# Swelling Mechanism in Clay-Bearing Sandstone | 2007-09

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# Swelling Mechanism in Clay-Bearing Sandstones

Timothy Wangler[1], George W. Scherer[2]

[1]Princeton University Dept. of Chemical Engineering
[2]Princeton University Dept. of Civil and Environmental Engineering
Eng. Quad. E-319, Princeton, NJ 08544 USA

## Abstract

Swelling clays in stone can generate damaging stresses during a wetting or a drying cycle, which leads to deterioration of building stones such as Portland Brownstone. There are two primary types of swelling identified for clays: short-range, ordered intracrystalline swelling, and long-range, continuous osmotic swelling. Identification of the swelling mode is important for understanding and ultimately preventing swelling damage. Through comparison of XRD and swelling experiments with cationic pretreatments and organic solvents, we demonstrate that intracrystalline swelling is the primary mode of swelling present in three different stones, including Portland Brownstone. The results highlight the importance of the counterbalancing cation to the swelling process, and a method for characterizing the intracrystalline swelling in sandstones is developed. Finally, the implications of long-term swelling behavior for stones are discussed.

## I. Introduction

Swelling clays are known to be an issue in many engineering problems, such as borehole stability, tunneling, and foundation stability [1-3]. They also appear in sandstones often used in historic monuments and buildings, and wetting and drying cycles lead to stresses that can cause damage [4]. Their unique behavior in the presence

of water and their interactions with other adsorbates makes characterizing their swelling properties of great importance. This paper details a study in which the mechanism of swelling clays in three sandstones is identified and characterized.

Clay swelling has been shown to be an issue in the deterioration of Portland Brownstone, an arkose sandstone appearing in many buildings and monuments in the northeastern United States [5]. It is also an issue in other stones throughout the world that appear in historic landmarks [6-7]. As can be seen in Figure 1, the microstructure of Portland Brownstone shows large grains of quartz and feldspar cemented together in a matrix that includes clays. X-ray diffraction (XRD) studies show that the primary clay present in Portland Brownstone is chlorite, along with illites and other non-swelling clays [8]. Weathering of chlorite has been shown to result in the creation of swelling layers interspersed within the nonswelling layers [9]. When XRD is performed on the whole rock, there is no detectable peak shift upon glycolation, so the swelling clay fraction is probably very small and is likely randomly distributed throughout the chlorite in Portland Brownstone. Since it is in the cementing phase, it is not necessary to have a large amount of clay to cause the observed dimensional change during a wetting cycle. Having the swelling clay in the cementing phase also has a drastic effect on the elastic and viscoelastic properties of the stone, as was demonstrated by Gonzalez and Scherer [5].

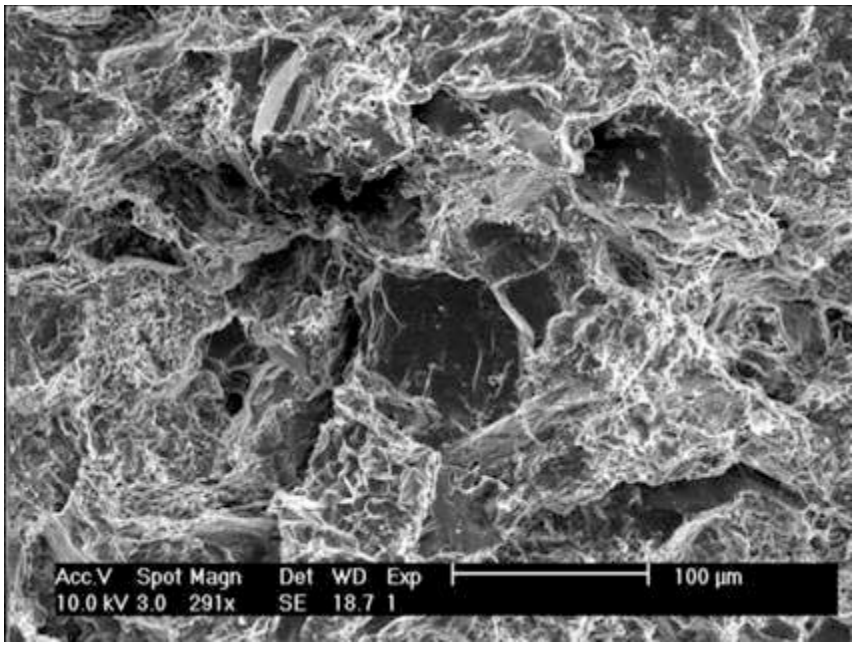



Figure 1. Portland Brownstone SEM micrograph.

Wendler developed a treatment to reduce swelling in stones that consisted of a diaminoalkane (DAA) molecule that would enter the interlayer and exchange for the alkali, which was tested in two separate studies [10-11]. Gonzalez and Scherer extended this treatment to Portland Brownstone and other swelling stones in another study, and also demonstrated the effect of sequencing and mixtures of diaminoalkanes [5]. In every treatment study, however, swelling was reduced, but never eliminated. It is well known that there are two different modes of swelling in clays: the initial, ordered, intracrystalline swelling from the hydration of the counterbalancing cations, and the long-range, purely electrostatic osmotic swelling [12]. Intracrystalline swelling is marked by discrete jumps in interlayer spacing, each corresponding to about 2.5 Angstroms, which is approximately one monolayer of water. When swelling enters the osmotic regime, interlayer spacing increases continuously with increasing water activity. It is also possible that residual

capillary strain from menisci formed during drying could cause swelling as those menisci are destroyed in a wetting cycle. Therefore the question of which swelling mechanisms are responsible for hygric expansion of sandstones should naturally be raised. Most of the evidence, such as the change in elastic properties of the wet stone as well as the effect of the DAA on the elastic and viscoelastic properties, seems to indicate that we are dealing with intracrystalline swelling to some degree, but in order to focus efforts on further reducing swelling strain, it is necessary to know if other mechanisms are at play. In this study, we demonstrate that we are dealing with almost exclusively intracrystalline swelling by means of various cation pretreatments and also by comparison of XRD studies of neat clay/polar organic solvent systems and our experimental swelling strains.

## II. Materials & Methods

Three different stones were used in this study: Portland Brownstone obtained from Pasvalco Corp. (Closter, NJ), a yellow sandstone from Aztec National Monument (New Mexico) provided by the Metropolitan Museum of New York, and Portage bluestone from Endless Mountain Quarry (Susquehanna, PA). All three types of stone were cut into samples approximately 5 x 5 mm square and ranging from 15-50 mm in height. Cationic pretreatments were performed by soaking a sample in an approximately 3 M solution of the chloride salt and then washing several times in DI water. All salts and solvents used in swelling were obtained from Fisher Scientific. Swelling experiments were performed on samples that had been oven-dried (60 C) and then equilibrated at ambient temperature in a sealed container to avoid ambient humidity. Using a linear variable differential transformer (LVDT from Macrosensors, Pennsauken,

NJ), linear expansion was measured as a function of time after the addition of the swelling fluid; in some experiments, the swelling solutions were syringed out and replaced with different ones.

## III. Results

The untreated hygric swelling of the three stones was first characterized and is tabulated in Table 1. Both the bluestone and the Aztec sandstone showed nearly double the amount of hygric swelling of Portland Brownstone, and the Brownstone used in this study had a very large swelling strain compared to Brownstones used in previous studies [4-5].

| Stone | Swelling Strain (mm/m) |
|---|---|
| **Portland Brownstone** | 1.0 |
| **Portage bluestone** | 2.1 |
| **Aztec Sandstone** | 1.9 |

Table 1. Untreated water swelling strains of stones used in this study.

### III.1 Elimination Experiments

Two experiments were carried out to test the mechanisms of residual drying strain and osmotic swelling. In the first experiment, decane was used as a swelling fluid. Decane is not expected to have any interaction with the clay, and the decane/water interface is of lower energy than the air/water interface, so any capillary pressure created by air/water menisci would be drastically reduced by contact with decane. In the second

experiment, a stone sample was fully swollen in water, and then the water syringed out and replaced with a concentrated (~1-2 M) salt solution. As the salt diffused into the stone's pore space, an osmotic effect would have resulted in a contraction of the stone as water flowed from the interlayer space (or possibly the interparticle space) into the pore space. Very minor swelling (~5% of the water swelling strain) was recorded with the decane experiment and almost no contraction observed with the salt solution experiment.

### III.2 Swelling after Cation Pretreatment

In these experiments, Portland Brownstone samples pretreated with various cations were subjected to swelling in pure water. The swelling curves for these can be seen in Figure 2. Potassium, ammonium, and cesium all depressed swelling for the duration of the experiment by 30-40%. All other cations tested (sodium, calcium, magnesium, lithium) swelled to close to the untreated swelling strain of 1.0 mm/m. This behavior was repeatable across the two other stone types.

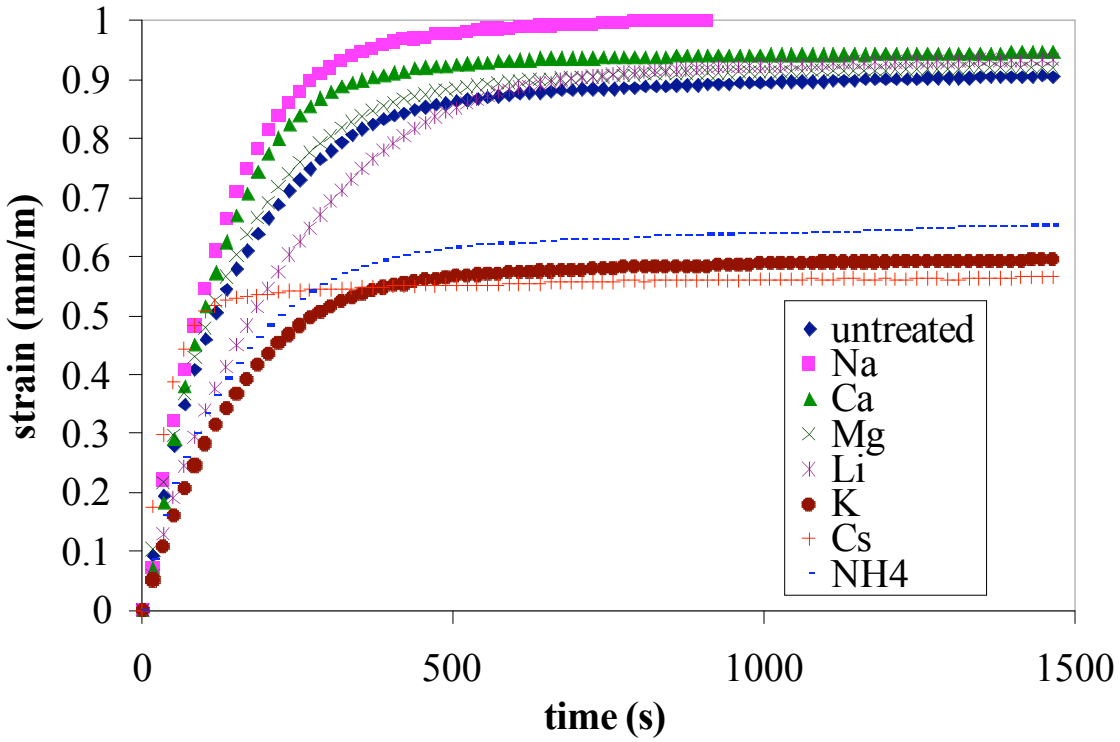



Figure 2. Portland Brownstone swelling with various cation pretreatments. K, Cs, and NH4 form the low-swelling cluster.

**III.3 Polar Organic Solvent Swelling**

In these experiments, cation-pretreated samples were first swollen with methanol or acetone, and then the solvent was removed and replaced with ethylene glycol. As the ethylene glycol diffuses into the stone, it enters the interlayer and displaces the methanol or acetone. Figure 3 shows the curve for Ca-pretreated Portland Brownstone and a sequential methanol-ethylene glycol-water addition. Upon addition of water, the Portland Brownstone swells to the full water swelling strain of about 1 mm/m. Figures 4a-c demonstrate the acetone-ethylene glycol sequence for calcium saturated samples of all

three types of stones. In all experiments, the ethylene glycol swelling strain was approximately twice that of the methanol or acetone swelling strain.

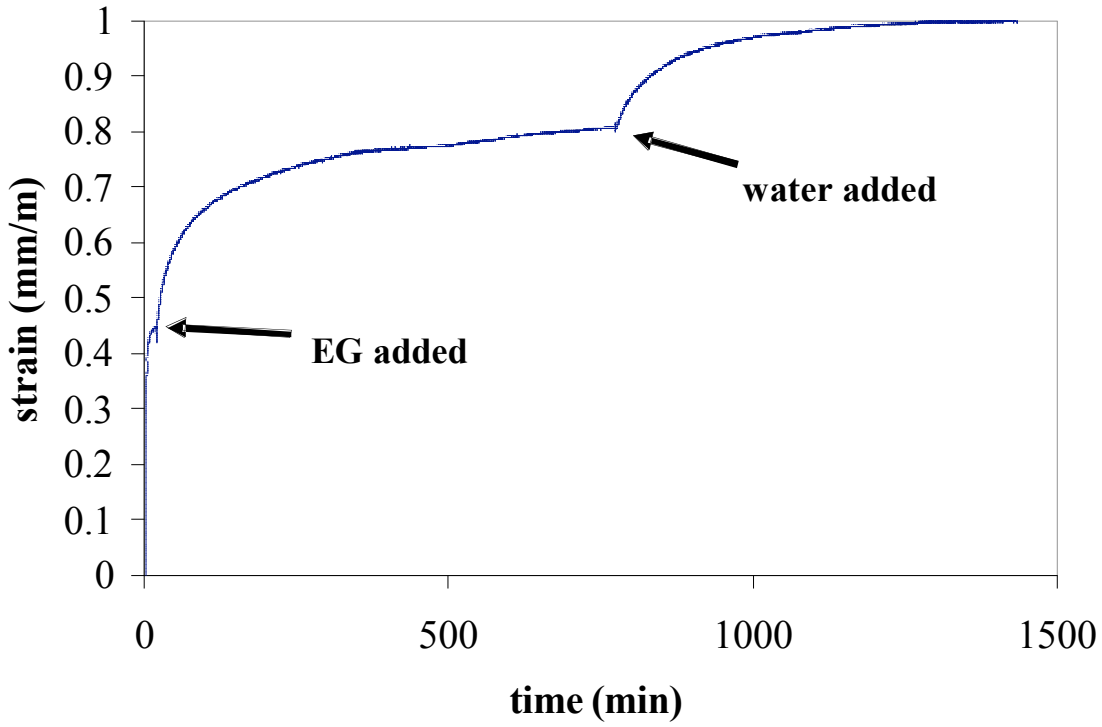
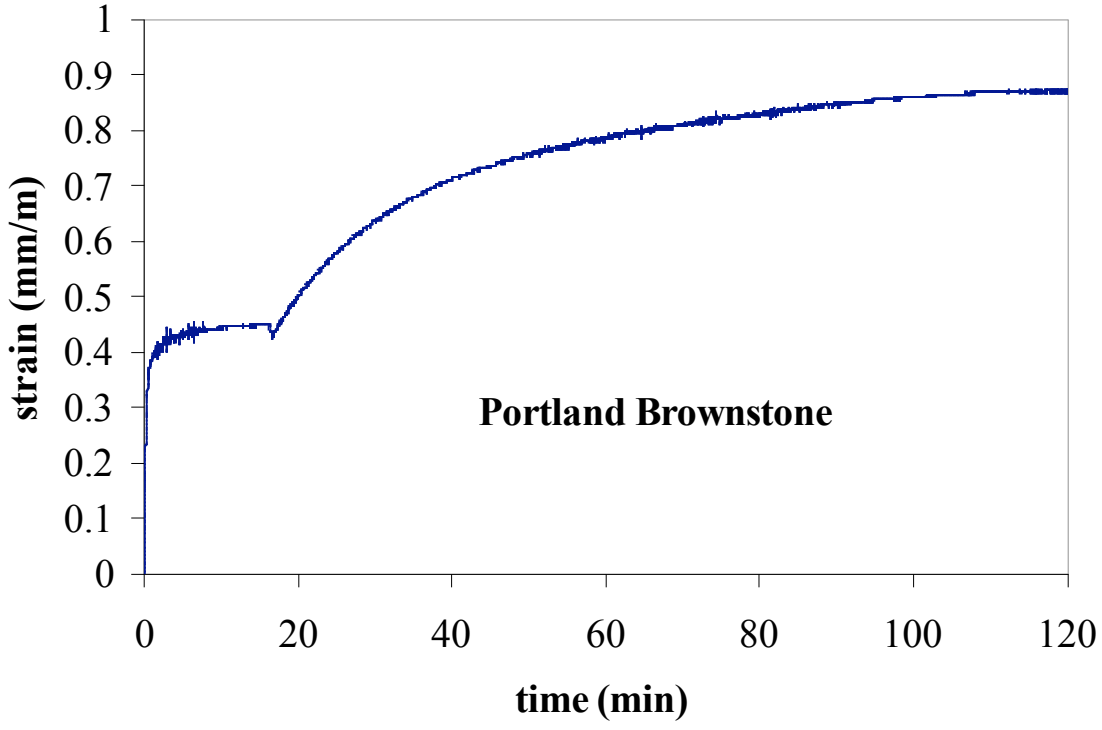
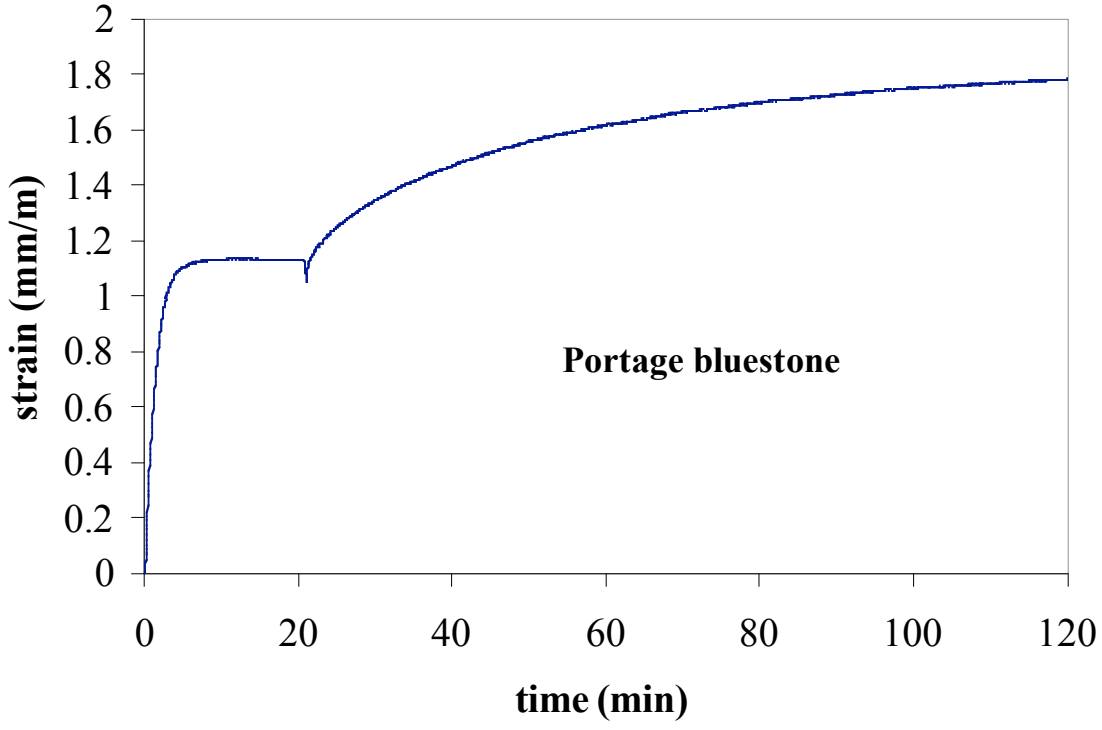



Figure 3. Portland Brownstone swelling upon sequential addition of methanol, ethylene glycol, and water. Ethylene glycol (bilayer) is nearly double the swelling strain of methanol (monolayer). The water swelling strain of this Portland Brownstone was 1 mm/m.


strain (mm/m)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
120
time (min)
Portland Brownstone


strain (mm/m)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
100
120
time (min)
Portage bluestone

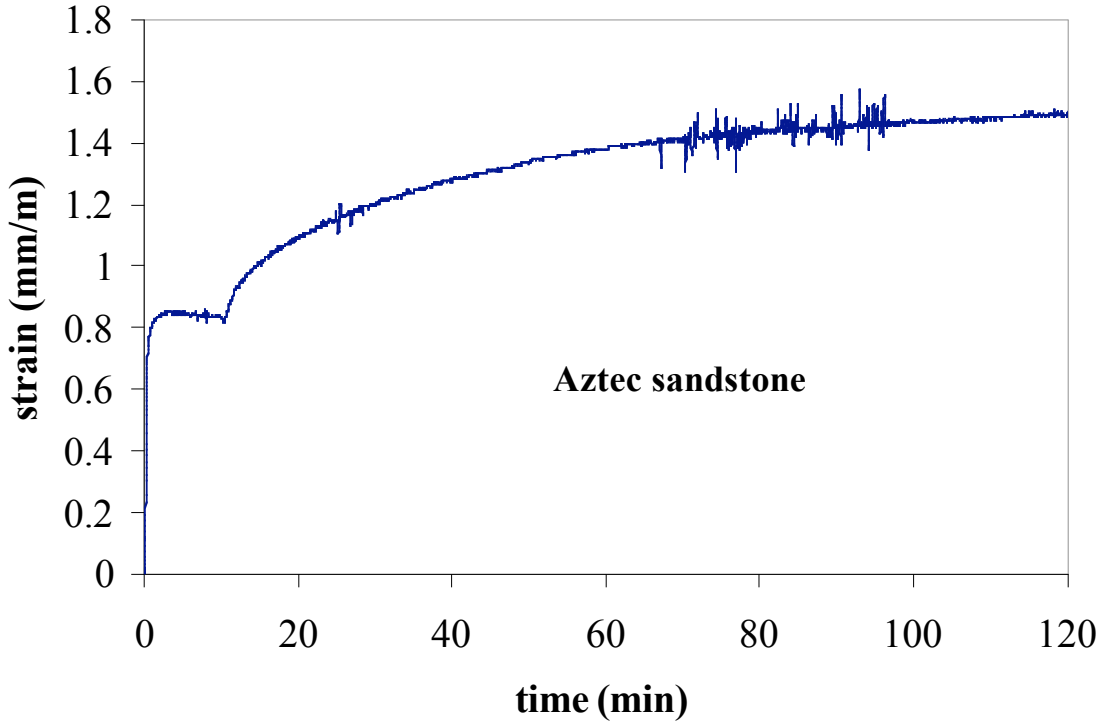



Figure 4 a-c. Sequential swelling experiment of acetone to ethylene glycol with Ca-pretreated stones. Ethylene glycol swelling strain is about double that of acetone, indicating a doubling of the clay interlayer spacing.

**IV. Discussion**

The elimination experiments were both useful in adding to the evidence that intracrystalline swelling is the predominant swelling mechanism at play. The lack of contraction on exposure to concentrated salts demonstrates that osmotic swelling is not significant in these stones. Capillary pressure also makes an insignificant contribution to the dilatation of these stones; nevertheless, the decane swelling experiment may prove useful in characterizing a baseline level of swelling strain that may come from residual drying strains in some stones.

The effect of the cationic pretreatments on the swelling strain is good evidence of intracrystalline swelling. Potassium and ammonium "fixation" to clays has been well known to soil scientists, and simulations have demonstrated that potassium and cesium both form "inner-sphere" hydrates in the clay interlayer, meaning that the cations remain close to the negatively charged surface during hydration and thus inhibit intracrystalline swelling [13-14, 1]. These experiments help to underscore the importance of the counterbalancing cation to the swelling process. It should be stressed that these experiments were conducted over relatively short periods corresponding to the time required to saturate the sample. It is possible that more swelling occurs at longer times, as will be discussed further in this paper.

The most enlightening results of this study come from the polar organic solvent swelling experiments. It has been demonstrated that swelling clays form monolayer or bilayer complexes with acetone and methanol depending on the counterbalancing cation and the duration of exposure to the solvent [15-16]. The interlayer spacings of these systems are typically 13-14 Å for a monolayer and about 16-17 Å for a bilayer. It is also well known that ethylene glycol will usually form a bilayer complex with swelling clays of about 17 Å [17]. In fact, ethylene glycol is typically used as a test for swelling clays in XRD studies for this reason. The results of this study show a doubling of the swelling strain upon the sequential addition of ethylene glycol to a methanol- or acetone-swollen sample, indicating a transition from a monolayer to a bilayer. This is the clearest evidence of intracrystalline swelling, and also underscores the importance of the counterbalancing cation to the process, because of the different layer spacings associated with different ion-solvent complexes.

If it is assumed that all swelling layers are identical, then the fact that two swelling strains can be matched to corresponding interlayer spacings permits calculation of a scaling factor relating the increase in strain on the macroscopic level to an increase in interlayer spacing. Additionally, the amount of swelling clay layers per unit length of stone can be estimated. The results of all these calculations for a Ca-stone-acetone-ethylene glycol system are shown in Table 2; the method of calculation is explained in the Appendix.

**Acetone / EG Experiment (Ca Pretreated)**

| | Interlayer Spacing (Å) | | Swelling Strain (mm/m) | | Scaling Factor (mm/m-A) | Swelling Layers/mm |
|---|---|---|---|---|---|---|
| **Stone** | **Acetone** | **EG** | **Acetone** | **EG** | | |
| **Portland Brownstone** | 13.5 | 17 | 0.45 | 0.85 | 0.11 | 1100 |
| **Portage bluestone** | 13.5 | 17 | 1.12 | 1.85 | 0.2 | 2000 |
| **Aztec Sandstone** | 13.5 | 17 | 0.83 | 1.49 | 0.19 | 1900 |

Table 2. Scaling factors relating proportional increase in stone linear dimension with increase in interlayer spacing. Interlayer spacings from [15-17].

The calculated constant of proportionality relating interlayer swelling to swelling strain leads to a variety of other useful information regarding the characterization of swelling in these stones. It demonstrates that maximum swelling is restricted to about a 10 Å layer spacing increase, or 4 “pseudo-monolayers” of water. The fact that calcium, a known osmotic swelling inhibitor, does not inhibit swelling at all is also confirmed by this. Swelling seems to begin from an almost fully dehydrated state. Typically, swelling clays will have one or two monolayers of water in neat clay XRD studies performed at

ambient relative humidities, depending on the cation. In fact, the high field strength of calcium means that calcium-treated swelling clays have two monolayers of water (basal spacing of 15 Angstroms) at relative humidities as low as 20% [18]. At the relative humidities of the experiments in this study (~30-35%), these data indicate that all cations are almost fully dehydrated, so the pressure of the stone matrix pushing the clay layers together must act to squeeze the last interlayer of water out during drying. For example, the elastic modulus of Portland Brownstone drops from 9.1 GPa in the dry state to 4.1 GPa when fully saturated [19]. The stiffness of the wet stone is attributed to grain junctions that do not contain much clay, and the network of these junctions forms a rigid skeleton. This skeleton would be expected to apply a static load on the clay-containing grain boundaries that would inhibit expansion; it also seems to be capable of preventing hydration of the interlayers at moderate humidity levels.

The net result of this work is that one can envision a series of tests to characterize swelling in clay-bearing stones. If there is a background of swelling from residual drying strain, the decane test is useful in characterizing that. Then, performing swelling experiments with acetone, methanol, ethylene glycol (or other solvents that have had their interlayer spacings with swelling clays characterized) can demonstrate whether intracrystalline expansion causes macroscopic swelling. Of course, this requires that all swelling clay layers behave in the same way, which means that they must not only have the same mineralogy, but must contain the same cations. It is advisable, therefore, to pretreat the stone with concentrated salt solutions to ensure that the interlayer cations are uniform, before testing with organic solvents. In terms of characterization of the swelling

of Portland Brownstone, a stone whose swelling clays have been undetectable in XRD experiments up to this point, this test has been invaluable.

An important feature of these stones that has not been well characterized is the behavior of these stones at long times. The fact that extended duration of exposure to monolayer-forming solvents can lead to bilayers means that the long time swelling behavior of these stones should be investigated, as the stone may swell more when exposed to a particular solvent for an extended period of time. In fact, initial experiments (as shown in Figure 5) indicate that a bilayer begins to form with methanol exposure at long times. This could confound the experiments detailed here if additional layers begin developing in the duration of the experiment. The implications for stones of interest in conservation are significant, because stones can stay wet for an extended period of time, even after a rainstorm ends. Additionally, these stones have been shown to be viscoelastic materials by Gonzalez and Scherer [5], and if what is resisting the entry of more water into the interlayer space of the stone is the pressure exerted by the stone on the interlayer, then it is possible that more water may enter the interlayer (even entering the osmotic regime) as the stone relaxes viscoelastically. Because of this, the behavior of different cation-stone-water systems at extended periods of time should be investigated in the future.

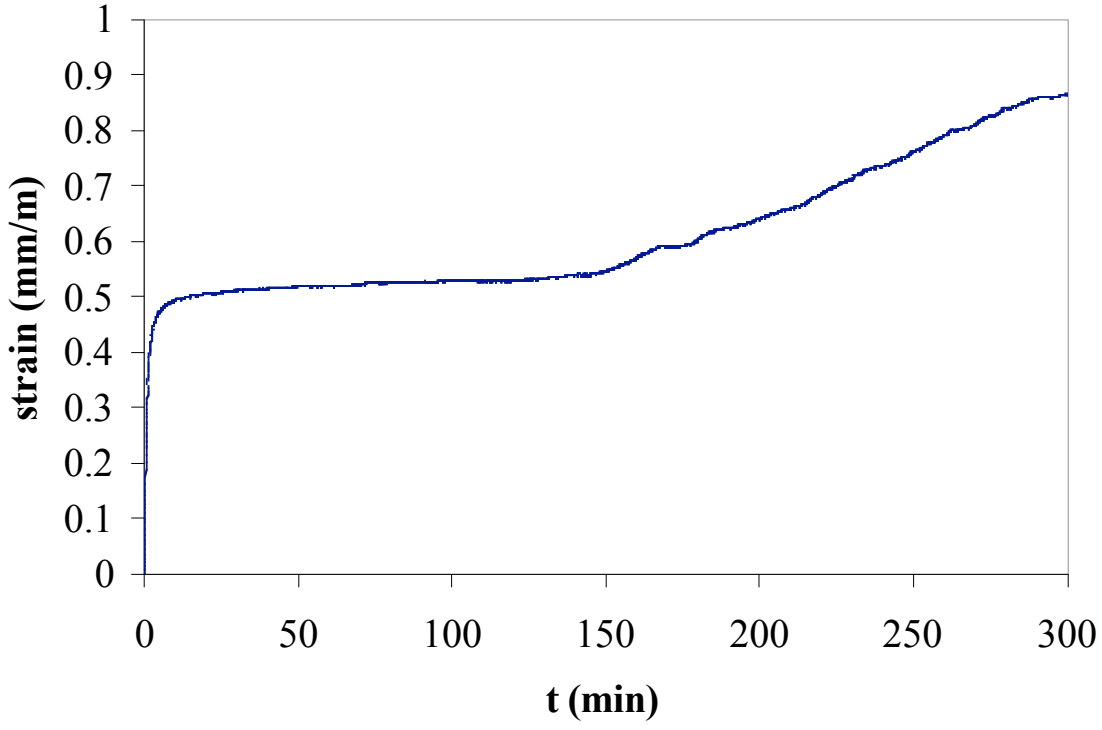



Figure 5. Bilayer formation at extended times with Portland Brownstone pretreated with calcium and wetted with methanol.

**V. Conclusion**

These experiments demonstrate that intracrystalline swelling is the primary mode of swelling in three clay-bearing sandstones, including Portland Brownstone, and a potentially useful test in the characterization of this problem has been developed. This is quite important in terms of focusing effort on swelling reduction and mitigating damage by this mechanism. The importance of the counterbalancing cation to the swelling process has been highlighted. Further work should investigate the counterbalancing cation's effect on other stone properties in order to increase understanding of this problem, to devise new treatments, and to improve current treatments. Finally, it will be

necessary to characterize the long time swelling behavior of these stones in order to further develop an understanding of the swelling and damage mechanism and for evaluation of treatments.

**Acknowledgment**

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**Appendix**

To estimate the swelling layers per unit length, one must assume all swelling layers have the same interactions with the solvent. The scaling factor relating linear dimension change to interlayer spacing change is calculated by

$$\frac{\varepsilon_{s,2} - \varepsilon_{s,1}}{d_{001,2} - d_{001,1}}$$

where $\varepsilon_s$ is the swelling strain, $d_{001}$ is the interlayer spacing, and the numerical subscripts refer to a particular solvent. This scaling factor gives the prescribed increase of the stone's linear dimension with a particular interlayer spacing increase, so the number of swelling layers per unit length is simply the amount of individual interlayer spacing increases necessary to produce a particular change in the stone's linear dimension. For example, Portland Brownstone will produce a 0.11 μm expansion per mm of stone with a 1 Å layer spacing increase, therefore there are (0.11 μm / 1 Å)*10000 Å/μm = 1100 interlayer expansions, or swelling layers.

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