to the limestone produced a considerable structural expansion in the layers where the sepiolite and palygorskite minerals were concentrated. Additionally, the ESEM experiment using the clay alone demonstrated the role of the fibrous clays in the buildup of swelling pressure in the presence of small amounts of salts, and the resulting damage to the stone structure. These results also confirm that swelling of fibrous clay particles by adsorption of H_2O molecules and Na ions on the clay particle surfaces, creating an electrical double layer and resulting in repulsion forces between adjacent clay fibers, is the principal damage mechanism of the limestone.

It should be mentioned that, within the Egyptian limestone, the clay grains are not well cemented (as oppose to the calcite grains) and, thus, the clay fibers can attract water to all of their surfaces, whereas the carbonates react as a more homogeneous block. Additionally, sepiolite and palygorskite both have a very large external surface areas (Jones and Galan 1988) and can adsorb large amounts of water on their external surfaces, which contributed to the slaking of the stone. The contrast of clay-carbonate aggregate behavior will result in a differential decay concentrated within the clay-rich areas, hence resulting in the delamination of the stone along the clay-rich planes.

Regarding the role of the salts in the decay of this Egyptian limestone sculpture, it must also be considered that hygroscopic salts promote water condensation at relative humidities lower than 100%. Deliquescence of either NaCl and $NaNO_3$ can take place at 75% RH, but deliquescence of a mixture of both salts occurs at relative humidities of ~60% (Arnold 1981; Price and Brimblecombe 1994). This means that liquid water can be present within the pore system of the Egyptian limestone at relative humidity values >60%. Thus, when relative humidity in the museum goes above this value, damage to the limestone sculptures by swelling may be produced, resulting in the formation of flakes and scales observed in the samples studied and wherever this stone type was used for sculptural purposes.

Results of the compression tests show that the strength of the limestone is strongly reduced in the presence of water. In fact, the wet strength of the limestone is 10 times smaller than the dry strength. Kowalski (1975) reported that water promotes a considerable reduction of the stone strength because it reduces the bonding energy between grains and at the same time induces stress-corrosion phenomena, resulting in crack propagation. Hence, in the presence of water the swelling pressure of the clays can easily overcome the wet strength of this stone.

Some treatments that were designed to stabilize the clay structure within the stone to avoid further damage by swelling/shrinking (such as application of surface coating or wax treatments) were not successful (Charola et al. 1982; Bradley and Middleton 1988; Miller 1992). Among possible alternative solutions is the strict environmental control of the temperature and relative humidity in the storage room. A treatment that would reduce the swelling capacity of the clay by exchanging the counterion (Na) for another with fewer hydration layers around the cation (Ca or Mg), in theory, should stabilize the clay structure by inducing aggregation of the clays and reduced swelling (Permien and Lagaly 1995). However, a practical method for accomplishing this without water-induced destruction of the stone has not been proposed. Other possible conservation methods involve the application of surface active agents (surfactants) that have been reported to influence both the rheological and swelling properties of clays (van Olphen 1977; Permien and Lagaly 1995). By being fixed on the clay surface, these surface active agents influence the counterion distribution in the Stern and the diffuse ionic layers, resulting in a reduction of the swelling capacity of the clays. Using a surfactant, Wendler et al. (1996) were able to reduce the swelling capacity of the clay-rich tuff used in the carved statues (Moai) on Easter Island (Chile).

CONCLUSIONS

Limestone from a Naga-el-Deir stela, which exhibits a high rate of decay due to spalling of carved surfaces, contains more than 10% (by weight) of clay minerals concentrated along the bedding planes. The clay mineralogy, morphology and composition were determined by using XRD and TEM-EDS. These data confirmed the presence of sepiolite (as a major clay mineral) and palygorskite (in minor amounts).

Wetting/drying laboratory tests using distilled water, relative humidity cycling, TMA and dynamic ESEM studies corroborate the working hypothesis that the hydration of sepiolite and palygorskite surfaces and the resulting swelling are ultimately responsible for the observed fissure development and damage suffered by this stone.

Dynamic ESEM analysis allowed direct observation at high magnification of the limestone damage process that occurred when water was applied. Swelling and shrinking of the clay alone was also observed by performing wetting/drying cycling in the ESEM chamber both in the presence of NaCl and without NaCl. Maximum swelling of sepiolite and palygorskite was achieved in the presence of monovalent counterions (Na), which suggests that an electrical double layer was established on the surface of the clay particles. Additionally, water strongly reduces the strength of the stone, thus facilitating stone disintegration due to even moderate clay swelling pressures. This results in considerable damage to the stone structure and large changes in the textural arrangement of the sepiolite and palygorskite. The interparticle swelling of sepiolite and palygorskite seems to be similar to that observed in other nonswelling clays such as illite and kaolinite.

It is recommended that, for conservation of artifacts of this composition, strict environmental control (especially low relative humidity) be imposed in museum storage rooms, and that extraction of the salt present using water or poultices, which has been done as a routine procedure for years, be discontinued since this promotes the damage generated by swelling of the clays. Conventional treatments, using coatings such as wax, have not been shown to be useful. New, unconventional treatments to avoid swelling of the clays should be considered for the protection of these sculptures. Further research is needed to develop effective and long-lasting solutions.

ACKNOWLEDGMENTS

This work was performed at the Getty Conservation Institute, and one of us (CRN) was supported by a postdoctoral fellowship (MEC, Spain) no. PF94 24232705, and by the DGICYT project no. PB 93/1090. We are indebted to M. W. Fang of the Phoebe Hearst Museum of Anthropology (Berkeley, California), who supplied the Naga el-Deir stela samples, and to M. Schilling, who performed the TMA. TEM-EDS analyses were performed at the Technical Services of the Granada University, Spain. We are indebted to B. McCarthy for the critical review of the original manuscript.

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(Received 21 March 1997; accepted 3 November 1997; Ms. 97-025)