

INTERNAL STRESS AND CRACKING IN STONE AND MASONRY

George W. Scherer

Princeton University, Civil & Env. Eng./PRISM, Eng. Quad. E-319, Princeton, NJ 08544 USA

Abstract: Internal stresses arise during weathering of stone and masonry as a result of crystallization of salts and ice, swelling of clay inclusions, and thermal expansion, among other causes. In this paper, we review the origin of the stresses and examine the unresolved questions regarding several of these mechanisms.

Key words: crystallization pressure, frost, salt, ice, clay, swelling pressure, stress, fracture

1. INTRODUCTION

Several phenomena are known to contribute to stress and damage during weathering of stone and masonry, but the details of the mechanisms by which they act are not clear. In this paper, we examine several important weathering processes (thermal expansion of calcite, freeze/thaw cycles, salt crystallization, swelling of clay inclusions), reviewing what is understood and identifying aspects that remain to be resolved. Only by understanding these mechanisms in detail can we hope to develop methods for preventing, rather than repairing, damage from weathering.

2. CALCITE THERMAL EXPANSION

The low porosity of marble makes it relatively resistant to weathering mechanisms other than acid rain^{1,2,3}. However, the porosity of marble can increase after heating/cooling cycles, owing to the peculiar thermal expansion behavior of the constituent crystals of calcite (calcium carbonate): they expand along two crystallographic directions, but contract along the third as the temperature increases⁴. As a result, each of the tightly packed grains in a sample of marble changes its *shape*, not only its size, during thermal cycles. Thermal expansion stresses tend to open cracks along grain boundaries, leading to an increase in porosity⁵, as shown in Figure 1. Opening of grain boundaries not only makes marble susceptible to invasion of moisture, it also causes expansion that can lead to warping of a thin plate of stone, if the grain boundary damage only occurs on one face. Warping of marble cladding has occurred on several notable buildings in recent years, requiring costly replacement. The cause of this phenomenon is controversial. Winkler² claims that it results from relaxation of residual geological stresses that are released when the stone is quarried, leading to slow creep. If this were so, it would be surprising to see all of the slabs on a building warp in the same direction, since there would be no control of their orientation when they are mounted on the building. It could be caused by weathering of one side of a thin slab that causes opening of grain boundaries. If expansion from weathering were the cause, then the slabs would be expected to warp in the same direction, as is generally observed; however, they should become convex as cracking of grain

boundaries expands the outer surface, and that is not always so. In the case of the Finlandia Hall⁴, the original slabs became concave outward, as if the protected side had expanded. This could indicate that the warping results from mechanical constraint: if a plate expands uniformly, but if constrained near an edge, it will bow toward the opposite edge, as indicated in Figure 2.

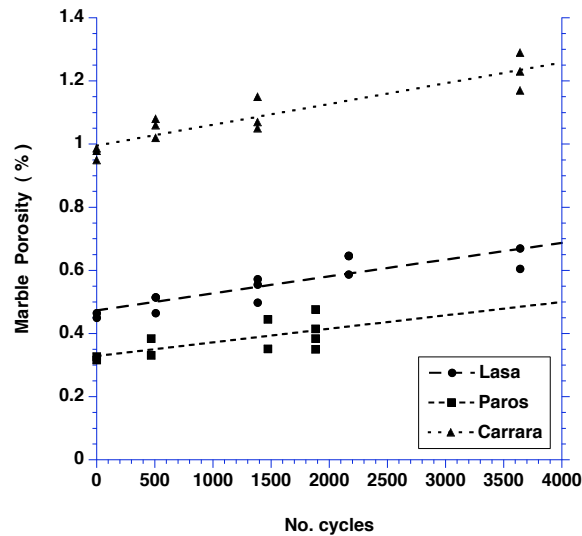


Figure 1. Change in porosity versus number of cycles between +35°C and -15°C for three types of marble. Data from Table 3, p. 13 of ref. 5.

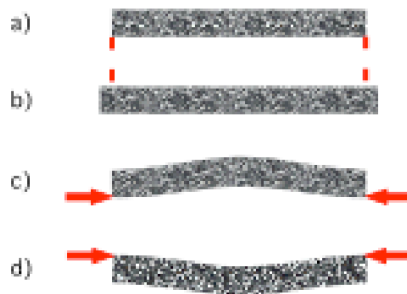


Figure 2. Warping of marble by constraint: a) original size; b) after uniform expansion; c) expansion constrained by clamping at lower edge; d) expansion constrained by clamping at upper edge.

3. FREEZE/THAW DAMAGE

Damage from freezing is commonly thought to result from the 9% increase in volume as water transforms into ice. The volume change can be highly destructive, if the liquid is entirely confined (as when a bottle of milk is forgotten in the freezer). A small object, such as a sculpture, might be chilled uniformly over its exterior surface, so that ice entraps the interior liquid. However, even in this extreme case, damage will result only if the saturation of the pores exceeds 91%; otherwise, the volume expansion can be accommodated by the vacant pores. A larger object, such as the wall of a monument, usually freezes from one direction (*viz.*, the exterior), so the ice pushes the water ahead. On the pore scale, it is possible that ice propagating through the pore network of a stone will

surround small pockets whose entries are very small; in that case, subsequent freezing would generate local stresses and damage⁶. It is not clear how important this mechanism is, but it could be quite significant when the freezing solution contains salt: since the salt cannot be incorporated into the ice crystal, the unfrozen brine becomes increasingly concentrated, and droplets of brine might become surrounded by ice. As the temperature drops, ice formation within the brine droplet would result in volume expansion that would exert stress on the surrounding stone.

Another mechanism for generation of stress during freezing is hydraulic pressure, as the volume change of the ice forces displacement of the adjacent liquid. Pressure builds up as the liquid is forced through the pores, and the pressure can be destructive if the growth is fast and the permeability of the body is low⁷. The pores in stone are generally too large to permit large stresses to arise in this way. Moreover, even when the pores are small (as in concrete), the rate of growth of ice rapidly decreases owing to the release of heat of fusion, which raises the temperature of the water/ice interface. The rate of growth is eventually controlled by the diffusion of heat, so it decreases in proportion to $t^{-1/2}$, with the result that the rate of displacement of the water is not sufficient to cause high stresses.

Frost damage can result from crystallization pressure, which is the stress exerted on the pore walls by the growing crystal^{8,9,10}. Although damage from growing crystals is widely recognized, some authors express puzzlement as to how a crystal can exert stress on a pore wall once it has made contact¹¹. The answer, probably first recognized by Taber¹², is that there is a thin film of liquid that surrounds the crystal, so that material is always available to permit growth (see Figure 3). The reason that growth is inhibited is that there is a repulsive pressure (or, disjoining force) between the crystal and the pore wall that is exerted across the liquid film¹³. The disjoining pressure between ice and minerals has at least two sources. First, the van der Waals forces are repulsive in this case, because the Hamaker constants decrease in order from ice to water to mineral¹⁴, so that a pressure of tens of MPa would be required to push ice into direct contact with most minerals⁹. Second, water molecules pack with a different structure in the vicinity of an interface^{14,15}, and this structure is probably not the same adjacent to ice and mineral surfaces; therefore, the liquid structure is disrupted when ice approaches a mineral and the energy of the system consequently rises. Analyses based on equilibrium thermodynamics⁹ indicate that crystallization stresses in the megapascal range (comparable to the tensile strength of stone) are expected when crystals grow in pores with diameters below 100 nm. Such pores are rare in stone, so this mechanism does not seem to account for the observed damage.

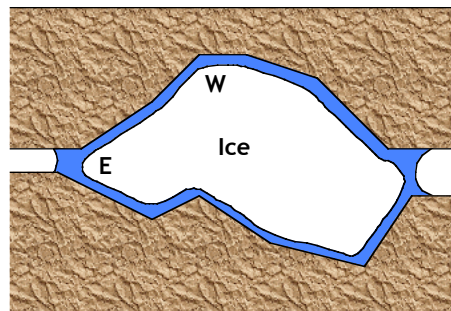


Figure 3. Isolated macroscopic crystal of ice, only in contact with surrounding film of water. As the temperature drops, it exerts high stress on the surrounding stone, limited only by the disjoining pressure in the film. The chemical potentials of ice and water must be equal near the pore entry (E) and near the pore wall (W).

To understand frost damage in stone, it might be necessary to assume non-equilibrium conditions. For example, consider the reasonable case in which an ice crystal extends through the pores of a stone over a volume of tens or hundreds of microns; a layer (perhaps a nanometer or so) of liquid surrounds the ice, owing to disjoining forces. When the temperature drops, the crystal tends to grow, so it pushes toward the wall against the disjoining pressure. Under equilibrium conditions, the chemical potential in the liquid film will be uniform, so the molecules of ice near the pore wall (W in Figure 3) and near the pore entry (E), which are in contact with the liquid, must also have the same potential. If the pore entry diameter is assumed to be in the micron range (so that its curvature has a negligible effect on the melting point of the crystal), then the pressure on the ice at E is negligible; ice near W will melt, and the molecules will be transferred to E as the temperature drops, so that the internal pressure of the crystal remains constant. However, to establish this equilibrium requires transport of molecules through a nanometric film over a distance equal to the size of the ice crystal. If this process is slow compared to the rate of cooling, then high transient stresses could develop. The characteristic time, t_e , for equilibration over a distance x by diffusion is approximately $t_e \approx x^2/D$, where D is the diffusion coefficient. For bulk water, $D \approx 2 \times 10^{-9} \text{ m}^2/\text{s}$, but the diffusivity is reported to be reduced by a factor of $\sim 10^3$ in films between mineral grains¹⁶ and $\sim 10^2$ in a thin film on a silica surface¹⁷, so we estimate $D \approx 10^{-11} - 10^{-12} \text{ m}^2/\text{s}$ in the water film around the ice. For diffusion through the film to equilibrate the pressure in an ice crystal with $x = 10 \text{ }\mu\text{m}$ would only take $t_e \approx 10\text{-}100 \text{ s}$, so it should easily remain in equilibrium with natural decreases in temperature ($\sim 5^\circ\text{C}/\text{h}$). However, if the isolated region of ice were 1 mm in diameter, the equilibration time would rise to the order of a day, so substantial stresses could be exerted on the pore wall during the period of equilibration of the ice. This phenomenon might cause damage on a very large scale, when ice is trapped in fissures in natural rocks, as well as creating cracks on the millimeter or centimeter scale in monuments.

4. SALT CRYSTALLIZATION

Salt crystals are also separated from the pore wall by a film of solution¹², but the van der Waals forces are attractive in this case, so the repulsion must arise from electrostatic forces or ordering of the water and ions against the solid surfaces. As in the case of ice, theories based on equilibrium thermodynamics⁹ predict megapascal stresses only in pores smaller than $\sim 100 \text{ nm}$. However, under nonequilibrium conditions, it is possible for an isolated macroscopic crystal of salt to exert high stresses^{18,19}.

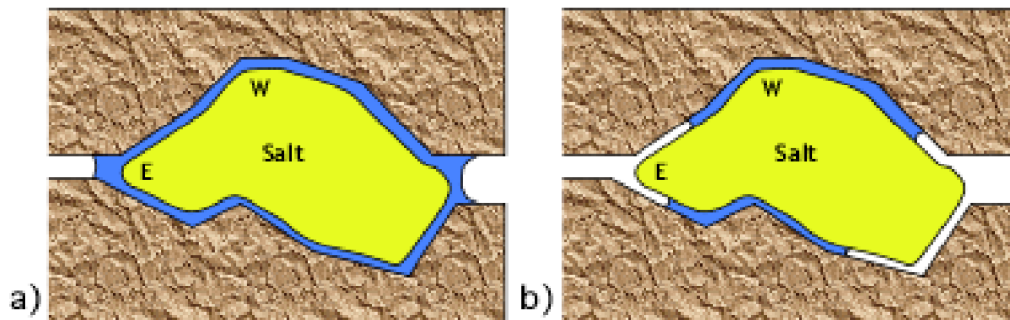


Figure 4. Macroscopic crystal of salt: a) surrounded by solution or b) partially dried.

Figure 4a shows a macroscopic salt crystal surrounded by a solution. If the supersaturation were to increase owing to a drop in temperature, the situation would be similar to that in Figure 3. Under equilibrium conditions, growth would occur near E to consume the supersaturation, and the ions in the film surrounding the crystal would diffuse to the site of growth; no significant stress would exist in this case. However, if the crystal were too large to permit the diffusion process to keep up with the rate of increase of supersaturation (corresponding to the rate of decrease in temperature), then high crystallization pressure could be exerted on the pore wall during the equilibration period.

The distribution of salt in the pores of a stone is controlled by several independent kinetic processes: supply of water (say, by rising damp or a leaky roof), evaporation, diffusion of dissolved ions away from the site of evaporation (*i.e.*, toward the source of invading water), and nucleation and growth of crystals. As water evaporates from a body with a pore size distribution, the larger pores empty first, while the smaller ones remain full by using their greater capillary suction to drain liquid from their larger neighbors²⁰. At equilibrium, the order of drainage during drying is identical to the order of invasion of the pores in a mercury intrusion experiment, since both processes involve the intrusion of a non-wetting fluid (*viz.*, air during drying and Hg during porosimetry). Therefore, the increasingly concentrated salt solution retreats into smaller and smaller pores in a predictable way. If the rate of evaporation is fast compared to the rate of redistribution of water among neighboring pores, then the large and small pores may empty almost simultaneously, but that is not expected for stones, owing to their high permeability. When the concentration of the remaining fluid (which, in the assumed state of equilibrium, has a uniform composition) reaches the solubility limit, macroscopic crystals become stable. However, for crystals to form in a pore with radius r , the solubility product, Q , must satisfy the Ostwald-Freundlich equation²¹,

$$\frac{2\gamma_{CL}}{r-\delta} = \frac{RT}{V_C} \ln\left(\frac{Q}{K}\right) \quad (1)$$

where γ_{CL} is the crystal/liquid interfacial energy, δ is the thickness of the film of solution between the crystal and the pore wall, R is the ideal gas constant, T is absolute temperature, V_C is the molar volume of the crystal, and K is the equilibrium solubility product. If the solution initially filling the pores is dilute, then a great deal of evaporation must occur to raise the concentration to the solubility limit; at that point, the solution will have retreated into relatively small pores, so a high Q may be needed to initiate crystallization. On the other hand, if the initial solution is nearly saturated, then precipitation may occur in the largest pores after very little evaporation has occurred. The stress generated during this process of evaporation at equilibrium has recently been analyzed by Coussy²².

If nucleation of crystals is difficult, then a different sequence of events is expected. The concentration will continue to rise until the threshold for nucleation is exceeded, whereupon crystals will form in all the liquid-filled pores. Crystals in the smallest pores will eventually have their growth arrested by the pore walls, while those in larger pores continue to grow. Since the solubility of a crystal increases as its size decreases, crystals that form in the smaller pores tend to dissolve as the solute diffuses to the larger crystals; this process of Ostwald ripening continues until the salt is transferred to the largest accessible (*i.e.*, solution-filled) pores¹⁹. The equilibrium state is the same as that discussed previously, but higher transient stresses are exerted in the smaller pores before those crystals dissolve. The kinetics of the transient may be further complicated by diffusion of solute

away from the drying surface. Buenfeld et al.²³ succeeded in modeling the chloride distribution subject to simultaneous wicking, continuous evaporation, and solute diffusion. However, Mayer and Wittmann²⁴ concluded that the rate of diffusion would usually overwhelm the natural (cyclical) rate of evaporation, so that it would be difficult for the pore solution to reach supersaturation. In such cases, crystallization pressure would only occur where isolated pockets of solution are left behind after the evaporation front passes, leading to the situation depicted in Figure 4b. Trapping of liquid during drying requires that a cluster of pores is surrounded by small pore entries; this can happen in any body with a distribution of pore sizes, but is particularly likely within clay inclusions which have much smaller pores than the surrounding stone.

5. SWELLING CLAY INCLUSIONS

Many sedimentary rocks contain clays, as isolated inclusions, as films around grains, or both. If the clays swell on exposure to moisture, damaging stresses can result^{25,26}. Some stones show expansions of several percent, but the failure strain of stone is typically $\sim 0.1\%$, so much smaller expansion can be destructive²⁷. Clays expand when water molecules enter between the sheets to hydrate the charge-compensating alkali ions²⁸. Since the initial spacing of the sheets is ~ 1 nm, insertion of a single layer of water molecules causes an expansion of $\sim 30\%$. Suppose that the clays form a film of thickness d around grains with diameter D , as in Figure 5a; if the strain in the clay is ϵ_c , then the strain in the stone is

$$\epsilon_s = \frac{d \epsilon_c}{D + d} \quad (2)$$

Therefore, when $d/D \ll 1$, the expansion of the stone can be orders of magnitude smaller than that in the clay. If the clay constitutes the cementing phase in the stone, the softening of the clay is directly translated into softening of the stone. For example, Portland Brownstone only expands by $\epsilon_c \approx 5 \times 10^{-4}$, but the modulus decreases by more than a factor of 2 when it is wet²⁷.

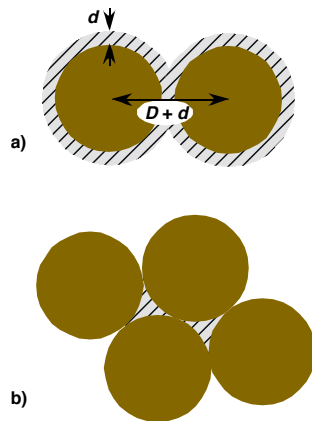


Figure 5. Clay may form a layer around grains of stone (a) or be isolated as inclusions between grains (b).

If the clay is rigidly trapped as inclusions between grains, as in Figure 5b, then it may not be able to expand at all. If it is loosely packed in the dry state, then it may swell and

exert stress on the surrounding stone. In that case, the strain in the stone can be calculated in the same way as one would calculate the thermal expansion of a composite containing isolated inclusions with an expansion coefficient larger than that of the matrix. For example, using the composite sphere model²⁹ (where the clay is the inner sphere and the stone is the outer sphere), the strain of the stone is estimated to be

$$\varepsilon_s \approx \frac{2v_c \varepsilon_c}{1 + K_s/K_c} \quad (3)$$

where v_c is the volume fraction of clay inclusions (assumed to be $\ll 1$) and K_s and K_c are the bulk moduli of the stone and clay, respectively. If the clay is very compressible ($K_s \gg K_c$), then the expansion of the clay causes little deformation of the stone.

If a clay-bearing stone is wetted by rain, its surface swells; when the water has only penetrated a small fraction of the depth of the body, the expansion of the surface is entirely suppressed by the dry interior, so high compressive stresses develop in the surface. If the body is thin, so that the water can penetrate to its center, then the dry interior is forced to stretch as the surrounding volume expands, so high tensile stresses develop in the interior. During drying, the stresses would reverse: contraction of the surface would create high tensile stresses near the outside of the body, while the wet interior would experience increasing compressive stresses. In this case, the most likely damage pattern would be “mud-cracking” (i.e., randomly oriented fissures) on the surface. This situation might occur for a tombstone or small sculpture, but not for the wall of a building. The compressive gravitational load on a building would suppress the expansion of the stone entirely (except for corners and protruding decorations), so the expansion during wetting would increase the compressive stress, but the interior would never experience tension; during drying, the compressive stresses would diminish to zero, but no tension would develop at the surface. If swelling of clays causes damage to a wall, it must result from buckling under compressive stress, which is consistent with the pattern of damage seen in structures made of swelling stone²⁷. Buckling will only occur if there are buried flaws that are several times wider than the thickness of the buckling layer³⁰. Such flaws could result from crystallization of salt or ice.

6. CONCLUSIONS

Several mechanisms are known to cause stresses, and many of their essential features are known, but some details are not clear. The cause of warping of thin marble plates is not understood. Freeze/thaw damage may have several causes, but most are not expected to cause high stresses in stone; it may be that trapping of liquid filled pores is important, particularly when dissolved salts lead to formation of brine pockets in the ice. Salt damage is one of the most serious, but least understood, causes of stone deterioration. How are large supersaturations produced? How easily do crystals redistribute from smaller to larger pores? What is the origin of the disjoining force? In the case of clay expansion, it is not clear whether damage requires clays to be in the cement between grains, or whether isolated inclusions can contribute. Once these details are understood, it may be possible to develop treatments that attack the cause, rather than the symptoms, of these damage mechanisms.

References

- ¹ E.M. Winkler, Weathering of crystalline marble, pp. 717-721 in *The engineering geology of ancient works, monuments and historical sites: preservation and protection*, Editor: Marinos, Paul G.; Koukis, George C. (A.A. Balkema, Rotterdam, 1988)
- ² E.M. Winkler, *Stone in Architecture*, 3rd. ed. (Springer, Berlin, 1997)
- ³ K. Lal Gauri and J.K. Bandyopadhyay, *Carbonate Stone, Chemical behavior, durability and conservation* (Wiley, New York, 1999)
- ⁴ S. Siegesmund, K. Ullemeyer, T. Weiss, and E.K. Tshegg, Physical weathering of marbles caused by anisotropic thermal expansion, *Int. J. Earth Sci.* **89**, 170-182 (2000)
- ⁵ G.G. Amoroso and V. Fassina, *Stone Decay and Conservation* (Elsevier, Amsterdam, 1983)
- ⁶ S. Chatterji, Aspects of the freezing process in a porous material-water system. Part 1. Freezing and the properties of water and ice, *Cem. Concr. Res.* **29**, 627-630 (1999)
- ⁷ T.C. Powers, The air requirement of frost-resistant concrete, *Proc. Highway Res. Board*, **29**, 184-211 (1949)
- ⁸ D.H. Everett, The thermodynamics of frost damage to porous solids, *Trans. Faraday Soc.*, **57**, 1541-1551 (1961)
- ⁹ G.W. Scherer, Crystallization in pores, *Cement Concr. Res.* **29** (8) 1347-1358 (1999); Reply to discussion of *Crystallization in pores*, G.W. Scherer, *Cement and Concr. Res.* **30** (4) 673-675 (2000)
- ¹⁰ G.W. Scherer and J.J. Valenza II, Mechanisms of Frost Damage, in *Materials Science of Concrete, Vol. VII*, eds. J. Skalny and F. Young (American Ceramic Society, 2005) 209-246
- ¹¹ S.Z. Lewin, The mechanism of masonry decay through crystallization, pp. 120-144 in *Conservation of Historic Stone Buildings and Monuments* (National Acad. Press, Washington, DC, 1982)
- ¹² S. Taber, The growth of crystals under external pressure, *Am. J. Sci.* **41**, 532-556 (1916)
- ¹³ C.W. Correns, Growth and dissolution of crystals under linear pressure, *Disc. Faraday Soc.* **5**, 267-271 (1949)
- ¹⁴ J. Israelachvili, *Intermolecular & Surface Forces*, 2nd ed. (Academic, London, 1992)
- ¹⁵ P. Gallo, M.A. Ricci, and M. Rovere, Layer analysis of the structure of water confined in vycor glass, *J. Chem. Phys.* **116** (1) 342-346 (2002)
- ¹⁶ P.K. Weyl, Pressure solution and the force of crystallization - A phenomenological theory, *J. Geophys. Res.* **64** (11) 2001-2025 (1959)
- ¹⁷ W.P. Halperin, S. Bhattacharija, and F. D'Orazio, Relaxation and dynamical properties of water in partially filled porous materials using NMR techniques, *Magnetic Res. Imaging* **9**, 733-737 (1991)
- ¹⁸ G.W. Scherer, Stress from crystallization of salt in pores, in *Proc. 9th Int. Cong. Deterioration and Conservation of Stone, Vol. 1*, ed. V. Fassina (Elsevier, Amsterdam, 2000) 187-194
- ¹⁹ G.W. Scherer, Stress from crystallization of salt, *Cement Concr. Res.* **34**, 1613-1624 (2004)
- ²⁰ G.W. Scherer, Fundamentals of drying and shrinkage, in *Science of Whitewares*, eds. V.E. Henkes, G.Y. Onoda, and W.M. Carty (Am. Ceram. Soc., Westerville, OH, 1996) 199-211
- ²¹ J. Freundlich, *Colloid & Capillary Chemistry* (Methuen, London, 1926) 154-157
- ²² O. Coussy, Deformation and brittle fracture from drying-induced crystallization of salts, submitted to the *Journal of the Mechanics and Physics of Solids*
- ²³ N.R. Buenfeld, M.T. Shurafa-Daoudi, and I.M. McLoughlin, Chloride transport due to wick action in concrete, *Chloride Penetration into Concrete*, ed. L.O. Nilsson and M.P. Olliver (RILEM, Paris, 1997) 315-324
- ²⁴ G. Mayer and F.H. Wittmann, Ein Modell zur Beschreibung des Wasser- und Salztransports in Mauerwerk, *Int. Zeitschrift für Bauinstandsetzen* **2** (1) 67-82 (1996)
- ²⁵ J.R. Dunn and P.P. Hudec, Water, clay, and rock soundness, *Ohio J. Science* **66** (2) 153-168 (1966)
- ²⁶ C. Rodriguez-Navarro, E. Sebastian, E. Doehne, and W.S. Ginell, The role of sepiolite-palygorskite in the decay of ancient Egyptian limestone sculptures, *Clays Clay Minerals* **46** (4) 414-422 (1998)
- ²⁷ G.W. Scherer and I. Jimenez Gonzalez, Characterization of Swelling in Clay-Bearing Stone, in *Stone decay and conservation*, SP-390, ed. A.V. Turkington (Geological Soc. Am., 2005) 51-61
- ²⁸ H. van Olphen, *An Introduction to Clay Colloid Chemistry*, 2d ed. (Wiley, NY, 1977)

²⁹ G.W. Scherer, *Relaxation in Glass and Composites* (Wiley, New York, 1986; reprinted by Krieger, Malabar, FL, 1992)

³⁰ J.W. Hutchinson, M.Y. He, A.G. Evans, The influence of imperfections on the nucleation and propagation of buckling driven delaminations, *J. Mech. Physics Solids* **48**, 709-734 (2000)