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Salt Weathering on Buildings
and Stone Sculptures

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Linking climate change, moisture dynamics and salt movement within natural building sandstones: implications for salt transport by diffusion

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ABSTRACT

Future climate change scenarios for much of the UK suggest that the key stone decay controls of temperature and moisture input will change. Seasonality in precipitation is projected to increase, essentially meaning that winters are due to become wetter, while summers are likely to become drier. For building stones, this translates into longer 'time-of-wetness' periods during winter that are linked not simply to surface wetness, but specifically to 'deep wetting'. Data from sandstone test walls in the wet west of Northern Ireland demonstrate the build up of internal moisture related to cumulative rainfall. During initial moisture penetration, salts can be re-distributed in solution, but once blocks become saturated it is likely that further re-distribution will occur through ion diffusion. This paper seeks to make links between climate change, stone moisture dynamics, and ion diffusion, experimenting to assess how quickly diffusion takes place in building sandstones and the potential deleterious chemical effects of salts held in solution.

Keywords: Climate change, Sandstone, Moisture, Ion diffusion

1   INTRODUCTION

Temperature and moisture are the underlying controls on processes of stone decay. Repetitive fluctuations of these variables drives decay and produces the patterns of decay we often associate with salt weathering – periodic wetting and drying of the stone surface, causing repeated crystallization / hydration / dehydration of soluble salts, bringing about granular disaggregation and sometimes flaking and scaling of the stone surface (depending on the nature of temperature cycling and depth of wetting) (Smith et al. 2011). The stone decay system is dynamic, and it is set within a world in which the nature of the atmospheric environment is changing (Smith et al. 2008). Thus, if the dynamics of the environment begin to change, the stone decay system must reflect that change. In the British Isles (especially the NW) there is a trend (already observable over the 1961 – 1990 base period) towards wetter winter conditions (Smith et al. 2011). This is projected to continue throughout the next century. Thus, a key question for stone decay scientists and conservators in this region must be: what is the knock-on effect of increased moisture input / 'time-of-wetness' for processes of stone decay (Smith et al. 2004), and perhaps particularly for mechanisms of salt weathering and patterns of salt distribution? What do climate change projections actually mean in terms of changes in decay at process and mechanistic levels? To answer these questions, 'downscaling' (see Wilby & Wigley 1997) is needed, not just in terms of understanding how climate may change at site level, but also experimentally to understand how decay processes and mechanisms may change as a result.

Longer periods of wetness linked to increased winter rainfall are not simply related to superficial surface wetness, but to the deeper penetration of moisture into porous building materials. This 'deep wetness' could potentially have a dramatic impact on the nature of salt weathering, in terms of mechanisms of transport and patterns of distribution through blocks, in natural stone structures in the NW British Isles. Turkington and Smith (2000) noted that the complete salt penetration of entire sandstone blocks from a building in Belfast coincided with inconsistent anion/cation ratios – this suggested the importance of ion diffusion of salts (sodium and chloride ions moving independently) during periods of saturation. Diffusion in solution is the process whereby ionic or molecular constituents move from an area of high concentration (activity) to an area of low concentration (activity) under the influence of random kinetic motion of the constituent molecules or ions. Diffusion occurs without any bulk water movement. If the solution is flowing, diffusion may still be a mechanism that can cause the mixing of molecular and ionic constituents. Diffusion ceases when there is no concentration gradient. Testing of this phenomenon is widespread in the study of chloride movement in concrete or brick (Shaát 1994; Poupeleer et al. 2003). However, investigation of ion diffusion in natural building stone is less well documented – possibly because moisture movement is more rapid in such porous materials, but also linked to the dogma that wetting and drying results in an almost constant flux of moisture, and that this is restricted to an alternating frequently wetted and thoroughly dried outer layer of stonework. It should be noted that, in an homogeneous material, ultimate uniformity of salt concentration may be achieved by ion diffusion, but this is unlikely in a mineralogically heterogeneous material – in the case of sandstones, it is likely that localized concentrations may emerge as anions, in particular, are fixed by, for example, clay minerals or organics. This paper suggests a method, adapted and refined from the study of chloride diffusion in concrete, to investigate the diffusion of salts within sandstones. The paper sets out to investigate how quickly ions move through sandstone and, crucially, the possible deleterious chemical effects that their passage might have on the stone itself (for example, the dissolution and transportation of amorphous silica or other cementing agents). Of course, after saturation, the complete drying out of a block in the summer months (along with salts that have been allowed to move deep into the block interior during a wet winter by diffusion) can mean that crystallized salts become trapped deep within stone, causing damaging subflorescence that may fuel retreat of the block surfaces (Smith et al. 2002).

1.1 The reality of 'deep wetting'

Walls constructed in the wet west of NI (Derrygonnelly) were instrumented with moisture sensors (see Smith et al. 2011 for details). One of the purposes of building the test walls was to begin to quantify 'deep wetness'. While not the central theme of this paper, it is helpful to set the process of diffusion in this context. Data collected from this test facility suggest that the prolonged and cumulative impact of rain events can have a profound effect on moisture levels deep within the stone – Figure 1 illustrate cumulative rainfall at Derrygonnelly for October and November 2010, with the arrival of the associated wetting depth on the SW-facing wall at 5cm, 15cm and 25cm shown (note that the cumulative rainfall for these two months is approaching 500mm). For further data on 'deep wetting', see McAllister et al. (this volume).

2 METHODS

2.1 Materials

The nature and impact of ion diffusion is investigated on Peakmoor Sandstone (one of the most widely used building sandstones in the UK, especially in restoration and conservation work). The characteristics of this stone are summerised in Table 1.
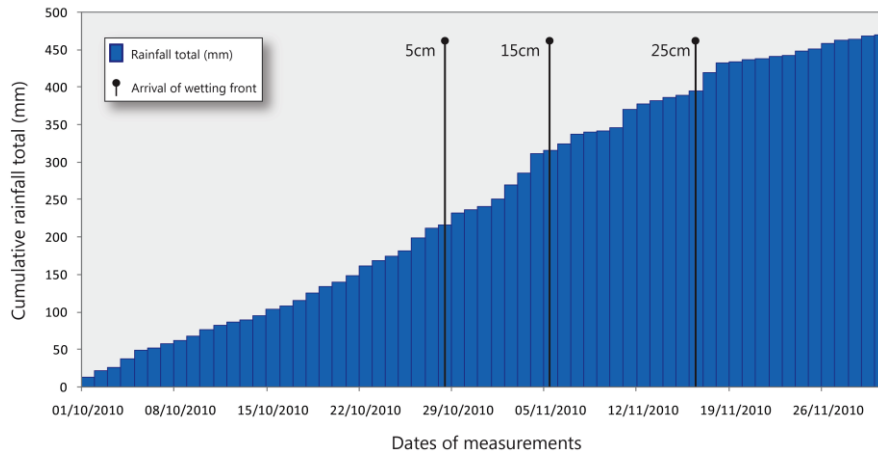
Figure 1. Cumulative rainfall in October and November at Derrygonnelly in the west of NI, with the arrival of the wetting front in the SW-facing test wall shown for 5, 15 and 25cm depth from the surface.

Table 1. Summary characteristics of Peakmoor Sandstone.

Colour	Buff
Porosity	16.46%
Saturation Coefficient	0.68
Water Absorption Capacity	5.07% (by wt)
Compressive Strength	72.5 MPa
Bulk Specific Gravity	2210 kg/m^3
Sodium Sulphate Crystallisation Test	1.07% mean wt loss

2.2   Pore water extraction from stone in a polluted urban environment

Before carrying out diffusion experiments on Peakmoor Sandstone, the strength of salt solution needed to be decided. The reason for analyzing pore water in a real building sandstone is to ascertain realistic solution strengths on which to base diffusion experiments. Choosing a realistic solution strength is essential to understanding how diffusion of salts (especially in terms of associated chemical impacts on sandstone) may proceed in the real-world buildings. To aid in deciding what solution strength to use experimentally, pore water was analysed from a building stone with a long exposure history in a polluted maritime environment (St. Matthew's Church, Belfast – see Smith et al. 2002). Three cores were dry cut from a sandstone block that had been removed from this salt-weathered urban church (at depths 0 – 10cm, 10 – 20cm and 20 – 30cm). The outer faces of these samples were carefully wrapped in waterproof tape to avoid leaching of soluble salts during saturation. To ensure saturation, each sample was treated separately by fitting a custom made high-density polythene (HDPE) container over the top of the stone and securely sealing it around all four top edges. The sample was then placed inside a vacuum desiccator onto which a 500 mL separating funnel and tube were fitted so that de-aerated de-ionized water could be transferred to the stone. Pressure inside the desiccator was reduced to 10-50 mbar and maintained for three hours. The water was released from the outer to the inner HDPE container while the system was kept under vacuum for a further hour and both containers were kept full until saturation was achieved. Air was allowed to re-enter the desiccator and the sample was kept under the above conditions for a further 16 hours before removal.

Following saturation, samples were crushed to remove the pore water. To achieve this, the sample was loaded to a maximum of 300 tonnes (at 5 tonnes per hour). Once this was completed, the load was removed and the pore water collected in a sealed container to avoid loss and contamination. Pore water samples were analysed using Ion Chromatography (IC) and Atomic Absorption Spectroscopy (AAS).

2.3 Diffusion cells

Although there are several methods for investigating diffusion, the method proposed in this paper is an adaptation of that described by Poupeleer et al. (2003). The aim of the experiment was *not* to achieve steady-state for calculating the diffusion coefficient, but rather to monitor diffusion over the period of the experimental run and investigate any associated chemical impacts. To achieve sample saturation (necessary for the diffusion experiment to work), a core of Peakmoor Sandstone (50mm thick, 100mm in diameter) was placed in a vacuum desiccator with both ends exposed. The pressure was reduced to 10-50mbar and held steady for three hours. Deaerated deionised water was added until the core was completely immersed. This vacuum was maintained for a further hour before allowing air to re-enter the desiccator after which the core was left for 16 hours.

The experimental diffusion cell set-up is illustrated in figure 2. Cell A was filled with a NaCl solution (0.15M, based on pore water extraction from St Matthew's Church) while cell B was filled with de-ionised water. The core of saturated Peakmoor Sandstone was placed (with the rounded edge sealed with silicone) between the cells. Because of the concentration gradient set up by this apparatus, ions diffuse from cell A to cell B, through the porous stone sample. Concentration measurements of the solution in Cell B were made using a minimum volume (50μL) and analysed by IC.

The experiment set-up requires the following assumptions: 1) The solution in the cell outside the stone sample is well mixed (this can be achieved with magnetic stirrers within the cells – see figure 2. 2) The water within the matrix of the core is immobile (i.e. the stone remains saturated). 3) The temperature of the solutions in the cells is constant (achieved by a climate cabinet). 4) Sorption is negligible (not necessarily true with mineralogically complex sandstones).
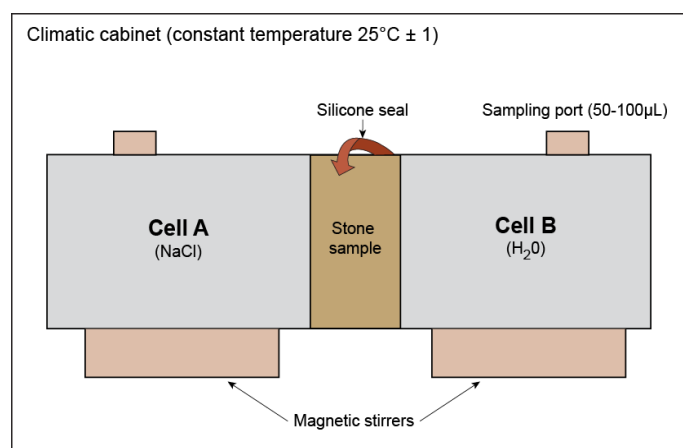

Figure 2. Experimental set-up for diffusion cell experiment.

2.4   Chemical analyses

A colorimetric technique was used for the detection of silica in the Cell B solution. This spectrophotometric method for analysing dissolved silica is based on the reaction between silicic acid and ammonium molybdate to form a yellow complex. The molar absorptivity of the complex is low and this is overcome by forming a reduced blue complex with oxalic acid and metol-sulpite solutions. This reaction prevents the reduction of excess molybdate and interference from phosphate. Absorbance is read at 810 nm.

The stone sample from the diffusion test had pore water extraction procedures described above carried out on it. Pore water from this sample was tested for pH, anion analysis (using IC) and cation analysis (using AAS).

3   RESULTS

3.1 Pore water analysis from stone in a polluted urban church

Figure 3 shows concentrations of anions and cations at sample depths of 0 – 10cm, 10 – 20cm and 20 – 30cm. Chloride, nitrate and sulphate ions are all present in abundance, but especially concentrated in the 10 – 20cm sample. Cations follow a similar pattern, with sodium, magnesium and calcium present in the highest concentrations.

3.2 Diffusion

Figure 4 shows results for the chloride diffusion experiment over 90 days. At the end of the experiment, the IC analysis showed 438ppm of chloride in cell B.

3.3 Chemical alteration in the sandstone

Colorimetric techniques have illustrated that silica is present (0.66ppm) in the final solution from cell B (when it was not detectable at all in the original salt solution). Though it is a very low concentration, its presence is significant in demonstrating that silica is being brought into solution (and experiencing limited re-distribution) in the presence of electrolytes (see Dove 1999). (Background Si in deionized water after during conditioning of the core was 0.2ppm). It suggests that the dissolution and transport of silica (possibly amorphous) from the sandstone matrix may be taking place over a period of just 3 months with a 0.15M solution of NaCl (although leaching may also play a role).
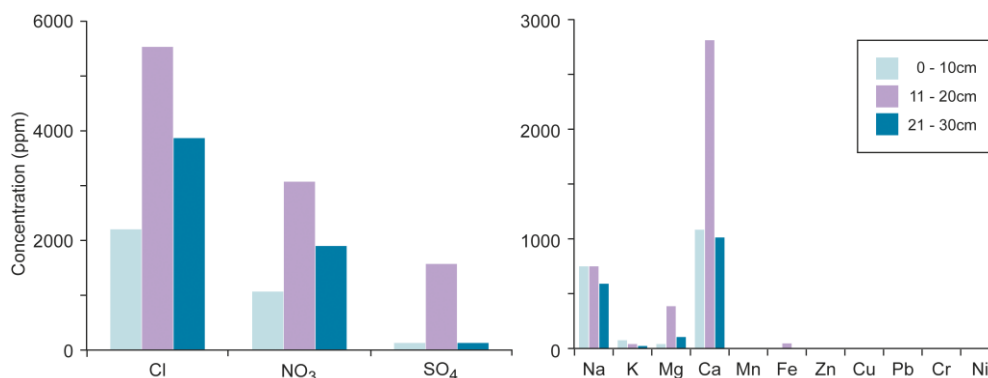

Figure 3. Result of pore water analysis from St. Matthew's Church, Belfast. Left – anion analysis by IC, Right – cation analysis by AA.

Pore water results from the Peakmoor Sandstone core (following the diffusion experiment) indicate that the highest concentration of salt was held in the core itself (3175ppm chloride). The pH of this pore water was measured at 8.12 – a strongly alkaline solution, potentially indicating the presence of amorphous silica. Silica levels in the pore water were confirmed to be over twice those in cell B (1.4ppm), using colorimetric analysis. Table 2 compares the concentration of elements in cell B with concentration in the pore water (Mg, Ca and K showing variable levels of dissolution and mobility).
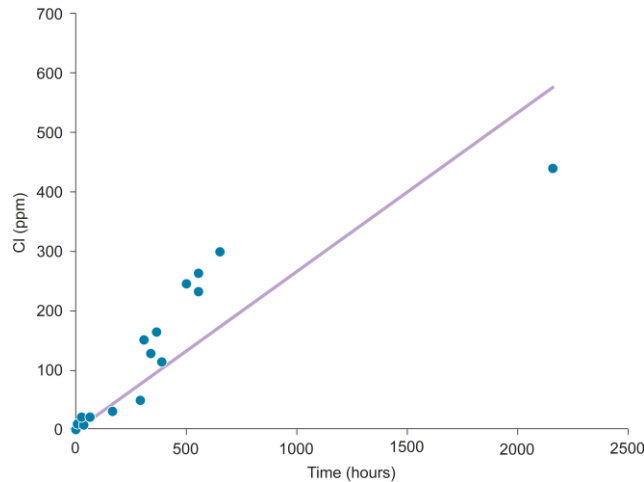

Figure 4. Concentration of chloride ions in Cell B over time ($R^2 = 0.71$)

Table 2. Concentrations of elements in cell B and pore water.

	SiO$_2$	Cl	Na	Mg	Ca	K
Concentration in cell B (ppm)	0.6	438	23	8.5	23	2
Concentration in pore water (ppm)	1.4	3175	4500	3.9	27	37

4   DISCUSSION

Pore water analysis from St. Matthews Church illustrates that salts have penetrated right through the sandstone block (though particularly concentrated from 10 – 20cm). Salts may have been transported in two ways – in solution flow, and also by diffusion of ions behind the wetting front. We are not suggesting that diffusion is the dominant mechanism by which the salt were transported to depth in this stone, unless saturation of the stone is achieved, whereupon ions would move only through diffusion (without bulk water flow). The reason for analyzing pore water in a real building sandstone was simply to ascertain realistic solution strengths on which to base diffusion experiments. The results show the nitrate is present in abundance, possibly reflecting the changing nature of pollution in Belfast – a reduction in sulphur, replaced by elevated vehicular pollution. The presence of nitrate may act as an effective 'fertilizer', potentially instrumental in encouraging biological colonization on buildings (Smith et al. 2011).

Although it is not the focus of the study, it is noted that the speed at which ion diffusion through the sample over the experimental run is more rapid than that recorded in concrete studies. This

is the traditional approach of engineers seeking to investigate how long it may take for salts to reach rebars in concrete structures. As stone decay scientists, however, we want to 'see inside' the stone – for example, what elements within the stone does the salt solution mobilize? IC analysis of the Peakmoor Sandstone core show that, by the end of the experiment, the highest concentration of salt was held in solution, within the stone core. Chemical activity is at the heart of salt weathering, and a full understand of how salts bring about stone decay should include chemical aspects (Goudie & Viles 1997). There is, of course, a complex interplay between chemical and physical salt decay – an interplay becoming more important with climate change in the NW UK – seasonality in precipitation is increasing, leading to possible block saturation during winter (chemical action of salts dominates to weaken stone) and drying out during summer (physical action of salts exploits weaknesses). The duration of this diffusion cell experiment is significant because it has demonstrated that 3 months of saturation using a realistic-strength salt solution may allow this kind of chemical activity to take place. Wetness data from experimental walls in the wet west of NI suggest that the duration of 'deep wetting' over a winter is at least 3 months (see McAllister et al. this volume). Walls became wet in October, and have showed little sign of drying out by March (with the wetting front already reaching 25cm by the end of November – though October and November were the wettest months recorded). As demonstrated in the chemical analyses of the cell B solution and pore water, silica was present, possibly suggesting that the amorphous silica cementing grains together had begun to be brought into solution (along with other elements in the stone matrix), compromising grain-boundary strength. The dissolution rates of quartz and amorphous silica in alkali and alkaline earth electrolyte solutions have been well documented (Dove & Rimstidt 1994) and results have shown that dissolution rates are enhanced in these solutions even at near neutral pH (Dove 1999). Some results from work to be published by the authors suggest that the presence of sulphate ions may increase silica dissolution significantly. Subsequent re-distribution of any silica present in the pore water upon drying has important implications for stone durability (Nespereira et al. 2010). Uneven silica cementation through a sandstone block may lead to spatially concentrated retreat (McCabe et al. In Press), with weaker areas weathering preferentially as salt crystals bring about granular disaggregation and surface loss.

5   CONCLUSIONS

In exploring the impacts of climate change on stone-built structures, there is a need to 'downscale', not only in terms of climatic projections to the site scale, but experimentally to investigate impact at process and mechanistic levels. The paper has briefly shown links between projected climate change scenarios, moisture dynamics within building stones, and mechanisms of salt re-distribution in blocks. Those with responsibility for the care of stone structures should be aware of these links and the implications of salts moving to depth in stones during long periods of saturation, both in terms of deleterious chemical effects (for example, potential dissolution and re-distribution of amorphous cementing agents), and subsequent physical damage at depth when stone does dry out during summer months.

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