



Review

Degradation and conservation of clay-containing stone: A review

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ABSTRACT

Significant progress in the understanding of the different degradation processes affecting building and ornamental stone has taken place in recent decades. However, some weathering phenomena still are not fully understood, which hampers the development of effective stone conservation treatments. One of these cases, stone damage associated with the presence of swelling clays, is reviewed here. Swelling clays cause damage when subjected to wetting/drying cycles, commonly resulting in stone scaling, flaking, spalling, exfoliation and/or delamination. Examples of this damage process and the mechanisms proposed for its development, as well as the key factors that control its origin, evolution and severity are presented and discussed. Alternative or complementary processes that may also lead to stone damage due to expansion/contraction cycles are also discussed. Finally, conservation treatments applied to halt or minimize clay swelling damage are reviewed. It is shown that traditional conservation materials such as polymers and alkoxysilanes applied to protect and/or consolidate damaged clay-containing stones typically have little effectiveness. Alternative treatments based on the application of clay swelling inhibitors, and a novel green conservation approach based on bacterially-induced formation of CaCO₃ cement and associated production of exopolymeric substances, recently proposed to prevent/control clay-related damage of tuff stone at the ancient Maya site of Copan, are presented and discussed.

1. Introduction

Significant progress in the fundamental understanding of the mechanisms and effects of the different weathering processes affecting cultural heritage materials, stone in particular, has been made over the last decades [1–3], while advancement in the development and application of different, many of them novel, conservation treatments has also taken place [1,4–7]. Among the different deleterious weathering processes affecting stone, humidity-related expansion and contraction upon cyclic wetting and drying has attracted considerable interest. In particular, physical weathering of clay-containing stones such as limestones, sandstones and volcanoclastic tuff has been often attributed to strains and associated differential stresses arising from cycles of swelling and shrinkage of clays [8–10]. Despite its recognized importance, our current knowledge regarding how this damage takes place is still incomplete. Even less is currently known on ways to halt or minimize its deleterious effects. Indeed, only a few conservation treatments have been developed and tested so far, which specifically tackle this damage process. Here we will present an overview of recent progress on the understanding of damage induced by clay swelling, as well as the conservation materials and methods developed and applied to prevent, halt

or minimize its effects.

2. Stone weathering

Building and sculptural stone is subjected to a range of physical, chemical and biological weathering processes that result in material degradation and loss, thereby endangering its survival [1,11–14]. Physical weathering processes, such as salt crystallization damage, freezing of water, differential thermal expansion, or moisture expansion associated with clay swelling, create stresses in porous building materials that result in crack opening and propagation, ultimately leading to material loss, or even structural failure [1,3,15–17]. Similarly, chemical weathering processes such as dissolution, hydrolysis, and/or redox reactions [18], associated with the interaction of aqueous solutions with the different mineral components of building materials can result in the weakening of sculpted or built stone structures leading to aesthetic changes and significant material loss [3,11]. This is even more marked in contaminated industrial areas and urban centers where air pollution contributes to chemical weathering upon interaction of acid pollutant gasses (i.e., SO₂, NO_x and CO₂) and particulate matter with the stone substrate of built structures or carved sculptures [19]. Last but not least,

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biodeterioration due to the interplay of chemical and physical weathering processes associated with the development of organisms, especially microorganisms, on and within building and sculptural materials can cause significant damage as well [13,20–22], but might also result in surface protection, as growing evidence is indicating [23–25]. Most of these weathering processes do not normally act alone. They tend to typically proceed in a synergistic way, leading to positive feedbacks that accelerate weathering, resulting in extensive material degradation.

In recent decades, it has been observed that all these weathering processes can be accelerated, directly or indirectly, by anthropogenic effects. Winkler [3] showed that increased air pollution since the Industrial Revolution has resulted in a marked increase in the rates of weathering (and material loss) of stone. This was exemplified by a porous calcareous sandstone sculpture at the Herten Castle, Westphalia (Germany), which in 1908, i.e., ca. 200 y after its emplacement, was in a relatively healthy state, but was almost defaced by the end of the 1960s due to acid rain and massive formation of black crusts (gypsum crusts) associated with air pollution. This example proved a direct link between human activities, particularly industrial-, heating- and traffic-related pollutant emissions to the atmosphere, and damage to cultural heritage. Moreover, the massive increase in anthropogenic CO₂ emission over the last 150 y and the associated climate change is also affecting cultural heritage in many ways [26]. For instance, it was predicted and later confirmed that the ongoing global warming is increasing the number of events resulting in deliquescence/precipitation of damaging salts affecting porous stone all over central and northern Europe [27,28]. Warmer and dryer conditions, especially in the Mediterranean area, could lead to salination of soils and ground water favoring capillary rise of saline solutions into monument walls, or increase evotranspiration leading to accumulation of salts in stone pores and resulting in increased salt damage [29,30]. Potentially, global warming and associated extreme weather events could foster not just salt damage, but other moisture-related decay processes such as clay swelling damage. In parallel, rising *T* can accelerate chemical weathering due to the fact that processes such as dissolution or hydrolysis show Arrhenius behavior (i.e., the rates of these chemical reactions increase with *T*) [18,31]. Similarly, biodeterioration could also be exacerbated by higher atmospheric CO₂ concentrations and global warming due to the fact that photosynthetic (micro)organisms (e.g., cyanobacteria) show enhanced bioactivity with rising CO₂ and most (micro)organisms accelerate their metabolism with increasing *T*. Indeed, climate change is having an impact on how biodeterioration affects building stones in different areas [32], for instance leading to stone “greening” in northern Europe [33]. These are just a few examples of what we will likely witness at a larger scale in the near future.

3. Clay swelling damage

3.1. The importance of clay swelling damage

Pioneering geomorphology research during the second half of the XXth c. underlined that several weathering forms affecting and shaping different rock outcrops in a range of natural environments could be related to expansion and contraction cycles due to humidity fluctuations in clay-containing rocks [34,35]. Polygonal cracking [36], tafoni [37], honeycombs [38], and spalling, as well as scaling and contour scaling [39] observed on sandstone outcrops in nature were related to the presence of clay minerals. Aiming at establishing a link between observed weathering features in natural rock outcrops and humidity-related processes, pioneering laboratory work using different clay-bearing rocks (sandstones and chemically weathered basalts) showed that crack development and damage could be achieved during wetting/drying cycles [40–42]. In parallel, mineralogical analysis of a range of building stone types showing surface flaking and scaling (i.e., detachment of sub-mm to mm-thick surface layers totally independent of the stone structure), exfoliation (i.e., detachment of multiple cm-thick

surface layers along stone bedding/structural planes), spalling (i.e., detachment of up to cm-thick layers sub-parallel to the stone surface), delamination (i.e., detachment of multiple thin stone layers sub-parallel to the stone surface), or contour scaling (i.e., detachment of mm- to cm-thick surface layers following the contour of stone surface features) (names of weathering forms after Vergés-Belmin [43]) (Fig. 1), revealed that, typically, they included clay minerals, normally in small quantities (commonly < 10 wt%) [8,9,44–51].

Importantly, such stones displayed a significant hygric and/or hydric expansion (i.e., expansion in contact with vapor or liquid water, respectively), which led to the conclusion that clay swelling/shrinkage following wet-dry cycles had to be involved in their degradation [8,9,52,53]. Stone expansion is easily quantified in the laboratory using a linear variable differential transformer (LVDT), which measures changes in the dimension of a stone sample (i.e., free swelling strain $\varepsilon = \Delta l/l$, where Δl is the length increase of a sample with initial length *l*) with an accuracy of (at least) $\pm 1 \mu\text{m}$ upon changes in relative humidity or upon immersion in water [10,51]. Such measurements showed that the free swelling strain of clay-containing stones could reach values of up to ~ 0.01 (i.e., 1% = 10 mm/m) [50], and, in extreme cases, values of up to ~ 0.05 [9,50]. Although there is not a well defined lower limit for the value of ε that can result in swelling damage, Jimenez-Gonzalez et al. [48] reported a threshold of 0.0015 for damage generation upon clay expansion considering that the product of this strain with the elastic modulus will typically exceed the (dry) tensile strength (or wet compressive strength) of most stone types.

Damage created by swelling clays present in building stone has been recognized for several decades as a major problem in the conservation of cultural heritage [50,51,54–58]. Damage to building and sculptural stone can occur even when the clay content in a particular stone is quite small [44,45,48,50,51,59]. Water penetrating within the pore system of the stone can produce swelling of the clays, and the resulting swelling pressure that macroscopically manifests itself as dimensional changes (expansion), can irreversibly damage the internal structure of the stone resulting in cracks formation and propagation (Fig. 2a). Repeated cycles of wetting and drying can lead to the almost complete destruction of the stone [8,9].

Much of the limestone, sandstone and tuff stones (among others) commonly used for building (e.g., dimensional stone) and sculptural purposes contains a small proportion of clays [46–48,50,54,59]. However, the clay content in some of these stone types can reach values of more than 10% [8,9,60]. Yet, even with ≤ 5 wt% clay, damage can be substantial, especially when the clays are concentrated along specific planes (e.g., bedding planes) surrounding the matrix minerals or being part of the stone natural cement [47,61] (Fig. 2b). This textural feature, resulting in an anisotropic swelling strain -maximum in a direction perpendicular to the plane where clays are concentrated and preferentially oriented- [62–64], and crack development (Fig. 2c) and widening/propagation (Fig. 2d–f) along such planes, seems to be particularly relevant. For instance, limestones with small amounts (1 up to 8 wt%) of swelling clay (smectite and illite/smectite interstratified clays) concentrated in stylolites, show extensive hydric swelling damage with cracks developing along the stylolite surfaces [65]. In some cases, proportions of swelling clays (smectite) ≤ 1 wt% have been claimed responsible for the limited durability of porous stones such as Melilli limestone, showing exfoliation damage in different monuments of Syracuse (Italy) [66]. In contrast, some limestones containing more than 30 wt% clay homogeneously distributed within the stone are very sound and stable [60].

Examples of this so-called clay swelling (or expansion) damage are numerous (Fig. 1). Just to name a few, it has been observed in limestone blocks at the Jaen’s Cathedral (Spain) (Fig. 1a–b)[62], ancient Egyptian limestone sculptures and stelae in the British Museum (London, UK), Metropolitan Museum (New York, USA) and Phoebe Hearst Museum (Berkeley, USA) [8,9], carved limestone rocks at the royal tomb of Seti I, Valley of the Kings, Luxor (Egypt) [67], or limestone rainscreen walls in

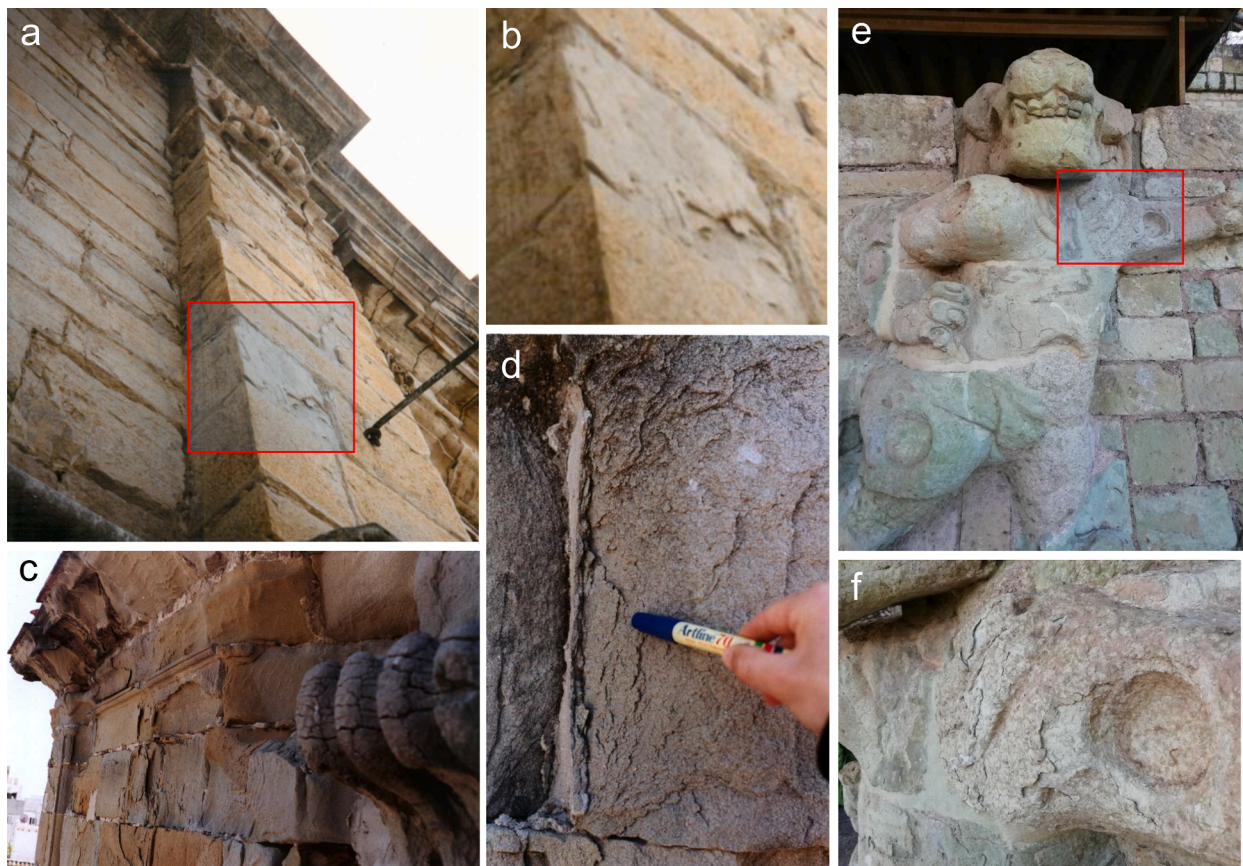


Fig. 1. Examples of stone damage associated with clay swelling/shrinkage. a) Micritic limestone at Jaen's Cathedral (Spain) showing scaling and delamination; b) Detail of the squared area in (a) showing scaling of the surface of the stone block. The stone includes smectites concentrated along the bedding planes (see below); c) massive fracturing and scaling of sandstone at Tarifa (Spain). See the cracks normal to the surface of carved areas on the right (i.e., resembling mud cracks); d) detail of scaling in sandstone. This stone includes smectite-illite interstratified clays, concentrated along bedding planes [47]; e) carved tuff stone figure at the Maya site of Copan (Honduras) showing scaling and loss of surface relief; f) detail (squared area in (e)) of scaling damage. This stone includes smectites (montmorillonite) [51]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

a modern building in Valencia (Spain) [68]; in several types of sandstones, such as Villamayor [58,69] and Tarifa (Spain) (Fig. 1c-d) [47,48], Meules (France) [70], Portland Brownstone (USA) [10], Villarod Molasse (Switzerland) [10], several German sandstones [49,71], Macigno sandstone (Italy) [46,72], Angkor Wat sandstone (Myanmar) [73,74] and Petra sandstone (Jordan) [75], as well as in sandstone used for roof tiling in NE Spain [76]; and very commonly, in volcanoclastic tuff stones [50]. This is for instance the case of tuffs making up the Moai sculptures in Rapa Nui (Easter Island) [45], Missions in California (USA) [77], ancient Roman and Ottoman constructions [78], as well as several monuments in central Europe [50,79,80] and Anatolia [50], including the Fairy Chimneys of Cappadocia (Turkey) [81], or some pre-Hispanic structures and colonial buildings in Mexico [82,83] and the Maya structures, sculptures and hieroglyphs in Copan (Honduras) (Fig. 1e, f) [51,84]. This phenomenon is rare in non-sedimentary stones such as igneous and metamorphic ones [85]. Nonetheless, humidity-related damage associated with minor contents of clay minerals in slate tombstones has been reported [86]. It has also been reported that the decay of the serpentinite (a metamorphic rock) stone used in the St. Maria dei Fiore Cathedral (Florence, Italy) is related to crack development upon expansion of the crysotile-antigorite-lizardite matrix in contact with water, despite the fact that these phyllosilicates are non-swelling [87].

Cyclic expansion and contraction of the outermost layers of the exposed stones in most cases leads to crack opening and propagation, ultimately resulting in material loss following delamination, scaling and/or spalling. Although such a type of physical weathering is typically related to the presence of swelling clays, there are reported cases where

moisture expansion damage (also resulting in delamination, scaling and/or spalling in the field) has also been observed in stones with no (swelling) clays. This has led to the hypothesis that other phases (e.g., zeolites) or mechanisms (e.g., solvation forces or the so-called disjoining pressure in micropores) can be involved in such a damage process [49,50,88,89]. In other cases, it is not totally clear what is the relative contribution of clay swelling to flaking or (contour) scaling damage as compared with other phenomena that can cause expansion (and contraction), as it is the case of thermal expansion [89–92]. Below we will evaluate the different processes proposed to explain this weathering mechanism, but first we will briefly describe the main structural and compositional features of clay minerals.

3.2. Clay minerals

Clays are phyllosilicates with size $< 2 \mu\text{m}$ and, typically, poor crystallinity [93,94]. They are made up of layers of two corner-sharing SiO_4 tetrahedra (the so-called Q^2 units) forming six-member rings, and layers of brucite ($\text{Mg}(\text{OH})_2$) or gibbsite ($\text{Al}(\text{OH})_3$) octahedra either sandwiched between two tetrahedral layers forming the 2:1 phyllosilicates, or bonded to a single tetrahedral layer, forming the 1:1 phyllosilicates (Fig. 3) [93]. In the case of the chlorite family the structure is slightly more complex, including a brucite and/or gibbsite layer between two 2:1 units, thereby forming a 2:1:1 (or 2:2) structure. Table 1 presents the structure types, as well as examples of the main groups and minerals, of the clay mineral family. Clays including Mg^{2+} or other divalent cations such as Fe^{2+} in the octahedral layer are named trioctahedral clays as 3

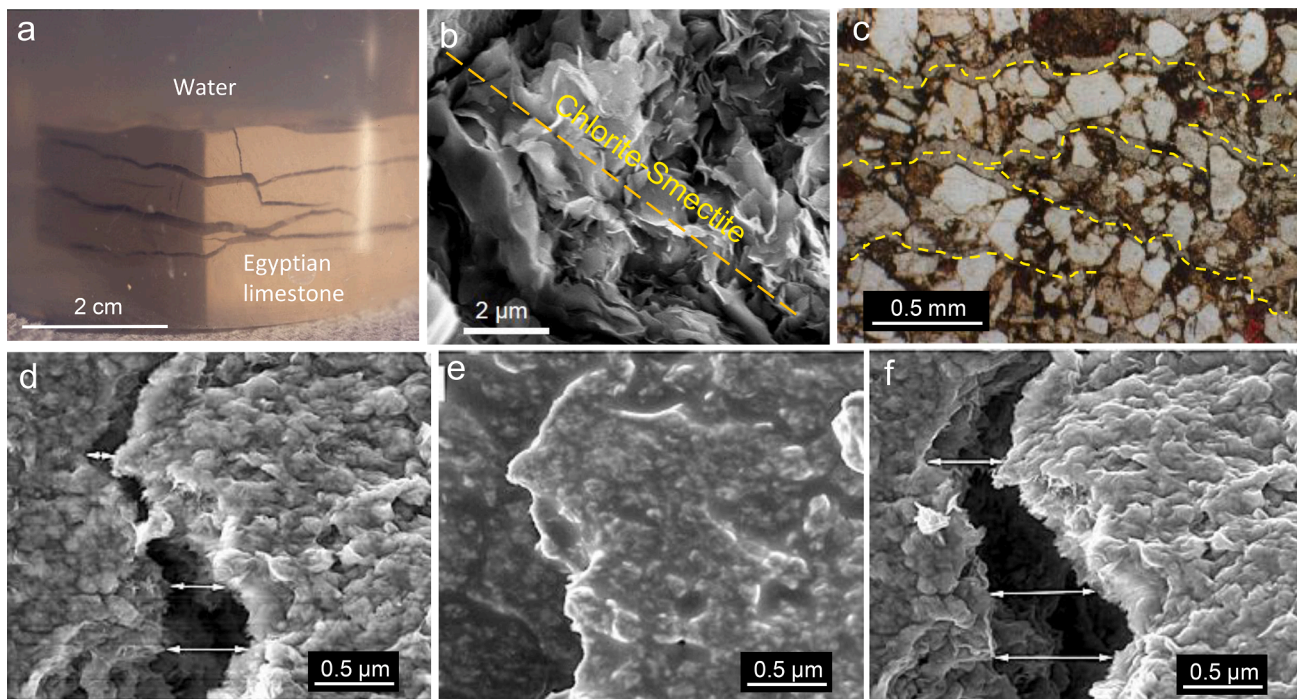


Fig. 2. Clay swelling damage development from the macro- to the microscale. a) Egyptian limestone block (remains of a fully degraded stela from the Egyptian collection of the Phoebe Hearst Museum, Berkeley, USA) developing multiple macroscale cracks sub-parallel to the bedding planes after immersion in DI water; b) Scanning electron microscopy (SEM) image of Tarifa sandstone showing chlorite–smectite mixed layer clay aggregates with a preferred orientation sub-parallel to the stone bedding plane (marked by the dashed line); c) Tarifa sandstone observed under the polarizing microscope (plane light) showing extensive cracking. The cracks (marked by the dashed yellow lines) are sub-parallel to the bedding plane of this stone; d–f) Sequential environmental SEM (ESEM) images of Egyptian limestone from the Phoebe Hearst Museum showing expansion upon pH_2O increase and T reduction within the ESEM chamber resulting in water condensation (transition from (d) to (e)) followed by a reduction in pH_2O and T increase resulting in drying (transition from (e) to (f)). Note the significant widening of the crack in (d) after a full wetting/drying cycle (f), demonstrating a permanent deformation (residual strain) and associated stone damage at the microscale. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

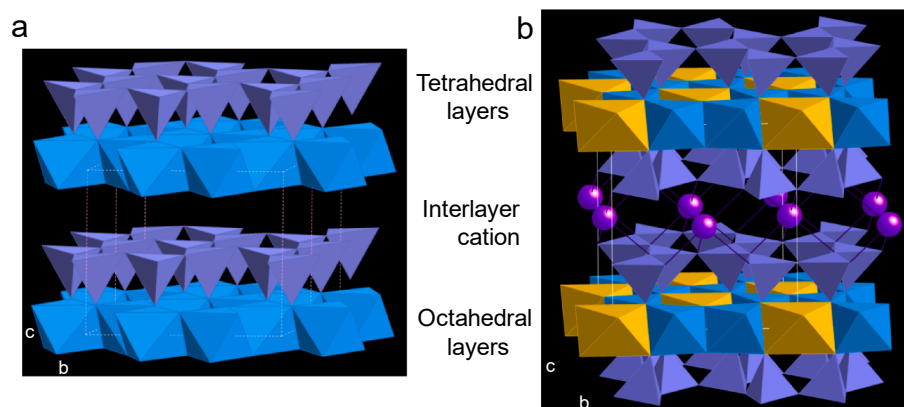


Fig. 3. Structure of (a) kaolinite and (b) montmorillonite projected along the $[100]$ direction. The violet tetrahedra represent SiO_4 units, the light blue octahedra represent $Al(O,OH)_6$ units and the yellow octahedra represent $Mg(O,OH)_6$ units. The interlayer cation in montmorillonite can change (e.g., K, Ca, Na). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

out of 3 octahedral positions are occupied by a cation. Those including Al^{3+} in the octahedral layer are called dioctahedral clays, as charge balance imposes that only 2 out of 3 octahedral positions are occupied by a trivalent cation. Examples of 1:1 di- and trioctahedral clays are kaolinite (Fig. 3a) and lizardite, respectively. Examples of 2:1 dioctahedral clays are illite and, among the group of smectites, beidellite, whereas saponite is a trioctahedral smectite, and montmorillonite (Fig. 3b) is a di-trioctahedral smectite as it includes both divalent and trivalent cations in octahedral positions. Most clay minerals display substitution of Si^{4+} in the tetrahedral layer by other cations such as Al^{3+} ,

and there might be also substitution of Al^{3+} (or Mg^{2+}) in the octahedral layer. Charge deficit associated with such a cation substitution is compensated by the incorporation of mono or divalent cations (Na^+ , K^+ , Li^+ , Ca^{2+} , Mg^{2+} , among others) in the interlayer space between 2:1 packets.

Depending on the structure, composition and layer charge of the clay mineral, cations in the interlayer can solvate (hydrate) or not. In the first case, the d_{001} -spacing or interlayer space (i.e., interplanar distance along a direction normal to the basal (001) planes of a phyllosilicate) can increase, and these type of clays are called swelling clays. Conversely,

Table 1
Classification and generalized structural formulae of clay minerals [94].

Structure	Group	General structural Formula	Nature of octahedral sheet	Mineral	Charge
1:1	Kaolinite	$Al_4Si_4O_{10}(OH)_8$	Diocahedral	Kaolinite Dickite Nicrite	0
	Serpentine	$(Mg, Al, Fe)_6(Si, Al)_4O_{10}(OH)_8$	Triocahedral	Lizardite Chrysotile Antigorite	0
2:1	Pyrophyllite-Talc	$Al_4Si_8O_{20}(OH)_4$ $Mg_6Si_8O_{20}(OH)_4$	Diocahedral Triocahedral	Pyrophyllite Talc	0 0
	Mica	$(K, Ca, Na)(Al, Mg, Fe, Ti)_4(Si, Al)_8O_{20}(OH)_4$	Diocahedral	Illite Phengite Glauconite	1.5–2
		$(K, Na, Ca, Ba)(Mg, Fe, Al, Ti, Mn)_6(Si, Al)_8O_{20}(OH)_4$	Triocahedral	Phlogopite Biotite	1.8–2
	Vermiculite (swelling clay)	$(Ca, Na, K)(Mg, Al, Fe, Ti)_6(Si, Al, Fe)_8O_{20}(OH)_4$	Triocahedral	Vermiculite	1.2–1.9
	Palygorskite-Sepiolite (fibrous clay)†	$(Ca, Na, K)(Mg, Al, Fe)_4(Si, Al)_8O_{20}(OH)_2(OH_2)_4$ $(Ca, Na, K)(Mg, Fe, Mn)_8(Si, Al, Fe)_{12}O_{20}(OH)_2(OH_2)_4$	Di/Triocahedral	Palygorskite Sepiolite	0.1–0.7 0–0.4
Smectite (swelling clay)	$(Ca, Na, K)(Al, Mg, Fe)_4(Si, Al)_8O_{20}(OH)_4$	Diocahedral Di/Triocahedral	Beidellite Nontronite Montmorillonite	0.5–1.2	
	$(Ca, Na, K)(Mg, Li, Fe, Al)_6(Si, Al)_8O_{20}(OH)_4$	Triocahedral	Saponite Hectorite Stevensite	0.5–1.2	
2:1/2:1	Interstratified clays (swelling clay)	$(Ca, Na, K)(Al, Mg, Fe)_4(Si, Al)_{16}O_{40}(OH)_8$	Diocahedral	Rectorite (Illite + Smectite)	variable
2:1:1/ 2:1		$(Ca, Na, K)(Mg, Fe, Al)_9(Si, Al)_8O_{20}(OH)_{10}$	Triocahedral	Corrensite (Chlorite + Smectite)	variable
2:1:1	Chlorite‡	$(Al, Mg, Li, Fe)_{10}(Si, Al)_8O_{20}(OH)_{16}$	Di/Triocahedral	Sudoite Cookeite	variable
		$(Mg, Al, Fe, Mn)_{12}(Si, Al)_8O_{20}(OH)_{16}$	Triocahedral	Clinochlore Chamosite	variable

†Fibrous clays can be either non-swelling or swelling [8].

‡Note that chlorites are considered non-swelling clays. However, the possibility that defective chlorites (with incomplete interlayer brucite/gibbsite layers) could be swelling clays was considered in the 1950–1970s, but it is believed that swelling is more likely due to the existence of a mixed-layer clay (chlorite-vermiculite) [93–95].

clays that cannot incorporate water (or other polar molecules) in the interlayer are called non-swelling clays. An example of the former are the smectites, while an example of the latter is illite. Swelling clays (e.g., vermiculite, smectites, and mixed layer clays including smectite packets interspersed with non-swelling clay packets of, for instance, illite or chlorite) can thus expand along the [001] direction when in contact with water molecules (or other polar solvent) resulting in high swelling pressure if they are constrained (i.e., within a stone matrix), which can cause significant strain (and associated differential stress) [48]. Repeated wetting/drying cycles due to humidity fluctuations or direct contact with liquid water followed by evaporation can lead to repeated swelling/shrinkage and damage to the stone materials containing such clays [9].

Due to their sheet-like morphology, small size, low crystallinity, and typically low concentration in building stones, the identification and quantification of clay minerals is not trivial. Indeed, the gold standard for their study is X-ray diffraction (XRD) [93], but conventional non-oriented powder samples (prepared after grinding a stone sample) do not normally allow a proper distinction of the Bragg peaks corresponding to the (most intense) 00 *l* basal reflections of clay minerals. In most cases, only a general, broad, low intensity *hkl* reflection at 4.49 Å is observed. This may have contributed to a general neglect of clays as a component in many stones, thereby overlooking their possible role in the stone's deterioration. A proper identification of clay minerals in a particular stone involves a somehow complex sample pre-treatment. After the stone is ground, the < 2 µm clay fraction needs to be separated by differential sedimentation (Stokes' law). If the stone is a limestone, it is necessary to eliminate the carbonates by acid treatment prior to the separation of the clay fraction. A high content in organics, which would have to be eliminated with H₂O₂ prior to XRD analysis, is

not expected in the majority of stone materials. Once the clay fraction has been separated, oriented aggregates have to be prepared and subjected to different treatments (e.g., solvation with ethylene glycol, EG, and/or dimethyl sulfoxide, DMSO, or heat treatment at 300–550 °C), in order to get intense 00 *l* Bragg peaks, and to differentiate clay phases. See Moore and Reynolds [95] for a detailed description on sample preparation and identification of clay minerals using XRD. Complementary techniques to identify and study clay minerals are, among others, Fourier transform infrared spectroscopy (FTIR), scanning and transmission electron microscopy (SEM and TEM, respectively), coupled with energy dispersive X-ray (micro)analysis, and thermal analysis including thermogravimetry (TG) and differential scanning calorimetry (DSC).

3.3. Clay swelling: How does swelling pressure develop?

There are two types of clay swelling (Fig. 4): (i) crystalline (also denoted as intracrystalline or innercrystalline) swelling, which involves the incorporation of successive H₂O monolayers in the (001) interlayer space of swelling clays. It is pH₂O-dependent and the increase in *d*₀₀₁-spacing is not continuous but stepwise [96]; (ii) osmotic (or intercrystalline) swelling, which can occur in any clay mineral (swelling or non-swelling), but it is most evident in swelling clays such as smectites [96,97]. It basically involves diffuse double-layer forces, according to the DLVO (Derjaguin-Landau-Verwey-Overbeek) model, interacting among individual clay platelets dispersed in an electrolyte solution [49]. Because at close to neutral pH clay particles have a negative surface charge, they tend to attract and adsorb counterions (cations) forming a Stern layer. To balance the ion activity between close-by (face-to-face) clay platelets, water from the bulk solution penetrates between them,

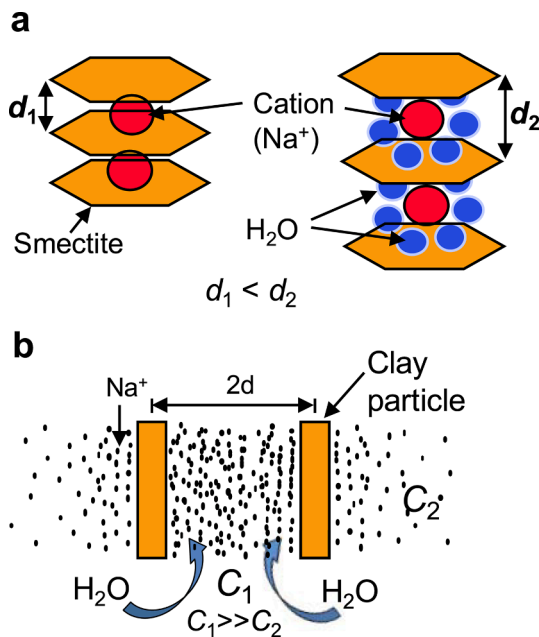


Fig. 4. Schematic of crystalline (a) and osmotic clay swelling (b). Based on Madsen and Müller-Vonmoos [98]. See text for details. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

leading to their separation. The collective effect is a measurable expansion of the clay aggregate [98].

Small angle (SAXS) and wide angle (WAXS) X-ray scattering analyses as well as computer simulations have shown that crystalline swelling of smectite (e.g., montmorillonite) involves changes in d_{001} from ~ 10 Å (fully dehydrated clay) to 11.5–12.5 Å for a monolayer water arrangement, 14.5–15.5 Å for a bilayer, and 18.0–19.1 Å for three water layers [99]. Additional water uptake induces the transition from crystalline to osmotic swelling, where $d_{001} \gg 20$ Å (even 30–40 Å) [96,99].

It has been commonly assumed that in the case of swelling clays such as smectites, osmotic swelling is responsible to a large extent of the observed expansion [98]. It has been shown, however, that the addition of electrolytes, which shield electrostatic DLVO interactions (i.e., reduction of Debye length) among clay particles, thereby reducing the extent of osmotic swelling [97], does not prevent clay-related expansion (and damage). Wangler and Scherer [100] have demonstrated that crystalline swelling of smectites (or smectite-illite interstratified) in clay-containing stones (Portland Brownstone) is the main cause for the development of swelling strain and the associated swelling stress and damage. Earlier experiments also demonstrated the key role of crystalline swelling in stone damage [62]: cycles of solvation with DMSO -known to increase the d_{001} -spacing of smectites from ~ 12 –14 Å up to ~ 18 –20 Å- and drying of smectite-containing Jaen's micritic limestone (Fig. 5a) resulted in extensive fracturing and delamination along the stone's bedding planes where the clays were concentrated (Fig. 5b). In the Jaen's Cathedral (Spain), crystalline swelling (in this case induced by H_2O incorporation in the smectite interlayer space) is manifested by the extensive spalling this clay-bearing limestone experiences (Fig. 1a-b).

The demonstration that crystalline clay swelling is a main mechanism for creating expansion and stone damage is important because it helps to select and apply appropriate treatments for the prevention of this deleterious phenomenon, for instance using crystalline swelling inhibitors (see below). Alternatively, if one tries to reduce osmotic swelling, one way to do so is adding a concentrated saline solution [71,97], which is not of practical application in the stone built heritage as deleterious salt weathering would be a side effect and a reduction in

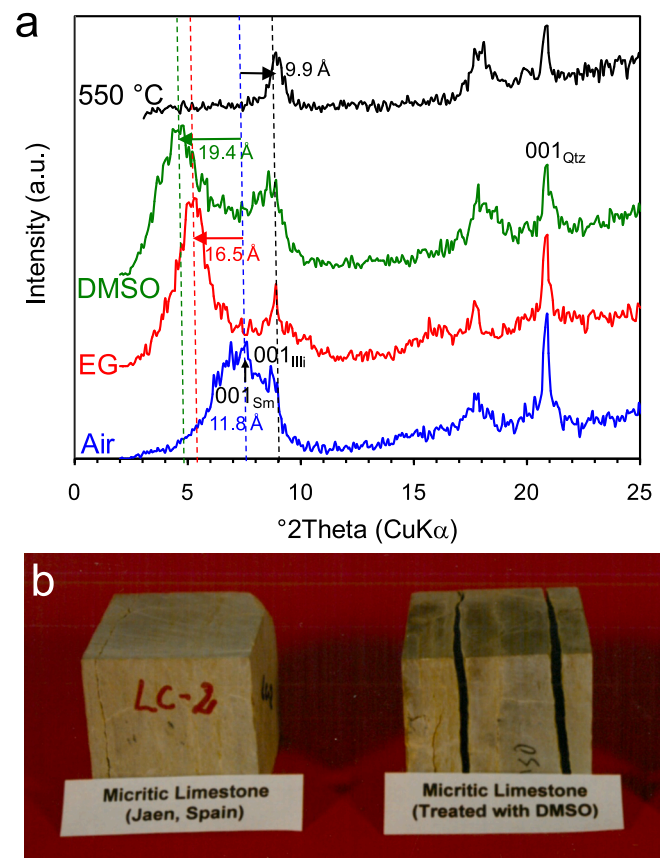


Fig. 5. Effect of cycles involving DMSO solvation and drying of Jaen's Cathedral (Spain) smectite-containing micritic limestone. a) XRD patterns of oriented aggregates of the clay fraction of Jaen's micritic limestone. The shift in d_{001} -spacing of smectite (Sm) from 11.8 Å (air dried) up to 16.5 Å and 19.4 Å upon EG and DMSO solvation, respectively, and its collapse to 9.9 Å upon 1 h heat treatment at 550 °C (shifts marked by vertical dashed lines and arrows) demonstrate the presence of this swelling clay. Note that the clay content in this stone is 9 ± 3 wt%, and the relative amounts of illite (Illi) and Sm determined from XRD are $33 \pm 3\%$ and $67 \pm 3\%$, respectively [62]; b) The image on the left shows a limestone specimen before testing, whereas the image on the right shows a limestone specimen after DSMO test (10 cycles involving DMSO solvation followed by oven drying at 110 °C). Note that the bedding planes (where smectites are concentrated) of both stone specimens are edge-on (i.e., cracks develop parallel to the bedding planes). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

crystalline swelling would not necessarily be achieved. The latter could even be enhanced if Mg or Na salts are used or naturally present in stone, as these cations (specially divalent ones) have a very high hydration capacity (if compared with K). Note also that whereas large concentrations of such salts can lead to the suppression of osmotic swelling, their presence in small concentrations could actually favor osmotic swelling, as there is a threshold electrolyte concentration that drives the transition from crystalline to osmotic swelling (i.e., 0.25 M NaCl) [96,97]. For instance, in the case of sepiolite fibers in Egyptian limestone, Rodríguez-Navarro et al. [8,9] have shown that osmotic swelling contributed to this stone's hydric expansion (Fig. 2a and 2d-f): the presence of a small amount of NaCl in this stone seemed to have enhanced such a damaging process, as the limited crystalline swelling of this fibrous clay (about 1% unit cell expansion) does not fully explain the huge free swelling strain experienced by this stone upon immersion in water (up to ~ 0.05). Even in the case of non-swelling clays, such as illite present in the limestone of the Romanesque portals of the Tournai Cathedral (Belgium), its osmotic swelling has been claimed responsible for the observed expansion/

contraction following wetting/drying and resulting in spalling damage [101]. Conversely, it has been observed that the presence of large amounts of NaCl in some tuff stones from historic monuments in Guanajuato (Mexico) reduces expansion (via osmotic swelling) as compared with other tuff stones with very similar clay mineralogy and content, but without salts, where large free swelling strains were observed [102].

A clear correlation between swelling clay content and hygric and/or hydric free swelling strain of clay-containing stones is generally observed [46,50,51]. Moreover, in the case of limestones including mixed-layer smectite-illite/glaucanite phases, free swelling strain is directly related to the amount of smectite layers in the interstratified clays [103,104]. Nonetheless, while most expansion during hygric and hydric tests in clay-containing stones is typically associated with swelling clays (undergoing crystalline swelling), at the last stages of stone saturation, non-swelling clays are reported to also contribute to the observed expansion (via osmotic swelling) [63]. In some isolated cases (e.g., [101]), the latter might even be the sole mechanism responsible for swelling damage.

3.4. How clay swelling damage is generated and progresses?

These are key questions that have been explored extensively. Upon contact with water, either water vapor (RH fluctuations) or liquid water (e.g., rain and rising damp), a clay-containing stone will experience expansion in the wet layer, which typically will be the outer surface layer of the stone exposed to the environment (Fig. 6a). Such an expansion will be opposed by the dry bulk stone underneath, which does not undergo dimensional changes. Therefore, the wet layer will be under compression (whereas the dry layer in contact with the wet layer will experience a certain tension stress). Under this conditions differential stresses will be generated and buckling can eventually develop (see below), resulting in scaling and material loss [10,48]. This is the scenario most common for the generation of clay swelling damage (at least in stone masonry walls). The stress created by the wet layer in contact with the bulk dry stone (assuming that the stone is a purely elastic material, and the thickness of the wet superficial layer is very small compared to the thickness of the core) can be calculated by [10,105],

$$\sigma_{wet} = \frac{E_{wet}}{1 - \nu_{wet}} (\epsilon_{RH} - \epsilon_s) \quad (1)$$

where E_{wet} and ν_{wet} are the Young modulus and the Poisson's ratio of the wet stone, respectively, ϵ_s is the free swelling strain of the saturated stone, and ϵ_{RH} is the strain of the dry stone in equilibrium at a certain relative humidity. In Eq. (1), $\sigma_{wet} < 0$, so the stress in the wet layer is compressive. According to Jimenez-Gonzalez and Scherer [10], if the stress is larger than the compressive strength of the wet stone, crack

development and damage will readily occur. But such a situation might be rare, as the wet compressive strength of most stones is significantly larger than the observed values of σ_{wet} [48]. Nonetheless, as we will discuss below, if the stone contains pre-existing flaws below the surface (for instance, due to salt damage), buckling could take place at a stress lower than the stone's wet compressive strength [105]. It could also be argued that failure might take place by tensile stresses normal to the plane separating the wet expanded surface layer and the inner dry stone, if such stresses overcome the tensile strength of the stone (see below).

Once a porous stone including swelling clays is saturated, for instance after a long period of rain, it will eventually start to dry from the outside in if the water supply ceases. The dry surface layer will shrink and be under tension, as the saturated (expanded) inner sections of the stone will oppose shrinkage (Fig. 6b). In such a case cracks normal to the stone surface can develop if the tensile stress associated with drying shrinkage overcomes the dry tensile strength of the stone. This situation has been observed in the field, for instance, in the case of the sandstone façade at the Church of San Mateo at Tarifa (Fig. 1c) showing polygonal cracks (i.e., drying cracks, also known as "mud cracks") [47]. These drying cracks will typically develop in (small) carved elements of clay-bearing stones where the exposed surface to volume ratio is very high, thus enabling full saturation (during a rain event) and fast drying [48,105]. This scenario is, however, not that common.

As drying progresses, the stress created by the thin dry layer in contact with the bulk saturated stone can be calculated by [10,105],

$$\sigma_{dry} = - \frac{E_{dry}}{1 - \nu_{dry}} (\epsilon_{RH} - \epsilon_s) \quad (2)$$

where E_{dry} and ν_{dry} are the Young modulus and the Poisson's ratio of the dry stone, respectively. In Eq. (2), $\sigma_{dry} > 0$, so the stress in the dry layer is tensional. If the stress is larger than the tensile strength of the dry stone, cracks will develop normal to the wet/dry interface. Since the stone is much weaker in tension than in compression, the drying event could be more damaging for the stone than the wetting event, as pointed out by Jiménez-González et al. [48]. Experimental results indeed show that stresses generated during the drying event of a fully saturates clay-bearing stone (Tarifa sandstone) can overcome the dry tensile strength of such a stone. It could thus be concluded that the most damaging event during a wetting/drying cycle would be the drying stage. However, as stated above, a prerequisite for damage generation during the drying stage is full saturation of the stone, which is not easily achieved during a wetting event in the field (i.e., rain event) unless the stone element is protruding and of reduced dimensions [48].

There is another scenario for damage generation during the drying event, which has been discussed by Demoulin et al. [105]. The authors report that in specific situations where fast evaporation occurs during

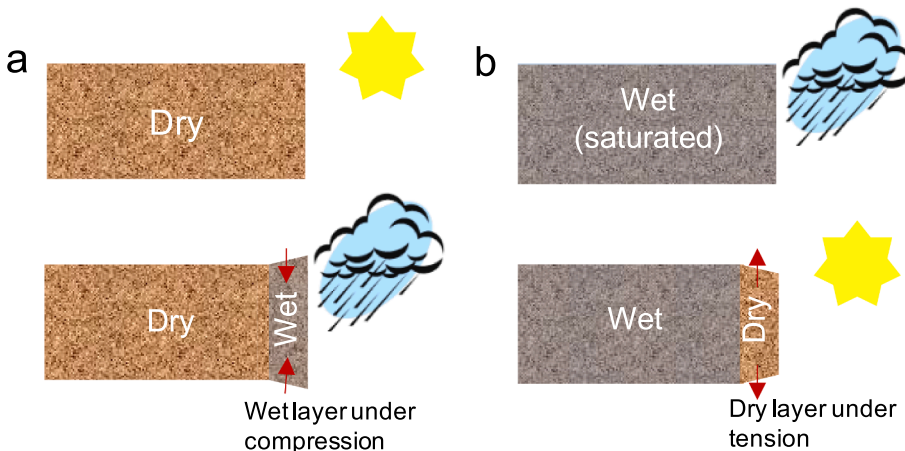


Fig. 6. Schematic of the expansion and contraction experienced by a clay-containing stone block upon wetting (a) during a rain event and subsequent drying (b). The wet layer in (a) at the beginning of the wetting period will be under compression, whereas the dry layer formed after full saturation of the stone block and the beginning of the drying period will be under tension. Modified after Jimenez-Gonzalez and Scherer [10]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the drying stage, such as in corners of a stone building, it is observed the development of cracks parallel to the exposed surface at a depth of few mm/cm that result in the scaling of curled, low curvature concave plates. Such a curling or peeling phenomenon, which according to Style et al. [106] develops via Mode I crack opening and propagation (i.e., the fracture plane is perpendicular to the normal force), is commonly observed in clay-rich soils undergoing polygonal cracking during drying. Note, however, that Demoulin et al. [105] suggest that peeling takes place via Mode II crack propagation (i.e., fracture occurs under the action of shear stress and propagates in the direction of shear) of a flaw parallel to the stone surface and located at a certain depth.

According to Wangler et al. [107], buckling during the wetting stage results from the suppression of the free swelling strain ϵ of a thin layer of stone over a flaw located at a depth t below the exposed surface, with width L . Buckling occurs when the compressive stress σ in the plane of the wet layer,

$$\sigma = \frac{E\epsilon}{1 - \nu^2} \tag{3}$$

is equal to the critical buckling stress, σ_c ,

$$\sigma_c = \frac{E}{1 - \nu^2} \frac{\pi^2}{3A_c^2} \tag{4}$$

where E is the elastic modulus of the saturated stone, ν is the Poisson's ratio of the wet stone, and A_c is the critical aspect ratio L/t where buckling occurs. Combining Eqs. (3) and (4), the critical aspect ratio is defined in terms of the free swelling strain:

$$A_c = \frac{\pi}{\sqrt{3\epsilon}} \tag{5}$$

It is thus possible to determine A_c knowing ϵ . Knowing the depth of the flaw, t , it is also possible to determine the critical flaw length L .

As an example, in the case of tuff stone at the archaeological site of Copan, where extensive scaling has resulted in massive loss of Classic Maya carved stone, stelas, and hieroglyphs, the thickness of tuff stone scales is $\sim 0.5\text{--}3\text{ mm}$ (Fig. 7a-b). Using Eq. (5), critical flaw lengths L of 14.5 mm up to 87.1 mm were calculated for the smallest and largest scale thickness, considering the average hydric strain ϵ of 0.0039

determined for this tuff [51]. However, for the development of such critical flaws, a mechanisms that triggers the nucleation and propagation of cracks that eventually coalesce forming such a critical flaw must exist. It could be claimed that weathering phenomena such as salt damage could be responsible for the formation of such a critical flaw [107]. However, the fact that expansion/contraction of the aforementioned tuff during wetting/drying cycles leads to non-zero residual strains after each cycle (Fig. 7c) is evidence for the formation and propagation of microcracks due to swelling of smectites present in this tuff in concentrations of up to 8 wt% [51].

In general, swelling stresses during the wetting stage will result in damage when the swelling pressure exerted by the clays overcomes the wet strength of the clay-containing stone [10]. Note that the wet strength of a saturated stone is a fraction of its dry strength [8–10,52,85]: In the case of limestones including swelling clays, a strength reduction upon wetting of up to 70% (proportional to smectite content) has been reported [108], whereas in the case of sandstones including glauconite and mixed layer illite–smectite a 59% reduction in compressive strength upon water saturation has been noted [109]. In theory, crystalline swelling pressures of up to 400 MPa, down to 110 MPa and 27 MPa for the first, second and third-fourth H₂O monolayers entering the interlayer space, respectively [98], can be generated by smectites. However, actual measurements of swelling stress generated by smectite-containing stones show values of only a few MPa [110] or even lower [48,49]. These values are very similar to those reported for the case of osmotic swelling of smectites (i.e., $\sim 2\text{ MPa}$ [98]). It is likely that such relatively low measured swelling pressures are in part due to stress relaxation [10]. However, stress concentration at the matrix-clay interface within a stone can likely reach much higher values, leading to microcrack opening and propagation (e.g., micro-cracks typically with $\sim 1\text{ }\mu\text{m}$ openings, as reported elsewhere [111]), eventually resulting in large flaws and macroscale damage. Also, it has been suggested that during the wetting stage, the presence of flaws would enable fracture propagation along a plane parallel to the exposed stone surface at stress values below the compression strength of the wet stone [10]. Ultimately, flaking, scaling and delamination occur in the field as has been thoroughly reported [10,47,50,51,62].

An alternative model for the development of fractures parallel to the

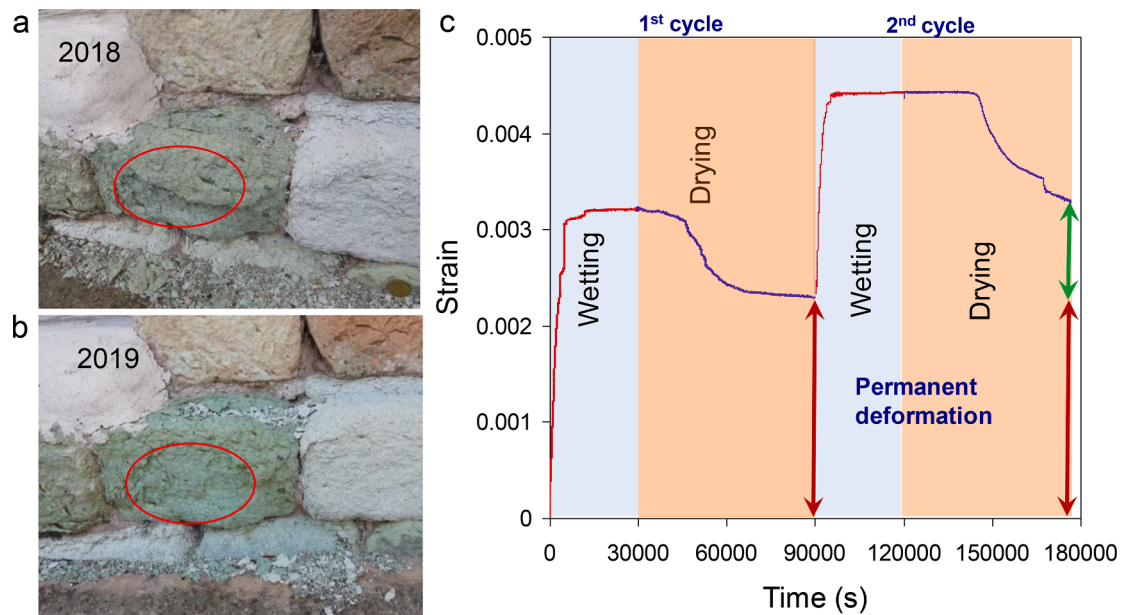


Fig. 7. Massive scaling and material loss of smectite-containing tuff stone at the Maya site of Copan (Honduras). a) View of tuff stone blocks at Structure 10H-18 showing surface scaling in 2018, and b) same area pictured in 2019. See the massive stone loss in the form of flakes and scales (red circled area) and their accumulation at the bottom of the wall; c) free swelling strain of Copan tuff stone during wetting/drying cycles. Note the existence of a residual strain after each cycle. Modified from Elert et al. [51]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

wetting front in clay-containing stone (limestone) subjected to capillary water infiltration was recently proposed, which considered that contraction at the height just above the water front can result in the development of significant tensile stress [112]. Hassine et al. [112] performed local strain measurements (using strain rosettes) during capillary water absorption in cylindrical limestone blocks and observed differential strains among the wet and dry sections. They reported an initial contraction in the vertical direction and expansion in the horizontal direction when the capillary front reached the rosette strain gauges. As the capillary front was passing the strain gauge position, they subsequently observed an expansion, a contraction and a final expansion phase (in the vertical direction). The authors explain the initial vertical contraction as a Poisson effect: as the lower saturated section expands the dry upper section contracts, whereas the second vertical contraction is due to local desaturation due to water evaporation from the stone surface. Basically this model describes the same situation indicated by the buckling model presented above [107], i.e., the existence of a compressive stress just below the capillary fringe -compatible with a vertical contraction of the dry stone just above the capillary fringe-, leading to fracturing along the wet/dry interface. However, Hassine et al. [112] model underlines that failure of the stone resulting in spalling occurs when the tensile stresses associated with the vertical contraction overcome the tensile strength of the dry stone. This is a situation much more plausible than that contemplated by previous models [10,48] that suggest that failure would occur when compressive stresses in the wet layer overcome the wet compressive strength of the stone. Indeed, the model proposed by Hassine et al., [112] may enable the development of local flaws that can eventually propagate according to the buckling model proposed by Wangler et al. [107] (i.e., both models can act sequentially).

It is important to underline that damage during wetting/drying cycles associated with clay swelling/shrinkage does not necessarily act alone in the deterioration of dimension stone. It has been shown that other weathering mechanisms such as salt crystallization damage can contribute or act in a synergistic way to clay swelling damage. For instance, Janvier-Badosa et al. [113] showed that in the case of limestones (tuffeau) used as dimension stone in the Castle of Chambord (Centre-Val de Loire, France), cracks that developed at a depth of ~ 1 cm following swelling of glauconite clay, favored the concentration of calcium sulfates at such a depth, resulting in salt damage when gypsum crystallized. The combined action of these two phenomena resulted in massive spalling. This study confirms previous research suggesting that the presence of clays can result in enhanced salt damage (and viceversa) [66,114].

3.5. Other expansion mechanisms: Solvation forces and zeolite swelling

In the case of some sandstones and tuff stones, a significant hygric expansion was measured even in stone varieties (specially tuff stones) without swelling clays [49,50,115]. This led to the hypothesis that surface forces (i.e., solvation forces), basically originating from DLVO interparticle interactions and involving a disjoining pressure, could explain the observed expansion during saturation with water. For such a disjoining pressure to develop, vicinal particles facing each other with flat parallel surfaces with adsorbed H₂O molecules would have to be at a distance of a few nm. Such a situation was assumed to occur in stones displaying abundant 'micropores' (diameter < 5 nm) (note that according to the International Union of Pure and Applied Chemistry, IUPAC, pores with size 2–50 nm actually are mesopores, whereas those with size < 2 nm are micropores), which led Ruedrich et al. [49], Wedekind et al. [50] and Pötzl et al. [115] to propose that the amount of micropores in sandstones and tuff stones was an indication of their susceptibility to moisture expansion. Such a model was already proposed by Schultz and Shi [116] to explain the observed hydration swelling of clay-free crystalline rocks with very low porosity (granites, diorites, gneisses and metabasites). Remarkably, the authors reported

strains of 0.0005, which could not be fully hindered by confining pressures of 15 MPa. The fact that the swelling was DLVO in nature was demonstrated by its reduction with an increase in ionic strength of the surrounding solution by adding CaCl₂. It is therefore likely that the observed hygric expansion of some sandstones and tuff stones (or other stones) lacking swelling clays is basically a solvation effect favored by the presence of very small particles (or microcracks) enabling the existence of micropores.

However, it should be also considered the possibility that expansion (and weakening) of stones due to water adsorption and (partial) saturation could be related to other physical phenomena. According to Yurikov et al. [117], Bentheim sandstone blocks with no swelling clays and just traces of kaolinite, underwent free swelling strains of 0.0001 and an associated strength reduction of 20% when the RH rose to 98%. The authors concluded that upon water adsorption changes in surface stress due to hydraulic pressure generation (of the order of several MPa) in compliant nanopores on grain contacts led to tensile stresses and the observed strain, as well as the stone weakening.

Zeolites are abundant phases in most tuff stones, being -along with clays- a typical product of the hydrothermal alteration of the volcanic glass present in the tuffs [118]. It has been suggested that their expansion/shrinkage could contribute to spalling and scaling in tuff stones [89,119,120]. Zeolites reportedly swell upon hydration and shrink following dehydration, as H₂O molecules can enter/exit their zeolitic channels [88]. Extensive XRD studies by Bish's group showed that zeolitized tuff (from Yucca Mountain, USA) experienced unit cell volume changes of up to 8% (yet, typically < 2 %) when fully dehydrated. Dehydration was generally reversible, as was the unit cell shrinkage [88,121]. However, in this case dehydration was achieved at high T (up to ~ 300 °C) and under vacuum, conditions that are not relevant for tuff stone decay in monuments. Nonetheless, Bish et al. [122] reported clinoptilolite unit cell expansion of 1% following exposure to 100% RH and saturation in liquid water at room T . Such an expansion is minor if compared with that of smectites (unit cell expansions of ~ 30 % upon water saturation) [51]. But could be a contribution to the observed damage of some tuff stones.

Lubelli et al. [89] proposed that spalling and scaling damage of Ettringen tuff stone (Germany) could be due in part to expansion of Ca-phillipsite, present in significant amounts in this volcanoclastic rock. XRD analyses showed a slight shifting of some Ca-phillipsite Bragg peaks to lower 2θ angles (i.e., larger d -spacings) upon exposure to high RH atmosphere or liquid water. These observations pointed to an expansion of the zeolite unit cell, which could explain the observed hygric and hygric expansion (ϵ of up to 0.0012) of the tuff stone. However, the shifting in Bragg peak position and the resulting change in unit cell dimension of Ca-phillipsite was not quantified, which makes it difficult to gauge the actual role of this zeolite in the observed expansion. Unfortunately, in the cases where zeolite swelling was claimed to be responsible for the expansion of tuff stones, no extraction of the clay fraction and detailed quantification and analysis by XRD (using oriented aggregates) was performed, which precludes an evaluation of the possible contributing role to the observed expansion of (swelling) clay minerals vs. zeolites. For instance, in the pioneering study by Kranz et al. [123] expansion following hydration of tuff from Yucca Mountain (ϵ up to 0.0022) was fully ascribed to the presence of zeolite minerals, despite the fact that the authors mentioned the presence of "minor amounts of smectite".

In an attempt to evaluate whether zeolite expansion was a contributing factor (along with the expansion of swelling clays) in the decay of Copan tuff stone, Elert et al. [51] performed detailed XRD analysis of the zeolites present (clinoptilolite, analcime and mordenite) in different varieties of Copan tuff stone following saturation in water of the powdered tuff. Only in the case of mordenite a unit cell expansion of 0.2% was observed upon saturation in water at room T . This value was considered negligible, as compared with the ~ 30 % expansion undergone by montmorillonite, as d_{001} shifts from 15 to 19.5 Å upon hydration

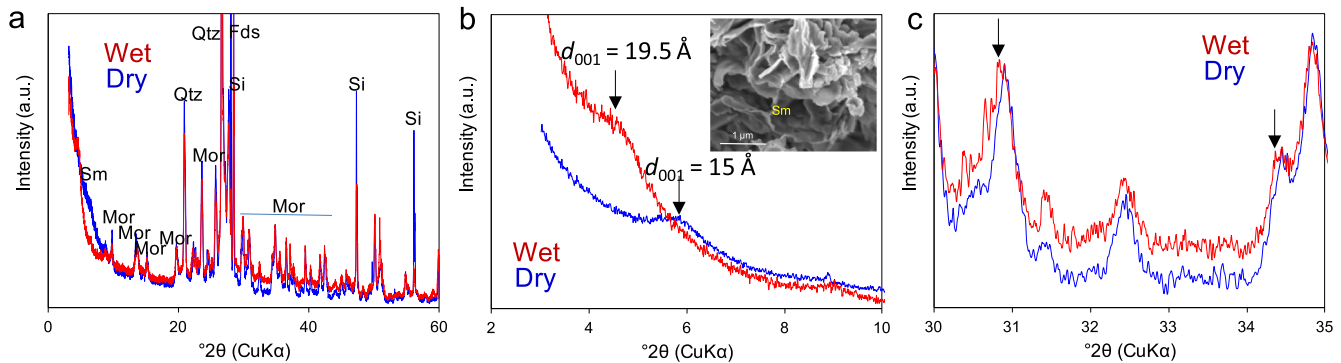


Fig. 8. XRD patterns of dry and wet Copan stone. a) full 2θ explored area; b) detail of montmorillonite 001 Bragg peak shifting to lower 2θ angles upon hydration. The inset shows a SEM image of montmorillonite platelets in the tuff stone; c) minor shifting of some mordenite Bragg peaks (arrows) following hydration. Legend: Sm, smectite; Mor, mordenite; Qtz, quartz; Si, silicon (std.), Fds, feldspars. Modified from Elert et al. [51]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(Fig. 8). It is therefore unclear at present what exact role, if any, zeolites play in the swelling damage of tuff stones.

3.6. Moisture expansion vs. Thermal expansion

Another possible mechanism accounting for the development of flaking or scaling phenomena in building stone is thermal expansion [3,14]. In the case of clay-containing stones it is however difficult to single out the individual contribution of clay swelling and thermal expansion on the developed damage. In general, it has been observed that the contribution of thermal expansion to flaking and scaling damage of sandstones and tuff stones is typically very minor as compared to moisture expansion [89]. Weiss et al. [91] states that in most cases the thermal expansion curve of sedimentary stones such as tuff or sandstone is quite straight, showing no residual strain after a heating/cooling cycle, thereby suggesting that thermal damage should be negligible (if any) in these cases. Actually, Benavente et al. [92] reported a negative correlation between thermal expansion coefficient and weight loss of several limestone and sandstones, whereas they found a positive correlation between swelling clays content and weight loss upon wetting drying cycles. However, in the case of sandstone blocks at Angkor Temples, Wedekind et al. [90] suggested that thermal expansion, not clay swellings as previously thought [73,74], was the main cause of the observed contour scaling. The authors reported that secondary precipitation of calcite at the stone surface/sub-surface occurred forming a crust (~4 mm in thickness) with different thermal and moisture expansion properties than the underlying bulk sandstone. They claimed that differential stresses could thus develop between the surface crust and the inner section of the stone during heating/cooling cycles. These differential stresses would result in crack development and, ultimately, in the observed contour scaling. However, the maximum hydric expansion of the crust and bulk sandstone reportedly were 1.55 and 1.988 mm/m, respectively, whereas the thermal expansion values at 60 °C ranged from 0.5 to 1 mm/m and -0.2 to 0.05 mm/m in the crust and bulk sandstone, respectively. These values suggest that the possible contribution of thermal expansion may not be as significant as that of hydric expansion, and likely the two mechanisms probably acted in a synergistic way. Further research should be performed to validate that thermal expansion is a main contributor for the development of contour scaling at Angkor Temples. In any case, this study demonstrates that ascribing a particular damage form, as it is the case of spalling or (contour) scaling, to a particular expansion (or other damage) mechanism is not trivial.

There is another aspect of the study by Wedekind et al. [90] that deserves attention. The claim that a surface layer of newly formed calcite cement on a silicate stone might foster thermal damage could have important implications when applying consolidants based on the

formation of calcium carbonate cement. This is the case of nanolimes (alcohol dispersions of $\text{Ca}(\text{OH})_2$ nanoparticles [6]) or bacterial biomineralization of CaCO_3 (see below) [7,51]. However, in addition to the possibility that the thermal effect above discussed might be minor, and the fact that a successful consolidation using the above mentioned methods should not result in a compacted layer of CaCO_3 (as occurred in Angkor sandstone), one has to consider the recent results by Cai et al. [124]. The authors show that wetting/drying cycles of clay-containing sandstone resulting in partial dissolution of the stone's original calcite cement, weakened the stone, and fostered intergranular cracking due to clay expansion. These results suggest that the actual cementation of clay-containing silicate stones (e.g., sandstones and tuff stones) by conservation treatments producing calcium carbonate would in principle be beneficial rather than detrimental.

4. The conservation of clay-containing stones

4.1. Failure of previous conventional conservation treatments

The advanced decay observed in many stones affected by clay swelling damage led to the application of many types of conventional conservation treatments since several decades [1,4,125]. Basically, there are two types of materials that have been traditionally applied to degraded clay-containing stones: protectives and consolidants. Protectives are compounds (e.g., organic polymers and alkylalkoxysilanes) that impart hydrophobicity to the stone surface [1,4]. Their application aims at preventing the access of water to the interior of the stone in order to prevent clay swelling and the associated damage phenomena discussed in the previous section. In many cases, however, protectives form surface films that hamper water vapor permeability and do not avoid the movement of aqueous solutions within the pore system of the treated stones (e.g., in case of rising damp) [1], thereby not effectively tackling clay swelling damage. Conversely, consolidants (e.g., polymers and alkoxy-silanes) are applied to the damaged stone to regain, at least in part, the lost cohesion and strength [1,4-7]. By introducing a new cementing material within the pore system of the stone, the consolidant could increase the overall strength of the treated stone, making it more difficult for damage to progress upon wetting/drying cycles in a clay-containing stone. The consolidant could even seal existing flaws in a clay-containing stone, so that damage due to buckling would be less probable. However, as we will see below, little success has been achieved with these two types of conventional treatments when applied to stones affected by clay swelling damage.

Early in the 1970–1990s the consolidants/protectives of choice where typically polymers, especially acrylic resins and their copolymers, which tend to be incompatible with the inorganic substrates (stone, mortars and plasters) they were applied to [6,126]. Their application on

Egyptian sculptures and stelae made of Thebes marly limestone (belonging to the Egyptian collection of the Metropolitan Museum, the British Museum, as well as the Phoebe Hearst Museum), alone or in combination with alkoxysilanes [127–130], did not lead to any significant improvement [8]. This could be partly due to the fact that at the time it was believed that salt damage was the main cause of scaling and flaking observed in such Egyptian limestone sculptures and stelae, although some researchers suggested that clays could play a role in the observed damage [131]. The general non-accurate diagnosis of the decay mechanism led to the common practice of desalinating such artworks by immersion in water or using aqueous poultices, which was not effective in controlling damage and flaking and material loss continued at a rapid pace. In some cases sculptures and stelae even collapsed upon immersion in water as reported by Helm [132] who stated “In the fifties one relief was put in a water bath and left over a weekend, by Monday fragments of the surface had floated away from the stone”. As indicated above, such sculptures and stelae contained significant amounts of clays (sepiolite in particular) that underwent expansion and contraction upon moisture fluctuations, leading to continued crack development [8,9]. A proper understanding of the main cause of deterioration (clay swelling) helped design and implement a tight environmental control for the conservation of such emblematic pieces of art.

The general observation of the incompatibility of polymeric conservation materials when applied to stone or other inorganic substrates [1,126,133] resulted in their almost general phasing out during the 1990s and early 2000s, and their general replacement by (mainly) alkoxysilanes as the consolidants of choice [4]. However, the latter did not result in an effective, long-lasting protection or consolidation when applied to stone affected by clay swelling damage [125]. Reportedly, alkoxysilane treatments applied to clay-containing stones such as sandstones lost effectiveness after a few wetting/drying cycles [4,134]. Swelling/shrinkage of expansive clays (e.g., smectites), resulting in damaging stress generation, affected the matrix of such treated stones. This led to decohesion among the clays and other stone mineral phases, and the silica gel formed after hydrolysis and polycondensation of the alkoxysilane treatment. These drawbacks are even more apparent in cases where polymers were replaced by alkoxysilanes as consolidants for carbonate stones. Additional to the above mentioned failure of the treatment efficacy after a few wetting/drying cycles when swelling clays were present, a lack of bonding between the carbonate minerals in the substrate and the silica gel resulting from the alkoxysilane treatment (an issue that could be partly solved by using a coupling agent) was generally observed [135]. Although an apparent appropriate consolidation of a clay-containing marly limestone was reportedly achieved using alkoxysilanes (as compared with the poor performance and incompatibility of acrylic polymers) [135], this case seems to be the exception (possibly because the clays in this stone were non-swelling illite and chlorite), not the rule. Indeed, Ercoli et al. [136] reported that desalination followed by consolidation with tetraethoxysilane (TEOS) of a marly limestone (calcarenite) used in the construction of the cloister of the medieval Cathedral of Cefalù (Sicily, Italy) and including ~ 5 wt% clay (49% illite, 38% montmorillonite and 13% kaolinite), led to a significant increase in the intensity and rate of deterioration (massive scaling). Their XRD analyses showed that ethanol, which is slowly released during the curing of TEOS, was able to expand montmorillonite, concluding that both water (used for the desalination treatment) and ethanol (released by the consolidant) contributed to the observed damage enhancement.

Also in the case of silicate stones such as tuffs, the use of conventional (organic and inorganic) consolidants does not seem to result in an effective consolidation. Stück et al. [137] reported that treatment of different German and Hungarian tuff stones with silicic acid ester, elastic silicic acid ester and polymethyl methacrylate (PMMA) led to changes in thermal- and hygric dilatation that increased the sensitivity to weathering of these tuff stones, potentially jeopardizing their long-term durability. Similarly, recent results by Pötzl et al. [138] show that the

treatment with TEOS and tetramethoxysilane (TMOS) of different clay-containing tuff stones from Germany, Mexico and Armenia resulted in a higher hydric expansion, an effect that could be deleterious in the long term.

Although not discussed in the studies by Stück et al. [137] and Pötzl et al. [138], it is very likely that the increased hydric expansion after the alkoxysilane treatments was due to swelling of the newly-formed silica gel. Silica gel is a mesoporous amorphous material [139], and as such can experience swelling due to adsorption of water molecules, as it has been reported for a range of mesoporous materials (e.g., Vycor glass) [140]. Water adsorption in mesoporous materials can result in a reduction of surface energy of the solid substrate leading to surface relaxation and expansion (Bangham effect), and/or a variation in surface stress that ultimately result in a measurable strain [140]. Such a strain can lead to a significant stress: for instance, it has been reported that amorphous silica gel hydration can result in pressures of over 20–30 MPa [141], values higher than the tensile strength of most stones [3]. In this respect, attention should be paid to the pioneering work by McBain and Ferguson [142] on the relation between the water vapor sorption of different building materials and their weathering. They reported that the use of Gatton stone as a building stone was discontinued owing to its enormous disintegration on weathering. According to the authors this was related to the high water vapor sorption -and associated swelling- of colloidal silica present in this stone in concentrations of up to 40 wt%. Ultimately, the possibility that hydration of silica gel formed after alkoxysilane treatments induces expansion and damage needs to be further studied.

In conclusion, it could be stated that the above mentioned conventional treatments generally failed because they did not tackle the cause of the decay (clay swelling) but rather dealt with its effects (in a not very effective way). This prompted the search of novel conservation materials and treatments for this elusive problem.

4.2. Use of swelling inhibitors

Since the pioneering work by Bradley [143] and MacEwan [144], it was known that organic molecules could be intercalated in the interlayer of clay minerals, especially expansive clays such as smectites. A large number of organic compounds were successfully incorporated or “pillared” in the interlayer space of smectites. The replacement of (typically hydrated) interlayer cations (Na^+ , K^+ , Ca^{2+} , or Mg^{2+}) by positively charged organic molecules with alkyl chains, and therefore with a low hydration capacity, can lead to swelling inhibition. This idea was first demonstrated by Weiss and Kantner [145] who replaced interlayer cations in smectites with alkylammonium ions. Such an effect has long been exploited in the field of civil engineering and the petroleum (oil drilling) sector to stabilize and consolidate clay-rich expansive soils and to prevent formation damage [146]. However, its application in the field of cultural heritage is relatively new [147]. One of the first examples is the case of the treatment of Easter Island tuff with a surfactant. Wendler et al. [45] successfully applied a dialkyl ammonium surfactant (diaminobutane dihydrochloride, $\text{C}_4\text{H}_{12}\text{N}_2 \cdot 2\text{HCl}$) as a swelling inhibitor to reduce the swelling of the smectite-rich tuff making up the famous Moai statues. Subsequently, Jimenez-Gonzalez and Scherer [10] and Jimenez-Gonzalez et al. [48] used a cationic surfactant, diaminoethane dihydrochloride ($\text{C}_2\text{H}_8\text{N}_2 \cdot 2\text{HCl}$) as a swelling inhibitor for Portland Brownstone, Villarlod Molasse and Tarifa sandstones. A ~ 50% reduction in free swelling strain was observed after treatment, which implies a ~ 50% reduction in swelling stress (compressive, tensile or shear) [48].

Wangler and Scherer [148] tested several surfactants, including α , ω -diaminoalkanes with variable carbon chain length (2–8), as swelling inhibitors for Portland Brownstone, showing that it was very difficult to achieve a swelling reduction larger than 50% in this sandstone that contains swelling (mixed layer) clays. The authors suggested that this was caused by an incomplete coverage of the interlayer space of the clays. Coverage was enhanced by using copper (II) ethylenediamine

complex solution, reaching a 70% free swelling strain reduction. But greater reductions could not be achieved. Ultimately, the authors could not rule out the possibility that the remaining strain was due to hydration of the external surfaces of the clay particles. This shows that the treatment with swelling inhibitors apparently can only reach a certain degree of effectiveness. Indeed, the study by Akoğlu and Caner-Saltik [149] on the treatment of clay-containing Mount Nemrut sandstone using a range of surfactants showed that the best performing one, diaminoalkane (DAA) only achieved a swelling reduction of 40%.

Combination of the swelling inhibitor treatment with other conventional treatments was also explored and showed promising results. Caruso et al. [150] demonstrated that the application of swelling inhibitors before TEOS consolidation reduced swelling damage of Villarlod molasse over several wet/dry cycles. However, the inhibitor pre-treatment reduced but did not fully prevent TEOS failure upon treatment of such a clay-bearing stone. Pötzl et al. [138] reported a reduction of hydric expansion when tuff stones were pre-treated with a swelling inhibitor before consolidation with TEOS and TMOS. However, in most cases, the anti-swelling agent could not compensate for the increase in swelling strain induced by the alkoxy silane treatment (specially in the case of TEOS). Much research is thus needed to find a proper combination of effective, long-lasting swelling inhibitors and an appropriate consolidant for clay-containing stones.

4.3. Bacterial protection and consolidation of clay-containing stone

Bacterial biomineralization of carbonates is a relatively novel and very active area of research, which is finding important applications in the conservation (protection and consolidation) of the stone built and sculptural heritage [7,151–153]. Early in the 1990s Adolphe et al. [154] patented a method for the consolidation of carbonate stones based on the precipitation of CaCO_3 on their surface and within their porous structure induced by bacteria. An inoculum of bacteria able to precipitating CaCO_3 , that is, a carbonatogenic bacteria culture, was applied along with a nutritional solution on the substrate to be treated. After a few days a certain degree of consolidation was achieved following bacterially induced CaCO_3 precipitation [155]. This method, commercially named Calcite, found only limited application over the following years. This was likely due to the fact that the method initially used a pathogenic bacteria (*Bacillus cereus*, which can provoke diarrhea), included a carbohydrate carbon source which can lead to undesired proliferation of deleterious acid-producing bacteria, and the culturing and application of the bacterial treatment was complex, requiring microbiologists in addition to conservators.

These drawbacks were overcome by a new bacterial conservation treatment developed by researchers at the University of Granada. This new method is based on the selective activation of indigenous carbonatogenic bacteria already present in the stone substrate to be treated [156]. By applying a patented sterile nutritive solution (M-3P), which lacked carbohydrate C sources [157], the selective activation of

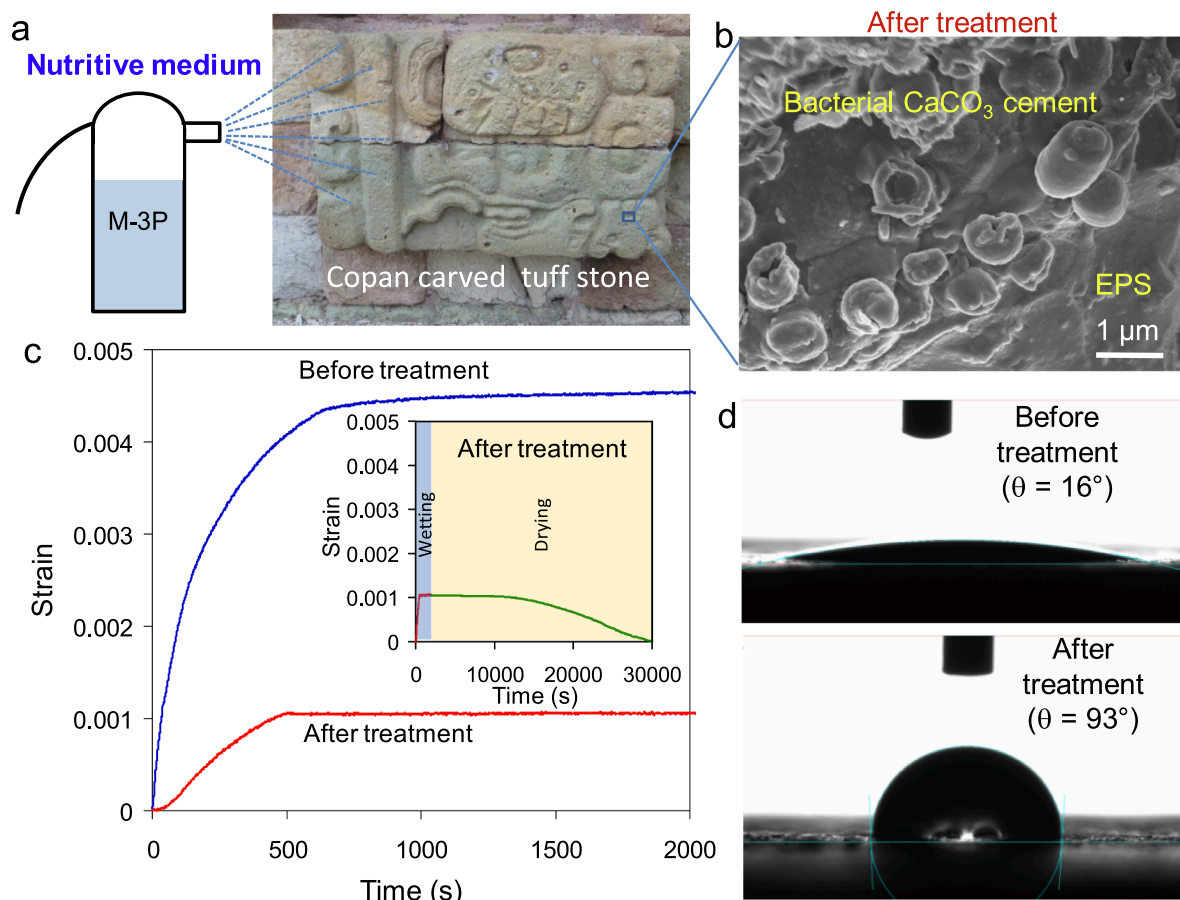


Fig. 9. Bacterial protection and consolidation of Copan tuff stone. a) Schematic of the treatment application (nutritive solution, M-3P); b) SEM image of calcified bacterial cells after treatment application, along with EPS; c) free swelling strain reduction after bacterial treatment of Copan stone blocks collected on site and treated in the laboratory. Note the absence of residual strain after a complete wetting/drying cycle (inset). In the case of the untreated stone there was a residual strain of ~ 0.001 after a complete wetting/drying cycle; d) contact angle of Copan tuff stone before and after bacterial treatment. Modified from Elert et al. [51]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

indigenous bacteria able to produce CaCO_3 cement was achieved, thereby obtaining a significant strengthening of decayed stones, both in the laboratory and in field trials in several carbonate and sandstone substrates [7,158]. Similar results were obtained by others [159]. Importantly, culture-dependent and culture-independent (molecular/genomic) analysis of indigenous bacteria in a range of substrates (stone and mortars) in many locations and environments, demonstrated that carbonatogenic bacteria are very abundant and that the treatment never induced the proliferation of deleterious (acid producing) microbiota [7,84]. These results warrant that this bacterial treatment can be safely and effectively applied in a range of substrates and locations worldwide.

After extensive testing in southern Europe [7,158,159], this treatment has recently been successfully applied in a complex, very challenging situation: the highly deteriorated clay-containing volcanoclastic tuff stone used for the building and carving of the Maya site of Copan (Honduras) exposed to a hot and humid tropical environment [51,84] (Fig. 9a).

Copan is one of the most remarkable Classic Maya centers in Mesoamerica and included as a UNESCO World Heritage Site [160]. Copan was built using a volcanic tuff of Tertiary age (ca. 5–30 Ma), extracted from local outcrops. Stone damage due to scaling and spalling after excavation of the different structures, carved stone sculptures, and stelae progressed at a rapid pace over the XX and XXI centuries. Consolidation with acrylic polymers (Paraloid B 72 and Mowital) and alkoxyxilanes was implemented in the 1980s and 1990s, but proved ineffective in the long term [161,162]. It was believed that biodeterioration was the main cause of alteration, although it was pointed out that Copan tuff stone included expansive clays which might contribute to its deterioration [162]. Our recent study [51] confirmed the presence of up to 8 wt% smectite (montmorillonite) in the stone varieties most prone to scaling and flaking, and disclosed a clear correlation between free hydric swelling strain and smectite content.

Once it was unambiguously demonstrated that clay swelling/shrinkage was the main culprit for the observed damage, the patented bacterial conservation treatment (sterile M–3P nutritional broth) was applied to the tuff stone on a trial site at Structure 10/18 in the Copan Acropolis (Main Group), as well as under laboratory conditions on tuff stone samples collected at the Maya site. In all cases, a significant proliferation of carbonatogenic bacteria took place, resulting in CaCO_3 biomineralization (Fig. 9b). The newly formed bacterial carbonate effectively consolidated the damaged tuff stones, at least to a depth of ~7 mm, as demonstrated by peeling tape test and drilling resistance measurements (DRMS), without altering the stone appearance as shown by color measurement [51]. Unexpectedly, a significant reduction in the free swelling strain of bacterially-treated Copan tuff stones and the absence of residual strain after each wetting/drying cycle was observed (Fig. 9c). In parallel, the water contact angle of treated tuff stone increased drastically from ~0° up to ~90° (Fig. 9d).

Altogether, these results showed that the activation of the indigenous carbonatogenic bacteria present in Copan stone following the application of the nutritive solution M–3P not only consolidated the stone but imparted hydrophobic (protective) and swelling inhibition properties to the substrate. Such a protection was linked to (i) the hydrophobic nature of copolymeric substances (EPS) formed by the activated bacteria [163], and (ii) the interaction of EPS with smectites, leading to EPS incorporation within the interlayer space of such swelling clays, and the reduction in their swelling capacity. XRD and small angle XRD (1D SAXS) results showed that bacterial EPS acted as a swelling inhibitor. Although these are preliminary results, they are very promising as they offer a new possibility for the protection and consolidation of stones containing swelling clays. Importantly, such a bacterial treatment has been demonstrated to be effective not just on calcareous substrates in mild Mediterranean environment, but also on silicate substrates and in harsh tropical conditions.

5. Concluding remarks

Despite the significant progress that has taken place over the last decades in the understanding of the different weathering mechanisms affecting building and sculptural stone, there are still some aspects of specific weathering processes that are not fully understood. This is exemplified by the damage associated with moisture expansion of clay-containing stones leading to scaling, flaking, spalling and delamination.

Although there is compelling evidence for the damaging role played by clays in general, and swelling clays in particular, on the development of strain and associated differential stress upon both crystalline and osmotic swelling of these phyllosilicates, other possible mechanisms for expansion leading to similar damage have been proposed. The latter include zeolite swelling and DLVO-related solvation forces (disjoining pressure) in micropores, both associated with moisture fluctuations, as well as thermal expansion. The evaluation and quantification of the individual contribution of each of these phenomena on the observed weathering patterns of clay-containing limestones, sandstones and tuff stones requires further research. For instance, it would be enlightening to perform expansion test in tuffs containing both zeolites and swelling clays using, in addition to water, other polar molecules with larger sizes (that can enter in the interlayer of the swelling clays but not into the zeolitic channel), in order to evaluate the relative contribution to expansion of clays vs. zeolites. The use of modern high-resolution technologies for the non-destructive in situ analysis of swelling and shrinking of the most sensitive clay (or zeolite) components in these stones, for instance using ESEM, in situ TEM with liquid cell, orptychographic X-ray nanotomography [164] would be important to get a more clear and detailed picture on the mechanisms of hydric/hygric expansion damage.

It is also shown that a proper understanding of the damage mechanism associated with the presence of clays in ornamental and building stone is key for the design and application of effective conservation treatments. In fact, an incomplete understanding of the fundamental mechanism(s) leading to moisture expansion, or the improper diagnosis of this deleterious phenomenon, has led to the application of conventional protection and consolidation treatments that had limited effectiveness, or even exacerbated damage. This is exemplified here by the case of the ancient Egyptian limestone sculptures at the Metropolitan Museum, the British Museum, and the Phoebe Hearst Museum.

The recognition that crystalline swelling of clays is a main contributor to the macroscopic expansion observed in clay-containing stones has opened a new way for preventive conservation treatments using swelling inhibitors, alone or in combination with other consolidants such as alkoxyxilanes. Much research is still needed in this regard, including the testing of alternative, more effective swelling inhibitors in combination with other consolidants, especially inorganic ones such as nanolimes or phosphates. Furthermore, the impact of newly formed calcium carbonate and calcium phosphate cement on the expansion (i.e., moisture expansion vs. thermal expansion) of treated clay-containing stones, particularly non-carbonate ones (sandstones and tuffs) needs to be evaluated.

It has also been shown that the novel approach for the conservation of clay-bearing stones by means of bacterial biomineralization is highly promising as this treatment not only consolidates the stone by the precipitation of new bacterial calcium carbonate cement, but it also tackles the root of the problem by limiting clay swelling. This is due to the fact that activated carbonatogenic bacteria are capable of producing abundant EPS, which renders the substrate hydrophobic, and by its incorporation in the swelling clay structure (smectites) reduces their swelling capacity. Further research is warranted to evaluate the long term effectiveness of this novel approach for the conservation of clay-bearing stones. Such a biobased and ecological method for the conservation of cultural heritage is in line with recent green and sustainable approaches for the conservation of a range of materials, involving not only consolidation but also cleaning and protection [165,166].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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