Special Session S24
Natural stones, usage and testing

Scientific Annals, School of Geology, Aristotle University of Thessaloniki Proceedings of the XIX CBGA Congress, Thessaloniki, Greece	Special volume 100	399-405	Thessaloniki 2010

CLIMATE CHANGE AND WET WINTERS: TESTING THE DIFFUSION OF SOLUBLE SALTS IN BUILDING STONE UNDER SATURATED CONDITIONS

McCabe S.[1], Smith B.J.[1], McAlister J.J[1]., Viles H.A.[2], Curran J.M.[3] , Crawford T.[4]

[1] School of Geography, Archaeology and Palaeoecology, Queen's University Belfast, BT7 1NN, UK
[2]School of Geography and the Environment, Oxford University Centre for the Environment, Oxford OX1 3QY, UK
[3] Consarc Design Group, Belfast, BT7 2JD, UK
[4] Geography Department, Methodist College, Belfast, BT9 6BY

Abstract: Controls on stone decay processes are rapidly changing as a result of changing climate. As such, there is a need to understand decay, not just in a dynamic world, but also in a world where the nature of the dynamics themselves are changing. Future climate change scenarios for the northwest of the United Kingdom (NW UK) typically project both increased short-term uncertainty in day-to-day weather conditions and an underlying trend towards wetter, warmer and longer winter conditions. The result of this is that natural stone used in buildings and monuments is wet for long periods of time – over a wet winter, it is possible that entire blocks become saturated. Usually the movement of salts is associated with moisture flux, but this paper investigates an alternative mechanism of salt movement – when blocks are saturated and a concentration gradient is set up, ions must move by diffusion. Because of the increasingly likely scenario of block saturation (in NW UK), this paper proposes a way of testing salt diffusion through natural building stones, modified and refined from studies testing chloride diffusion in concrete, to determine how quickly salts may diffuse through natural stone and any associated deleterious chemical effects. A concentration gradient is set up, whereby salts diffuse through a saturated sandstone sample from a 'cell' containing a 0.55 molar solution to another 'cell' containing de-ionized water. The increase in concentration in the cell containing de-ionized water can be measured at intervals using Ion Chromatography. Preliminary tests have shown that both salt and stone types are important controls for the rate of diffusion. Emphasis is placed on the need to adapt laboratory studies to more accurately reflect the environmental conditions under investigation.

Keywords: Climate change, salt weathering, ion diffusion

1. Introduction

Controls on stone decay processes are rapidly changing as a result of changing climate. As such, there is a need to understand decay, not just in a dynamic world, but in a world where the nature of the dynamics themselves are changing (Smith et al., 2008), and thus, a need to adapt stone decay experiments in the laboratory to reflect the environmental conditions being investigated. Future climate change scenarios for the northwest of the United Kingdom (NW UK) typically project both increased short-term uncertainty in day-to-day weather conditions and an underlying trend towards wetter, warmer and longer winter conditions (Betts, 2002; Hulme et al., 2002). Buildings appear to have responded to these changing climatic conditions by 'greening' – recent observations have shown an increase in algal 'greening' of external sandstone walls (a material that has shown itself to be particularly sensitive to changes in environmental regime, especially moisture related) in many places in the NW UK (Smith et al., 2004) (see Fig. 1a and 1b). The authors hypothesize that this is caused by a combination of increased moisture and decreased air pollution, and thus reflects recent changing environmental conditions. Beyond this blatant aesthetic and physical change, it is likely that chemical weathering will be enhanced in the NW UK due to increased 'time-of-wetness' (Viles, 2002; Smith et al., 2004). Prolonged and more deeply penetrating wetness should also affect other agents of decay through allowing deep-seated salt penetration and surface algal colonisation.

Fig. 1. Greening of sandstones as a response to increased ‘time-of-wetness’, St. Mark’s Church, Belfast (see also Smith et al., 2004). Greening represented by shading – a (up) shows greening related to surface roughness, b (down) shows patchy greening on a facade.

There is a need in current research to more directly relate changing climatic conditions to effects on a building façade. A first attempt to relate future climate change to effects on built heritage has been carried out in the Noah’s Ark project (http://noahsark.isac.cnr.it), using one Global Climate Model (GCM) and one emission scenario. One of the aims of the Noah’s Ark project was to research, predict and describe the effects of climate change on Europe's built cultural heritage over the next 100 years. However, the project “does not involve downscaling” (Grossi et al., 2007) and there are, therefore, inherent difficulties in applying the results to ‘site specific’ localities. Initial work by the Noah’s Ark project produced model-based maps of changing sandstone moisture contents showing current very dry conditions across Europe and even drier trends in future (NOAH’s ARK, 2007). However, variability in climate across, for example, the UK, is difficult to pick up in these outputs. This is illustrated in the fact that UK-specific studies (for example, Crawford, 2007), using statistical downscaling, do predict increases in winter wetness in NW UK over the next 50 to 100 years that will exaggerate the moisture content of stone masonry. GCMs are simply not appropriate for answering these questions – they were developed to predict synoptic-scale, general circulation patterns of the atmosphere (Crawford, 2007). Thus, the relevance of GCMs decrease as resolution increases – to understand how the changing climate will impact sites or buildings, they are of little use. Predicting the impacts of future climate change on surface and deep-seated wetness of sandstone masonry is a highly complex task, and necessitates downscaling global predictions to a local level and consideration of probabilistic models.

2. Downscaling

"So-called ‘downscaling’ techniques have… emerged as a means of bridging the gap between what climate modellers are currently able to provide and what impact assessors require" (Wilby and Wigley, 1997, 530).

“Even if global climate models in the future are run at high resolution there will remain the need to ‘downscale’ the results from such models to individual sites or localities for impact studies” (DOE, 1996). Statistical downscaling consists of a search in observed climate baselines for a statistical relationship between the surface climate variable to be downscaled (‘predictand’) and the potential ‘predictors’ (frequently the large-scale upper air variables) and a subsequent application of that relationship to GCM-produced data for future climate change (Huth, 2005). The approach is based on the concept that regional climate is conditioned by two factors: the synoptic climate state, and local physiographic features. Thus, local climate information is derived by first determining a statistical model which relates large-scale climate variables to local characteristics. Then the large-scale output from a GCM experiment is fed into this statistical model to estimate corresponding local climate variables (Wilby et al., 2002; Wilby and Dawson, 2004; Crawford, 2007).

Projecting future climate change in the NW UK is far from straightforward. Large prediction uncertainty is related to choice of climate model, choice of emissions scenario, and choice of downscaling technique. However, several robust downscaled predictions have emerged from work carried out by, for example, Crawford (2007). Temperatures are likely to increase across all months (though for weathering in the NW UK, this is possibly a secondary concern behind the role of moisture). Precipitation regimes are likely to become much more seasonal, as a function of wetter winters and markedly drier summers (see Fig. 2, illustrating increased seasonality in precipitation across different models and emission scenarios at a site in the west of Northern Ireland, Killyclogher). The number of extreme rainfall events, and their contribution to the overall total, is likely to increase in winters in response to a more zonal synoptic pattern, with increases also found in late summer in response to convective activity (Crawford, 2007).

3. Weathering implications of wetter winters

Investigations into how salt weathering impacts natural stone have largely focused on how soluble

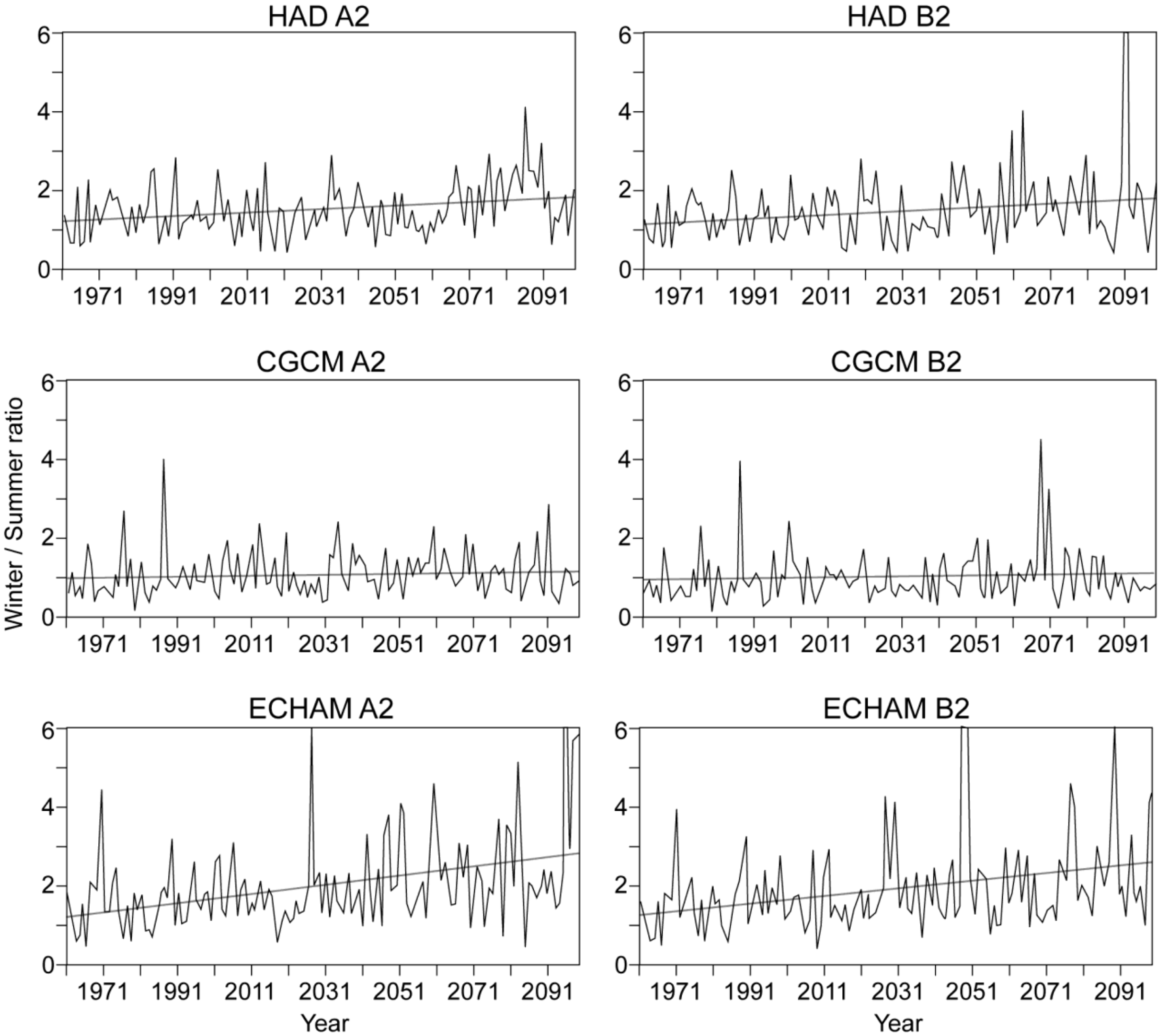

Fig. 2. Shows projected increasing seasonality in precipitation (expressed as a winter/summer ratio) across different models (HAD/CGCM/ECHAM) and emission scenarios (A2/B2) for a site in west NI (Killyclogher) – a trend mirrored to varying degrees around the NW UK (from Crawford 2007). HAD = HADCM3, UK Met Office's atmospheric Unified Model; CGCM = CGCM2, the second version of the Canadian Centre for Climate Modelling and Analysis Coupled Global Climate Model; ECHAM = ECHAM4, the fourth in a series of models derived from the European Centre for Medium-Range Weather Forecasts model.

salts move into stone via moisture flux, with periodic wetting events quickly followed by drying (Goudie, 1986; Smith and McGreevy, 1988; Smith et al., 2005; McCabe et al., 2007; McCabe et al., 2008) – essentially, wetting and drying of the stone surface zone. However, with climate change bringing longer, wetter winters in the NW UK, it is likely (and reported anecdotally by architects) that the increased ‘time-of-wetness’ of stone blocks will, and may already be leading to block saturation. Essentially, during wet winters, a block may remain saturated for long periods of time (Turkington and Smith, 2000). Indeed, Smith et al. (2004) have posited that a positive feedback is setup, whereby algal growth (encouraged by the presence of moisture in the stone) keeps the block beneath it damp. This leads to the question, how do soluble salts behave if blocks become saturated and there is no moisture flux? Turkington and Smith (2000) have demonstrated complete salt penetration of entire sandstone blocks from a building in Belfast, coinciding with inconsistent anion/cation ratios suggesting the importance of ion diffusion of salts 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 is a mechanism along with dispersion 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, studies of this kind have perhaps neglected the diffusion of soluble salts within natural building stones – 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, but this is unlikely in a mineralogically heterogeneous material – in this case it is likely that localized concentration within the stone 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 test the diffusion of salts within sandstones – the rate at which the ions move and the possible deleterious chemical effects that their passage might have on the stone itself (for example, the dissolution and transportation of amorphous cementing agents such as silica or iron). With reference to the increasing seasonality of precipitation, it would be remiss not to make mention of the potential implications of summer drying following winter saturation – 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) can mean that crystallized salts become trapped deep within stone, causing damaging sub-efflorescence that can fuel retreat of the blocks surface following loss of surface material (see Smith et al., 2002 for a detailed conceptual model of block retreat).

4. Method – diffusion cells

Several methods have been proposed to investigate salt diffusion. Techniques include the use of different tracer solutions and various experimental set-ups. Non-intrusive methods such as dual-energy gamma radiation and magnetic resonance imaging (MRI) have proven quite successful. However, due to high expense and limitations for the large size (dimension) of physical models, these techniques are not employed on a routine basis to measure fluid flow in porous media. One area where method development has progressed is in reinforced concrete studies since chloride ingress is the main cause of rebar corrosion. A rapid chloride permeability test was introduced that used an electric current to accelerate the diffusion process (Whiting, 1981). This method was later adapted to introduce effective or apparent diffusion coefficients where both salt flow and chemical reactions between salt ions and cement paste were taken into account.

The method proposed is an adaptation of that outlined by Poupeleer et al. (2003). Cell A is filled with salt solution (0.55 molar in preliminary tests), while cell B is filled with de-ionised water. Between the two cells, a sample of saturated stone sits (preliminary tests were carried out on 20mm thick samples of Dumfries Sandstone and Portland Limestone, but different thicknesses may be used), with the rounded edge sealed with silicon. See Table 1 for a summary of stone characteristics. Because of the concentration gradient set up by this apparatus (see Fig. 3 for a schematic representa

Table 1. Characteristics of Dumfries Sandstone and Portland Limestone (after Warke and Smith, 2007).

Stone Type	Porosity (%)	Permeability mD)	Description
Dumfries Sandstone	18 - 25	Range: 200 - 1000 Mean: 600	Permian quartz and iron-rich red sandstone with well-defined bedding. Quartz 52%, feldspars 10.5%, clays 18% (smectites) and mica 1%
Portland Limestone	13 - 26	Range: 1 - 150 Mean: 15	Jurassic oolitic limestone. Calcite 57.8%, quartz 2.3% and clays 13.5%

tion), ions diffuse from cell A to cell B, through the porous stone sample. For high-durability concrete studies, this is very time-consuming (Poupeleer et al., 2003). This is not so with, for example, sandstone, which is generally much more porous and readily permits the movement of ions from one cell to the other. The use of IC to analyse the solution at regular intervals is a more refined and sensitive approach than conductivity meters used in previous concrete studies, allowing for early detection of ion diffusion and a much more accurate and absolute understanding of the phenomenon.

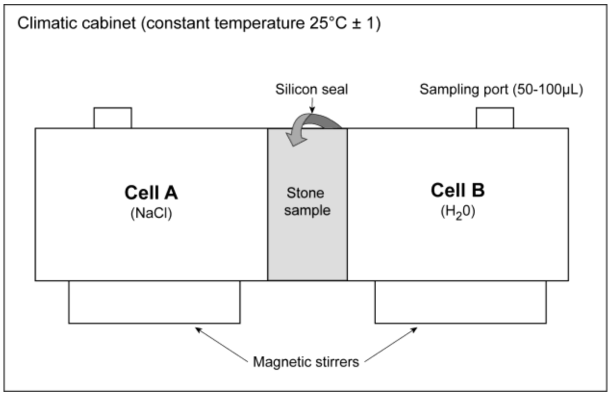

Fig. 3. Experimental set-up of diffusion cells, where ions diffuse through a stone core from cell A (salt solution) to cell B (de-ionized water)

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)
2. Concentration measurements of the vessel solution are made using a minimum volume (50-100μL) for ion chromatography analysis of chloride and other anions (nitrate, sulphate) when mixed salt solutions are included in the experiment
3. The water within the matrix of the core is immobile (the stone remains saturated)
4. The temperature of the solutions in the cells is constant (achieved by a climate cabinet)
5. Sorption is negligible

5. Preliminary Results

Fig. 4 shows the results for diffusion rates of chloride in Dumfries sandstone and Portland limestone. Preliminary tests using the methods described above (using 20mm thick stone sample of Dumfries Sandstone and Portland Limestone) show that salts diffuse through natural sedimentary stone relatively rapidly (when compared to dense concrete samples) – within a day, IC detects an increase in Chloride concentration in cell B in the test using Dumfries Sandstone (a range of 77.04 – 133.3 ppm/day from 3 different samples, explained by the large range in permeability, or connectivity of pores, exhibited by Dumfries Sandstone, Table 1). The rate of diffusion differs for different stone types, based on specific stone characteristics (porosity, permeability) – chloride diffuses much more slowly through the less permeable Portland Limestone (30.1 ppm/day). The type of salt (choride/sulphate/nitrate) also has an impact on diffusion rate. Previous work (discussed in Smith et al. 2005) has shown that chloride ions diffuse through the stone faster than sulphate ions (taking about 5 days to move through the sample), conforming with previous studies on sandstone buildings that showed chloride typically dispersed throughout blocks and sulphate concentrated near exposed faces (Turkington and Smith, 2000).

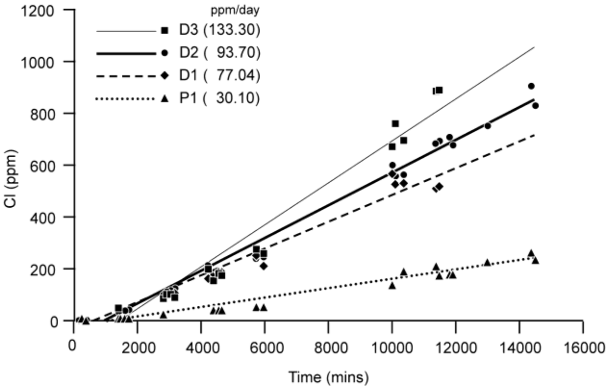

Fig. 4. Diffusion rates for 3 samples of Dumfries Sandstone (D1, D2 and D3), and Portland Limestone (P1). Measurements were made by placing a 20mm thick and 100mm diameter stone sample between an ionic source (0.55 NaCl) and a neutral solution and measuring ion content of the neutral solution side at regular intervals using Ion Chromatography (IC)

6. Discussion

“The chemical behaviour of soluble salts is at the heart of salt weathering and must be understood before a real appreciation of how salts cause damage can be gained” (Goudie and Viles, 1997). To understand salt weathering fully, an appreciation of chemical damage is necessary. With most current research in this area focusing on mechanical damage through crystallization/hydration, this perspective can become lost. Thus, one recent study on salt weathering stated that “if salts are presented in porous system of masonry materials in the form of solution, they are mostly not dangerous” (Pavlik et al., 2008). However, if chemical damage is to take place, it is necessarily when the salt is in solution. The majority of sandstones are largely composed of crystallized quartz (SiO_2) grains. These grains are usually cemented together by silica in a less well-crystallized (amorphous) form. This cement may also contain iron oxides or hydroxides. Silica polymorphs undergo hydrolysis ($SiO_2 + 2H_2O = H_4SiO_4$) and it has been shown that the dissolution rates of quartz and amorphous silica are increased 50-100 times when alkali and alkaline earth cations are introduced into otherwise pure solutions (Icenhower and Dove, 2000). Thus, the weakening of inter-granular bonds of amorphous silica by salts in solution is an essential ingredient in paving the way for physical damage manifesting itself in granular disintegration when crystallization does occur. While the effect of cations on the dissolution rate of silica has been thoroughly investigated, however, only a few studies have been carried out on the impact of anions – one important study has shown the solubility of amorphous silica to increase in the presence of sulphate (Bai et al., 2009), but this area requires further work.

Supporting this perspective of damage caused by salt in solution, another recent investigation into irregular silica cementation and the strength of a particular sandstone when wet and dry showed that compressive strength was significantly reduced (from ‘moderately strong’ to ‘weak’) when masonry was wet for long periods of time (Nespereira et al. *in Press*). Thus, another area that would provide a fuller understanding of the impact of ion diffusion on sandstones, not seen in previous concrete and porous media studies, is in the detailed geochemical analysis of the final solution in cell B (Fig. 3). Analysing the final solution will give an understanding of what is being removed from the stone by salt in solution.

Future work, then, will involve the final cell B solution being analysed for Si, Al and Fe concentrations after ion diffusion using various single electrolytic solutions and their mixtures. Sensitive colorimetric techniques are being developed for Si and Al while Fe will be determined using atomic absorption spectrometry. Sensitive colorimetric techniques are chosen since the availability of the ICP atomic emission spectrometry technique is still limited and costly. The ICP technique also suffers serious drawbacks when high levels of salts are present in solution. Detection limits of 0.005 and 0.02 mg/L are possible for Al and Si respectively using colorimetric analysis. These techniques will be employed in an attempt to study the mobility of the above cations plus Ca, Mg, Na and K as a result of the diffusion process. The experimental set-up outlined could also enable a study of the effects of different electrolytic/organic acid mixtures on sandstone as a result of the ion diffusion process.

7. Conclusions

- In response to changing environments, the nature of decay processes change
- Downscaled projections show increased seasonality in precipitation for sites in the NW UK, across different models and emission scenarios
- In NW UK, longer wetter winters mean that sandstone blocks in buildings may become saturated for long periods of time
- Increased seasonality means that complete drying out of blocks in summer following winter saturation could leave damaging sub-efflorescences deep within the stone
- There is a need to adapt laboratory testing of stone to reflect the changing nature of decay regimes – the authors suggest the outlined ion diffusion test method as a means of understanding how soluble salts move in sandstone under saturated conditions and the chemical damage that can be done to the stone while the salts are in solution
- Diffusion rates vary with type of salt and stone properties – future work will be carried out on salt mixtures, different stone types, and the analysis of the dissolution of cementing agents, for example, amorphous silica and iron

Acknowledgements

Thanks to Gill Alexander for help in the preparation of figures. This research was funded by EPSRC grant EP/G01051X/1 (and partly by the Dept of Employment and Learning, NI).

References

Bai S., Urabe S., Okaue Y., Yokoyama T. 2009. Acceleration effect of sulfate ion on the dissolution of amorphous silica. Journal of Colloid and Interface Science 331, 551-554.

Betts N. L, 2002. The climate of Northern Ireland. In: Smyth, A., Montgomery, W. I., Favis-Mortlock, D. and Allen, S. (eds), Implications of Climate Change for Northern Ireland: Informing Strategy Development. Norwich, The Stationary Office Ltd, 26 – 42.

Crawford T., 2007. Future climate change: modelling the implications of shifts in rainfall characteristics for runoff in Northern Ireland. Unpublished PhD Thesis, Queen's University Belfast.

Deprtment of the Environment, 1996. Review of the potential effects of climate change in the United Kingdom. HMSO, London, p. 247.

Goudie A. S., 1986. Laboratory simulations of 'the wick effect' in salt weathering of rock. Earth Surface Processes and Landforms, 11, 275-285.

Hulme M., Jenkins G. J., Lu X., Turnpenny J. R., Mitchell T. D., Jones R. G., Lowe J., Murphy J. M., Hassell D., Boorman P., McDonald R. and Hill S., 2002. Climate Change Scenarios for the United Kingdom: The UKCIP02 Scientific Report, Tyndall Centre for Climate Change Research, School of Envirnmental Sciences, Univ. of East Anglia, Norwich, UK, 120 pp.

Huth R., 2005. Downscaling of humidity variables: a search for suitable predictors and predictands, International Journal of Climatology 25, 243 – 250.

Icenhower I.P. and Dove P.M., 2000. The dissolution kinetics of amorphous silica in sodium chloride solutions: effect of temperature and ionic strength, Geochim. Cosmochim. Acta, 64, 4193-4203.

McCabe S., Smith B. J. and Warke P. A., 2007. Preliminary observations on the impact of complex stress histories on the response of sandstone to salt weathering: laboratory simulations of process combinations. Environmental Geology, 52, 251-258.

McCabe S., McKinley J. M. and Smith B. J., 2008. Simulating initial stages of salt accumulation and organisation within building sandstones. In: Lukaszewicz, J. W., Niemcewizc, P. (eds), 11th International Congress on the Deterioration and Conservation of Stone. Nicolaus Copernicus University Press, Torun, 173-180.

Nespereira J., Blanco J. A., Yenes, M. and Pereira D., In Press. Irregular silica cementation in sandstone and its implication on the usability as building stone. Engineering Geology, *in press*.

Pavlik Z., Michalek P., Pavlikova M., Kopecka I., Maxova I., and Cerny R., 2008. Water and salt transport and storage properties of Msene sandstone, Construction and Building Materials 22, 1736 – 1748.

Poupeleer A. S., Carmeliet J., Roels S. and Van Gemert D., 2003. Validation of the salt diffusion coefficient in porous materials. International Journal for Restoration of Buildings and Monuments, 9, 663-682.

Shaát A., 1994. Int. Conf. on Corrosion and Corrosion Protection of Steel and Concrete, 446-460.

Smith B. J. and McGreevy J. P., 1988. Contour scaling of a sandstone by salt weathering under hot desert conditions. Earth Surface Proc. and Landforms, 13, 697-705.

Smith B. J., Turkington A. V., Warke P. A., Basheer P. A. M., McAlister J. J., Meneely J. and Curran J. M. 2002. Modelling the rapid retreat of building sandstones: a case study from a polluted maritime environment. In: Seigesmund, S., Weiss, T. & Vollbrecht, A. (eds), Natural Stone, Weathering Phenomenon, Conservation Strategies and Case Studies: 347 – 362, Special Publications 205. London: Geological Society.

Smith B. J., Warke P. A. and Curran J. M., 2004. Implications of climate change and increased 'time-of-wetness' for the soiling and decay of sandstone structures in Belfast, Northern Ireland. In: Prikryl, R. (ed.), Dimension Stone, Taylor&Francis Group, London, 9-14.

Smith B. J., Warke P. A., McGreevy J. P. and Kane H. L., 2005. Salt weathering simulations under hot desert conditions: agents of enlightenment or perpetuators of preconceptions? Geomorphology, 67, 211-227.

Smith B. J., Turkington A. V. and Curran J. M. 2005. Urban stone decay: the great weathering experiment? Geological Soc. of America, Special Paper, 390, 1-9.

Smith B. J., Gomez-Heras M. and McCabe S., 2008. Understanding the decay of stone-built cultural heritage. Progress in Physical Geography, 32, 439-461.

Turkington A. V. and Smith B. J., 2000. Observations of three-dimensional salt distribution in building stone. Earth Surface Processes and Landforms, 25, 1317-1332.

Warke P. A. and Smith B. J. 2007. Complex weathering effects on durability characteristics of building stone. In: Prikryl, R. and Smith, B. J. (eds), Building Stone Decay: From Diagnosis to Conservation, Geological Society, London, Special Publications, 271, 211 – 224.

Wilby R.L., and Wigley T.M.L., 1997. Downscaling general circulation model output: a review of methods and limitations. Progress in Physical Geography 21, 530-548.

Wilby R., and Dawson C. W., 2004. Using SDSM version 3.1 – a decision support tool for the assessment of regional climate change impacts. Version 3.1 User Manual, Nottingham, Environment Agency of England and Wales.

Wilby R., Dawson C. W., and Barrow E. M., 2002. SDSM – a decision support tool for the assessment of regional climate change impacts, Environmental Modelling & Software, 17, 147 – 159.

Whiting,D., 1981. A rapid measurement of chloride permeability of concrete, Public Roads, V. 45(3), 101-112).