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INFLUENCE OF ION EXCHANGE PROCESSES ON SALT TRANSPORT AND DISTRIBUTION IN HISTORIC SANDSTONE BUILDINGS

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ABSTRACT

Crystallisation of salts in the pores of stone is a major concern in the preservation of heritage buildings, monuments and sculptures, but the mechanism of transport and distribution of salts is still not properly understood. The fractionation and distribution of salts in the porous matrix has, in building material research, conventionally been attributed to the solubility and concentration of salts present in the groundwater. We propose another mechanism contributing to the control of the salt distribution based on the interaction of ions in the salt solution with the charged mineral phases within the stone. The transport of mixed salt solutions was studied in laboratory simulated flow-through experiments on two fluvial sandstones – a Permo-Triassic red bed sandstone and a Carboniferous sandstone, both from the UK. The experiments were carried out under non-evaporative conditions, eliminating the possibility of solubility-dependent crystallisation. The results indicate that the process of ion exchange significantly controls the transport of ions in the pores and leads to fractionation of solutes in the course of transport even in the absence of evaporation and crystallisation. The sandstones behave like a chromatographic column and retention of various ionic species is significantly controlled by ion exchange processes. A quantitative estimation of cation exchange capacity (CEC) indicates that sandstones with higher CEC have greater influence on retention and fractionation of salts in the course of capillary transport than those with lower CEC. Simple scoping calculations using a geochemical modelling code and the ion exchange properties based on those determined in the laboratory experiments, demonstrate that ion exchange can have a significant effect on mineral precipitation during evaporation.

Keywords: Salt transport and distribution, ion exchange, salt crystallisation, salt weathering, capillary rise, cation exchange capacity.

1   INTRODUCTION

It has been noted that salts are transported to different locations in porous building materials resulting in heterogeneous spatial distributions of salt (Arnold, 1982; Arnold and Zehnder, 1990 and 1991). These inhomogeneous distributions are a very important factor in stone decay due to crystallisation, as the damage is related to the location of crystallisation (Rodriguez-Navarro and Doehne, 1999). The crystallisation can take place at the surface (efflorescence) and/or within the pores below the surface of the stone (subflorescence). The transport and distribution within the porous network is generally considered to be a function of surface evaporation and

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solubilities of the salts present in the water. However, the processes that govern the transport and spatial distribution of salts in the context of historic buildings have not been thoroughly investigated.

The development of the fractionated distribution of salts within a building stone is usually explained as the result of the sequential crystallisation of salts as the water gradually advances through the stone and evaporates as it does so. Thus the crystalline phases are deposited in sequence according to their respective solubilities, while the most soluble solutes are concentrated in the remaining solution (Arnold, 1982; Arnold and Zehnder, 1990 and 1991; Matteini, 1991). This preferential precipitation of different salt phases from salt solution leads to fractionation, forming spatial sequences of different salts.

However, there is another possibility that is rarely discussed in the context of building materials – the effect of ion exchange. Ion exchange will give rise to a chromatographic effect in the migration of ions, and this could in principle strongly effect the distribution of saturation states, either increasing or decreasing the degree of saturation. Perhaps Wendler and Snethlage (1988, cited in Schäfer and Steiger, 2002) were the first to investigate cation exchange capacities (CECs) of weathered building stone and noted significant differences between CEC of weathered and unweathered zones. Schäfer and Steiger (2002) compared various techniques of CEC determination in building stone and also observed that the CEC in weathered stone is much less than that of unweathered stone, though this will not necessarily always be the case as weathering can increase the proportion of clays present. However, in these studies CEC measurement was used as an indicator of chemical weathering and partial dissolution of clays and other colloidal size minerals due to acid attack, and it appears that there has been no research to study the role of ion exchange processes in salt transport through building stones. Accordingly, the study described here was devised to determine the effect of ion exchange on ion distributions as water flows through building stones with the aim of determining the potential importance of ion exchange in determining the spatial distribution of crystallisation.

2 CATION EXCHANGE AND PREFERENTIAL RETENTION
2.1 Introduction

Many varieties of sandstone contain an appreciable percentage of clasts with large surface areas that have a significant capacity to exchange ionic constituents attached to their surfaces. These clasts can be detrital or authigenic mineral grains. They are often inorganic, sometimes amorphous (uncrystallised or poorly crystallised) and mostly composed of clay minerals and metal oxides and hydroxides (Freeze and Cherry, 1979). The imperfections/ionic substitutions within the crystal lattice and reactions at the particle surface result in a net positive or negative charge of the crystal lattice. This charge imbalance is compensated by a surface accumulation of ions of the opposite charge (the 'counterions') that form as a layer of exchangeable composition. Though almost all particles will have some excess surface charge, the most important for ion exchange are those with large surface areas. The nature of the surface charge is sometimes a function of pH. At low pH in oxides for example, a positively charged surface prevails whereas at high pH a negatively charged surface develops.

Ion exchange is usually taken to mean the phenomena associated with the presence of the excess charge on solid surfaces, with any specific bonding of solute to surface being referred to as 'sorption'. Often in practice it is difficult to separate the results of the two processes, and the surface interactions of the major aqueous species are assumed, as here, to be associated with ion exchange.

In ion exchange the selectivity or affinity of ions for the solid surface is governed by the structural and charge properties of ions. A typical order of decreasing selectivity (affinity to exchange sites) of common cations depending on the above mentioned conditions is expressed as (Blatchley & Thompson, 2010):

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Cs^+ > K^+ > Na^+ > Li^+$$
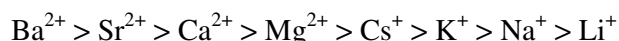
Cation exchange capacity (CEC) measurement is a common practice in soil science, geochemistry, hydrogeology etc. and there are many standard methods for CEC determination. Almost all of them follow the same principle – to measure the exchangeable cations by a displacement method. A number of solutions, for example ammonium acetate and barium chloride, have been used for displacing exchanged cations: the latter are then summed to provide an estimate of CEC (Bohn *et al.* 2001, White, 2006).

2.2   *Quantifying cation exchange reactions*

Several different models have been proposed to describe cation exchange reactions based on the assumption that the mineral surface has a constant total CEC at a given pH and the exchange reaction is stoichiometric and reversible. Cation exchange selectivity or the preference of the exchange phase for one cation over another is described by, for example, Appelo and Postma (2005):

$$mA^{n+} + nBX_m = mAX_n + nB^{m+} \qquad (1)$$

$$K_{A \backslash B} = \frac{[AX_n]^m \, [B^{m+}]^n}{[BX_m]^n [A^{n+}]^m} \qquad (2)$$

where $K_{A \backslash B}$ is the equilibrium constant, X represents the exchange phase of the cation and square brackets denote activities.

The cation exchange equilibrium constant describes the relative affinity of the exchanger for two considered cations. For example, in the case of a $Na^+ \backslash K^+$ exchange (i.e. A being Na in equation (1)), equilibrium constant values less than 1 would denote an affinity for K^+ greater than for Na^+ when aqueous activities of Na^+ and K^+ are equal, meaning a *preference* of the exchange sites for K^+.

Unfortunately, there exists no general model for determining the activity coefficients of ions on the exchange surfaces. As a result, various 'conventions' are used in estimating activities of attached ions, none of which is accurate in all situations. This means that it is usually found that measured 'equilibrium constants', better distinguished as 'selectivity coefficients', vary with exchanger composition, i.e. they

are not true thermodynamic constants (e.g. Essington, 2004). However, provided that the exchange compositions do not vary markedly during water movement, reasonable estimates can often, nevertheless, be obtained in practice by use of the selectivity approach (e.g. Carlyle *et al.*, 2004).

In this research the Gaines-Thomas convention (Gaines and Thomas, 1953), one of the most commonly applied conventions, was used for estimating ion activities on exchanger surfaces. This assumes that activities of the ions attached to the surfaces can be approximated by the equivalent fraction (i.e. activity = equivalents of sorbed ion per unit mass of dry rock /CEC expressed in equivalents per unit mass of dry rock).

3   MATERIALS AND METHODS
3.1   *Material Selection and Sampling*

This research was conducted on freshly quarried (non-weathered) blocks of sandstone from Locharbriggs Quarry, Dumfries, southern Scotland and Stoke Hall Quarry, Grindleford, Derbyshire, England. The Locharbriggs sample is a lower Permian, red sandstone sequence of fine to medium –grain-size and distinctive aeolian cross lamination. The Stoke Hall sample is medium grained, buff coloured sandstone from the 'Millstone Grit' of Carboniferous (Pennsylvanian) age. These particular samples were chosen because they represent two different types of sandstones used in historic buildings (red and buff coloured), and have been widely used in the UK.

The samples for flow-through experiments were cut into cylindrical cores using a water-cooled drill. The Locharbriggs samples were 20 mm long and 31.6 mm in diameter, and the Stoke Hall were 45 mm long and 31.6 mm in diameter. Smaller cores were used for the Locharbriggs samples as it was taking much longer to achieve full breakthrough. All the samples for the experiment were taken from the same block of stone to minimise the error due to possible variation in properties from one block to another.

3.2   *Material Characterisation*

Examination of the mineralogy of the samples was carried out qualitatively using polarised light microscopy (PLM) and semi-quantitatively using scanning electron microscopy with energy dispersive analysis (SEM-EDAX).

The mineralogy of Locharbriggs sandstone under polarised light microscopy appears to be predominantly quartzo-feldspathic or sub-arkosic. It is mainly composed of quartz, feldspars and very little rock fragments with scattered opaque minerals (probably iron oxides), which gives characteristic dark bands in concentrated zones. The grain surfaces and boundaries are coated with the iron oxide that gives the rock its red colour and a small proportion of clay minerals is present. The grains appear to be weakly cemented by edge to edge contact due to pressure-solution compaction and there is very little silica cement and no observable carbonate cement. This is consistent with the published mineralogical data, which indicate that the Locharbriggs sandstone mainly contains polycrystalline quartz, potassium and plagioclase feldspars, with a small amount of clays (illite, kaolinite and smectite) and rock fragments (Baraka-Lokmane *et al.* 2009). SEM-EDAX on our samples indicated that the

feldspars are invariably potassium feldspar and the dark minerals seen in PLM are iron oxides with other impurities. The elemental composition obtained in the EDAX spectra suggest that the clay fraction is kaolinite-dominated.

Stoke Hall sandstone, on the other hand, appears in thin section to be poorly sorted, medium to coarse grained with polycrystalline quartz as a dominant phase. It appears to have undergone a greater degree of pressure solution compaction leading to significant reduction in porosity. It is largely composed of quartz, plagioclase feldspars, biotite mica, rock fragments and clay minerals. There is little silica cement and no calcite cement was noticed. Most of the clays in this stone are present as aggregates in the pores. SEM-EDAX confirms that the feldspars are mainly sodic, and suggests that again in our samples kaolinite, which has a rather low exchange capacity, is probably the dominant clay.

Effective (open) porosity was measured using vacuum saturation method as per the procedures described in European Standard [EN 1936] and by Mercury Intrusion Porosimetry. The results indicated the average porosity of Locharbriggs samples was approximately 22% and that of Stoke Hall was approximately 11%. The hydraulic conductivity was measured using a falling head permeameter and the results indicated that average value for Locharbriggs is 6×10^{-7} m/s and that for Stoke Hall is 5×10^{-8} m/s, both rather low.

3.3   Experimental Methods

The cores were thoroughly washed with deionised water, dried for 24 hours in a ventilated oven at 110^{0} C and tightly wrapped in three layers of PTFE sealing tape and placed inside a suitable length of clear heat-shrinkable tube in such a way that about 3-4 cm of tube extended out at each end. Polyolefin heat-shrinkable tube with 38 mm bore and shrink ratio 2:1 above 95^{0} C was used. This sample assembly was then uniformly heated with a hot-air gun and the tube shrunk to seal tightly against the sides of the core. The surplus tubing forms a neck at each end that is used to attach the sample to the flow-through apparatus. Samples were then placed in a sealed vacuum tank and evacuated to below 2.0 kPa (15 mm Hg) maintaining the pressure for about 24 hours. After vacuum equilibration, deionised water was introduced slowly as the saturating liquid until the samples were completely immersed and the vacuum was maintained for another 24 hours. The samples were then returned to atmospheric pressure leaving them immersed under water for another 24 hours in a well-covered container.

The experimental setup was adapted from hydrogeochemical research (Kool *et al.*, 1989; Carlyle *et al.* 2004). It was designed to simulate salt solution transport under a non-evaporative regime in order to study the exchange properties of the sandstones and their influence on preferential retention of cations during saturated flow. The concentration of salts used was very low and, in the absence of any evaporation, no precipitation would have taken place within the pores. Therefore, any change in the chemistry of the output fluid will confirm the physical-chemical interactions of salt ions with the stone constituents. The entire experiment was carried out in two steps – firstly a flushing fluid with known chemistry was flushed through the sandstone samples under pressure from one end and the eluent was collected at the other end. This step was to ensure that all the exchange sites within the pores are in equilibrium

with the flushing solution and that effectively no other cation is present in the pores. In the second step all the cations adsorbed on the exchange site were stripped off by flushing the samples with strontium nitrate. In the standard CEC methods, high concentrations are required to desorb the ions as the rock is only exposed to one volume of displacing solution. There is a disadvantage, however, with this approach as the CEC can change with ionic strength. Using a flushing method, as here, much lower concentrations can be used, as the displacing solution is continuously replenished. Hence in the experiments a low concentration of $Sr(NO_3)_2$ (4.0 mM) was used, having an ionic strength only slightly in excess of the initial, conditioning solutions (12 mM compared with 9 mM). Strontium was chosen as its concentration in any initial solutions, and due to mineral dissolution, would have been negligible. The amount of cations displaced in the second step was used to estimate the exchange capacity of the sandstone samples and to calculate the selectivity coefficients.

The apparatus (see Figure 1) consisted of a constant flow rate peristaltic pump to drive the fluid flow and a fraction collector to collect the solution flushed out at fixed time intervals. The cores were connected to the peristaltic pump with a tube, one end of which was fixed to the sample through a perforated rubber bung and the other end of which was connected to the outlet of the pump. The inlet into the pump was connected to a fluid reservoir with a similar tube. The other end of the sample was connected to another tube which terminated in a fraction collector.
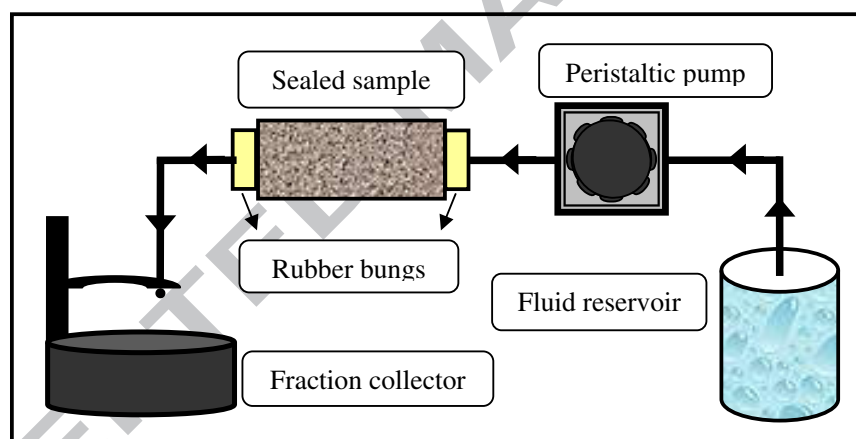

Figure 1: Apparatus for flushing experiments and CEC determination

The composition of the initial conditioning solution was chosen such that the ionic strength was consistent with fresh groundwater, and so that all four major cations were present in high enough concentrations to be easily measureable. All four major cations - sodium, potassium, magnesium and calcium - were thus prepared in 1.0 mM concentrations using analytical grade NaCl, KCl, $CaCl_2.2H_2O$ and $MgSO_4.7H_2O$ salts.

A very slow flow rate was maintained to avoid any pressure build-up in the sample or in the tubing, which may have resulted in leakage and failure of the system. The rate of flow through the sandstone core was 0.25 ml/minute, meaning that there was a 15 minute residence time. Ion exchange reactions are rapid, often with equilibration within 5 minutes (e.g. Ogwada and Sparks, 1986), but clearly equilibration at any one location within the core cannot be guaranteed. However, the success of modelling based on local equilibrium assumptions retrospectively provides some indication that equilibrium was approximated. The fraction collector was timed in such a way as to

collect approximately one pore volume of discharge as a single fraction in the plastic test tubes.

Five Locharbriggs samples were flushed initially with flushing fluid (four cation solution) until equilibrium between the solution and the full core was attained (a preliminary test indicated that flushing of approximately 60-70 pore volume was sufficient to attain equilibrium). All the cations adsorbed at the exchange sites were then displaced by a second flushing of 70 pore volumes of 4 mM strontium nitrate to measure the total mass of displaced cations for CEC determination. The pH of the flushed fluid was monitored and was noted to be between 6.5 and 6.9 for both types of sandstone. In the second flushing a total of 50 fractions was collected from each of the five Locharbriggs cores – the first 40 fractions equal to approximately one pore volume each and the next 10 fractions as 3 pore volumes each.

A similar experimental procedure was carried out on four Stoke Hall sandstone samples from the same block. However, because they have lower permeabilities and lower cation exchange capacities, they were saturated with the initial flushing fluid, flushed then for 30 pore volumes with this fluid, and then flushed with the strontium solution for about 48-49 pore volumes.

The fractions collected in the flow-through experiments were diluted by a factor of six and analysed for elemental concentration on a Dionex DX500 chromatograph using an IonPac CS12A cation exchange column and self-regenerating suppressor. 20 mM concentration of methanesulfonic acid was used as mobile phase for isocratic separation of cations. External standards were used at the concentrations 1, 5, 10 and 15 ppm for system calibration.

Each fraction was filtered with 0.2 μm syringe mounted filters and analysis was carried out for of all four cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) used in the experiments. The concentrations obtained from the analysis were plotted against the amount of salt solution flushed through the sample represented as number of pore volumes.

4   RESULTS
4.1   Differential Retention in Saturated Transport

It is worth briefly considering the breakthrough curves for the initial flush used to condition the cores as these illustrate the chromatographic effects of ion exchange.

Locharbriggs breakthrough curves of concentration (mM) vs. number of pore volumes for all the five samples are plotted in Figure 2. The results show that there is excellent repeatability. From initial to final fractions, the concentration of cations increases initially very quickly and then gradually attains the input concentration as the chemical equilibrium between injected solution and the sample is approached. The concentration changes of the cations in the effluent form a chromatographic pattern, with sodium and potassium achieving near equilibrium conditions much more rapidly than magnesium and calcium.

The concentration in the first pore volume is low because samples were saturated in deionised water and the water present in the pores contributed to the first pore volumes collected: note that the large apparent dispersion includes the effect of the

large water sample size (= 1 pore volume). The sum of cations (Figure 3) indicates that in the output concentration of ions is same as in the input solution (6 meq/L), which confirms that no dissolution or precipitation reaction is taking place within the samples.
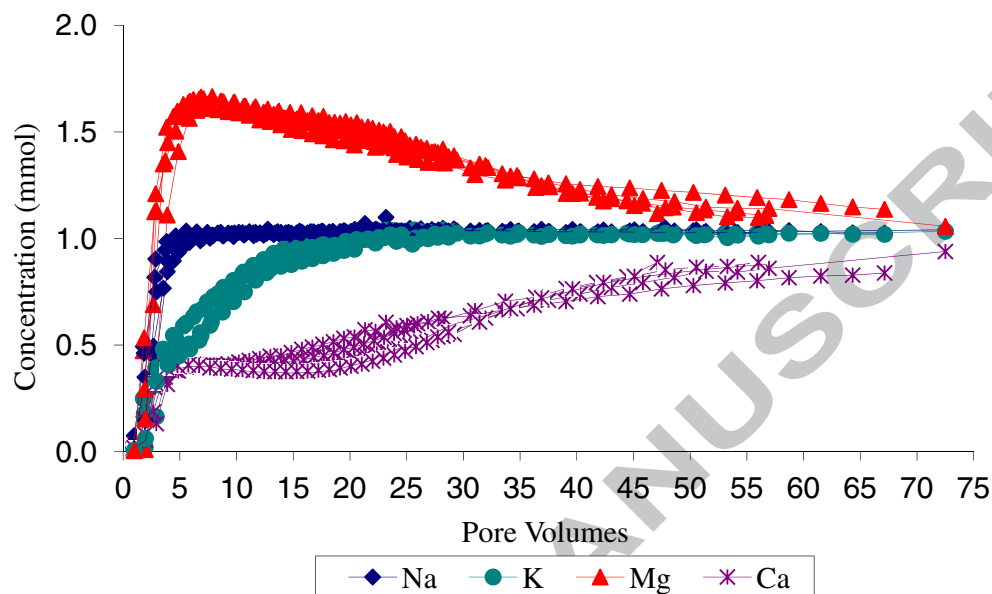
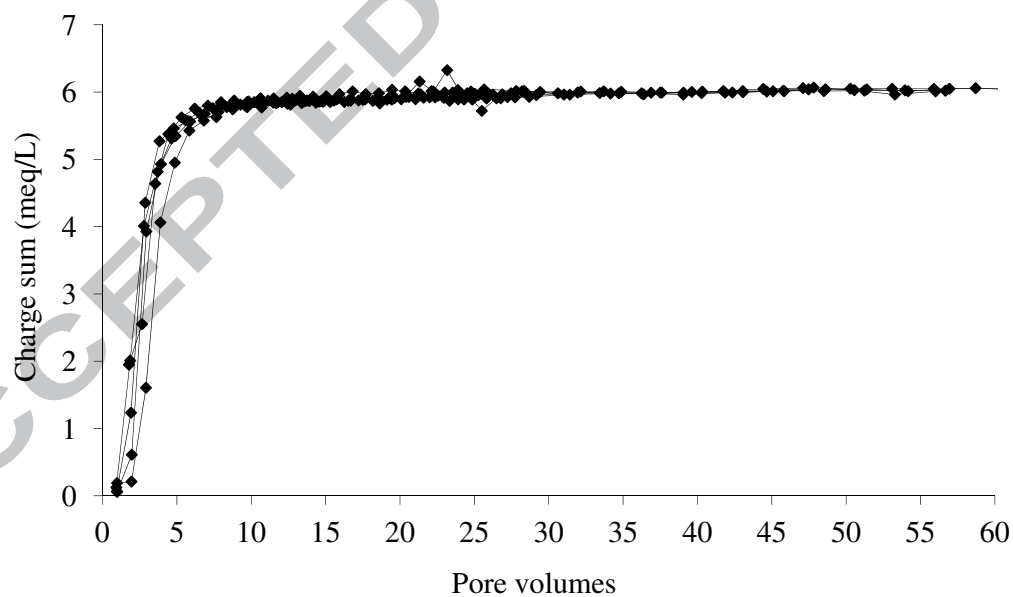Figure 2: Breakthrough curves in the initial flushing from the five Locharbriggs cores.

Figure 3: Sum of cations in the output fractions for the five Locharbriggs cores during the initial flushing phase of the experiments.

4.2   Cation Exchange Capacity and Selectivity

After flushing the sample cores with a salt solution of known chemistry as discussed in the previous section, the cores were flushed with the strontium nitrate solution: the resulting cation profiles were then modelled to obtain the CEC and selectivity coefficients assuming a Gaines-Thomas exchange model. The results obtained from the strontium displacement flushing are plotted in Figure 4a for the Locharbriggs sandstones and Figure 4b for the Stoke Hall sandstones. Breakthrough curves indicate that as the strontium is flushed into the cores, it exchanges for the cations already present on the exchange sites. This exchange follows the order of increasing selectivity of cations – Na^+ having the lowest selectivity is displaced first, followed by K^+. The higher selectivity cations Mg^{2+} and Ca^{2+} have higher affinity to exchange site as compared with Na^+ and K^+ but lower than Sr^{2+} (Blatchley & Thompson, 2010) and, therefore, their displacement is much delayed.

The cation exchange capacities were calculated as the sum of cations displaced by the strontium solution, and expressed in meq/100 g of sample dry mass (Table 1). The two sandstones used in this research have very different CECs. Locharbriggs has much higher CEC than Stoke Hall, which explains why the breakthrough is achieved relatively quickly in Stoke Hall as compared with Locharbriggs, despite the shorter length of the columns of the latter. However, it appears that in the Stoke Hall cores breakthrough has not been completely achieved and the breakthrough profile shows a tailing behaviour (above zero cation concentration towards the end of curve). This is discussed further in the next section when the geochemical modelling is described.
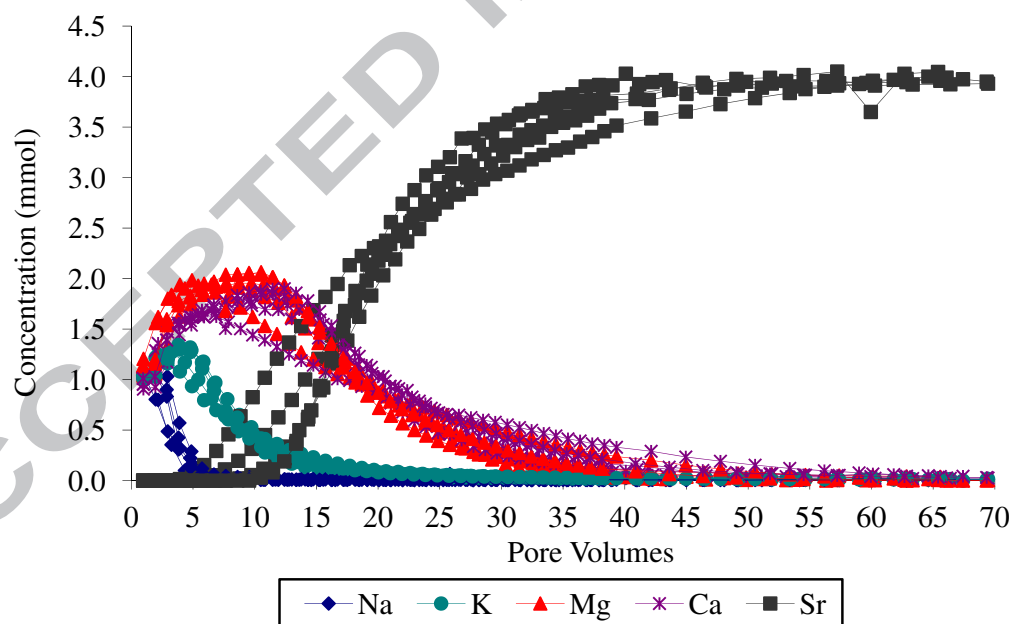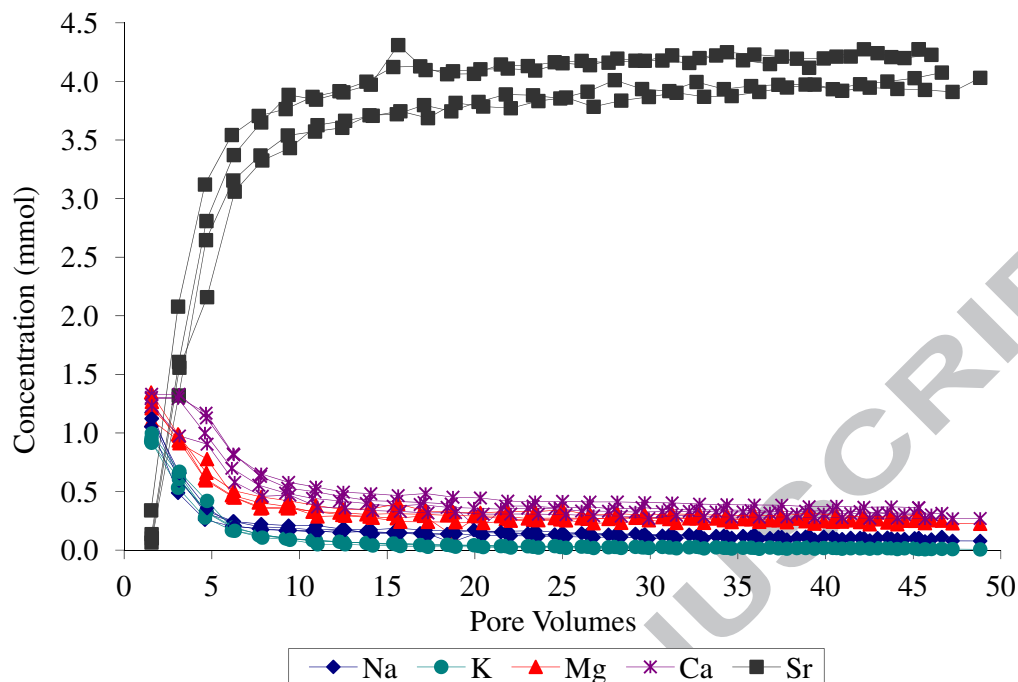
Figure 4a and b: Breakthrough curves in strontium displacement flushing from Locharbriggs (a) and Stoke Hall (b) cores

Sandstone	CEC – Min (meq/100g)	CEC – Max (meq/100g)	Average	St. Dev.	% RSD
Locharbriggs	1.75	2.01	1.88	0.09	4.91
Stoke Hall	0.38	0.45	0.42	0.03	7.34

Table 1: Cation exchange capacities of Locharbriggs and Stoke Hall sandstone samples

4.3 Geochemical Modelling

The selectivity coefficient can be back-calculated from the exchanger compositions and aqueous concentrations obtained from the experiments using equation (2). However, in this study forward modelling was used to obtain selectivity coefficient values. This approach has the advantages of convenience and also taking into account ion pairs and aqueous activity coefficients. A geochemical modelling program, PHREEQC (Parkhurst and Appelo, 1999), was used to simulate one dimensional dispersive transport of cations in the sandstone cores. PHREEQC is based on an ion-association aqueous model and is capable of simulating a wide range of equilibrium reactions between water and minerals, ion exchangers, surface complexes, solid solutions, and gases (Parkhurst and Appelo, 1999, Appelo and Parkhurst, 2002). The Gaines-Thomas model was implemented, and selectivity coefficients varied until the predicted breakthrough curves satisfactorily reproduced the experimental ones. CEC values were assigned the values calculated from the mass balances using the experimental data (Table1), dispersivity was determined by calibration, and average linear velocity was calculated by measured flow rate, cross sectional area, and porosity.

PHREEQC handles exchange reactions by splitting them into half-reactions, e.g.

$$Mg^{2+} + 2X^- = MgX_2 \qquad (3)$$

where X^- represents an unoccupied exchange site, though at all times the model assumes all sites are occupied (i.e. the activity of X^- is maintained at zero). The Na\NaX half reaction is defined as the point of reference with the log k value set to 0.0, k being the equilibrium coefficient for the half reaction: these half reaction equilibrium coefficients [e.g. $k = (MgX_2)/[(Mg^{2+})(X^-)^2]$] were used as calibration variables when undertaking PHREEQC calculations, and the full reaction selectivity coefficients calculated from them as required. k values were altered systematically starting from the most sensitive cation until a best fit, identified simply by visual assessment, with the experimental breakthrough curves was obtained. There will always be some equivalence in the interpretation when trying to fit model breakthrough curves to experimental breakthrough curves as different sets of values may produce the same result.

The log k values obtained from the best fits were used to calculate selectivity coefficients for different cations with respect, arbitrarily, to Na^+ by combining the two half reactions

$$Na^+ + X^- \rightarrow NaX \qquad (4)$$

$$\frac{1}{n}A^{n+} + X^- \rightarrow \frac{1}{n}AX_n \qquad (5)$$
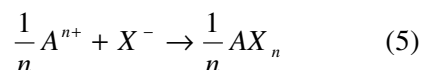
where A is one of the other cations present, to give the following full reaction

$$Na^+ + \frac{1}{n}AX_n \rightarrow \frac{1}{n}A^{n+} + NaX \qquad (6)$$
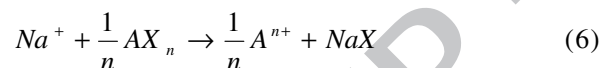
and the associated K value

$$K_{Na \backslash A} = \frac{[NaX][A^{n+}]^{1/n}}{[AX_n]^{1/n}[Na^+]} = \frac{k_{Na \backslash NaX}}{(k_{A \backslash AX})^{1/n}} \qquad (7)$$

The values calculated were then compared with values reported in the literature.

The fit between experimental data and PHREEQC simulated data for one of the Locharbriggs samples is represented in Figure 5. Because of the close repeatability of the experiments (Figure 2), the results from only one experiment are shown. The selectivity coefficients relative to Na calculated from the k values from the model fits are given in Table 2.
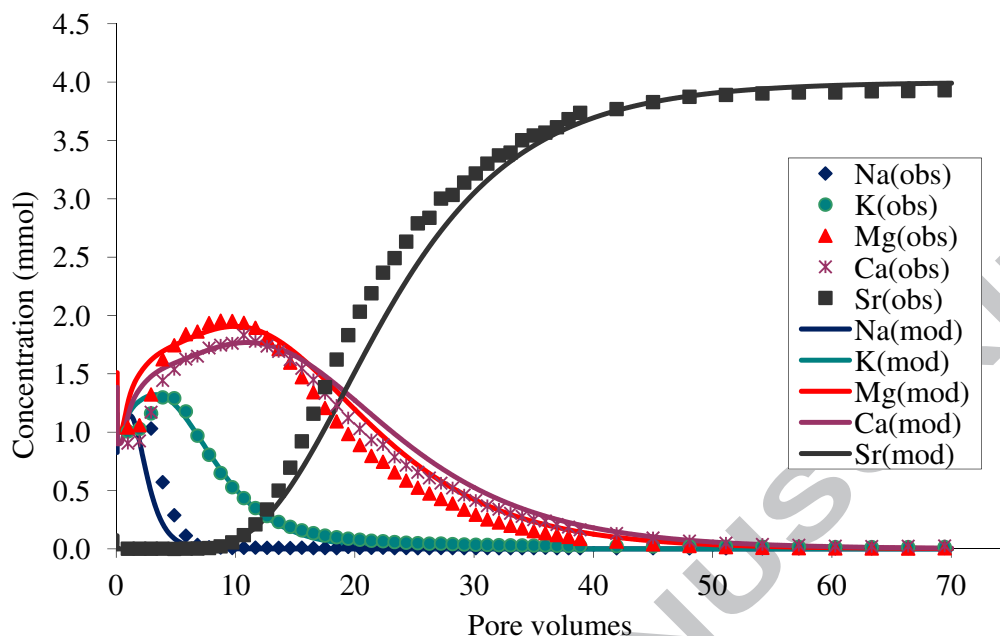
Figure 5: Experimental and modelled breakthrough curves for one of the Locharbriggs columns: dotted points – experimental; solid lines – PHREEQC model

The K values listed in Table 2 are in good agreement with those published by Appelo and Postma (2005), also given in Table 2. The selectivity coefficients between other cations (for exchange not involving Na^+) can be obtained by algebraic manipulation of the selectivity coefficient equations using the K values in Table 2.

Cation pairs	Modelled values	Published range
$K_{Na\backslash K}$	0.20	0.15 - 0.25
$K_{Na\backslash Mg}$	0.50	0.40 - 0.60
$K_{Na\backslash Ca}$	0.45	0.30 - 0.60
$K_{Na\backslash Sr}$	0.45	0.30 - 0.60

Table 2: Modelled K values for Locharbriggs sandstone compared with values published by Appelo and Postma (2005)

The Stoke Hall samples were less easy to model satisfactorily. Figure 6 shows that using the measured CEC and selectivity coefficient values for Na\K, Na\Mg, Na\Ca, and Na\Sr of 0.40, 0.63, 0.56, 0.63, respectively, the general style of the breakthrough curves has been reproduced, but that the model does not fully reproduce the data. One obvious feature of the experimental data that cannot be reproduced by simply varying CEC and K values is that the concentrations of Ca in particular remain constant rather than declining to effectively zero. Total cation concentrations increase during the experiment, indicating dissolution. The most likely dissolving phase would be calcite or dolomite: no carbonates were seen in thin section, but calculation indicates that the amount needed could have come from a carbonate phase effectively below the detection limit of the thin section analysis. Accordingly, the model curves shown in Figure 6 include calcite dissolution, assuming that before injection the conditioning and strontium solutions were in equilibrium with atmospheric carbon dioxide (at $10^{-3.5}$ bar). Though the model reproduces the stable Ca concentration, it does not reproduce the Mg and Na values, the implication being that another process is also occurring. In Section

3.2, it was observed that the Stoke Hall samples contain clay aggregates; this, and the tailing observed particularly in the strontium results, could indicate that there is a degree of physical non-equilibrium occurring – effectively there are zones of lower flow within the sandstones that are accessible only by diffusion. A similar situation has been found in UK Triassic Sherwood Sandstone Group samples by Bashar and Tellam (2006; 2011), who modelled their breakthrough curves using a dual region model. Though the interpretations of the breakthrough curves are less successful for the Stoke Hall samples, they are nevertheless instructive in indicating that dissolution and physical non-equilibrium effects should also be considered in the context of solute movement in building stones.
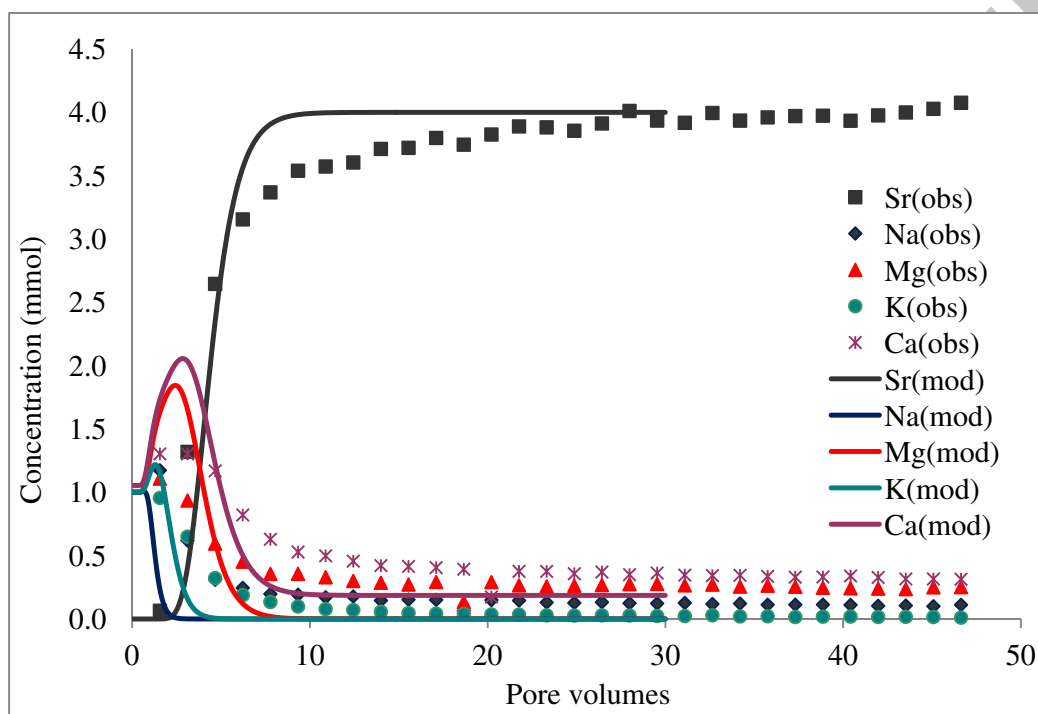

Figure 6. Experimental and modelled breakthrough curves for one of the Stoke Hall columns: dotted points – experimental; solid lines – PHREEQC model

5   DISCUSSION AND CONCLUSIONS

The transport and distribution of salts in historic buildings and monuments has previously been considered to be solely a function of rate of evaporation and solubilities of the salts present. According to this concept, differential distribution of salts can only take place when salts crystallize out from the solution in the order of their solubilities during the course of capillary rise of groundwater. It is well understood that environmental conditions play a significant role in crystallization of salts and the ECOS chemical model (Price, 2000) predicts crystallization of salts from mixtures depending on the environmental conditions (relative humidity and temperature). Although it is likely that the transport and distribution of salts is affected by environmental conditions and solubility, there is no conclusive evidence published so far to suggest that transport and distribution of salts is exclusively controlled by the solubility. Natural stone and groundwater are geochemically active systems and it is inappropriate to assume that there are no other physicochemical interactions taking place in the course of capillary transport. This study has examined ion exchange in this context, and quantified cation exchange properties in two

example building stones: the results appear to indicate that ion exchange could be significant.

This can be illustrated by the following scoping calculation. Taking the Locharbriggs sample CEC values, the maximum cation mass that could be taken up on exchange sites in a building stone of dimensions 30 x 30 x 30 cm would be a little over 1000 meq. Given that even calcite-saturated freshwater solutions are unlikely to carry more than about 5 meq/L Ca (and seawater contains only 20 meq/L), this is a potentially significant sink (or possibly in some cases a source): ignoring other cations, the CEC would have the same cation mass as around 40 pore volumes of calcite-saturated freshwater (10 pore volumes in case of seawater). Though this example is in some regards an extreme case, it does illustrate that CECs are not insignificant.

Computer modelling can be used to explore this further. Figure 7 shows the results of two experiments using PHREEQC considering limited degrees of evaporation. The first experiment (Figure 7a and b) models evaporation of a groundwater (Table 3) in equilibrium with a carbon dioxide partial pressure of $10^{-3.5}$ bar, allowing calcite and gypsum to precipitate; equilibration was enforced at all stages of evaporation, with the mass of water decreasing from 1 to 0.009 kg. This experiment is an approximate representation of what might happen in a building stone without carbonate cement but with good contact with the atmosphere. The second experiment (Figure 7 c and d) modelled the same system, but also maintained ion exchange equilibrium with the rock applying properties based on the measurements made during this study (Table 3).

In the first experiment, where ion exchange is not involved, evaporation induces calcite, but not gypsum, to precipitate (Figure 7a and b). This results in removal of Ca and inorganic carbon from solution, with the other ions increasing in concentration in proportion to the degree of evaporation. In contrast, when ion exchange equilibrium is enforced, both calcite and gypsum precipitate, and most ion concentrations are affected. The precipitation of calcite is 0.46 mmol compared with 0.14 mmol for the case without ion exchange; 0.79 mmol of gypsum also precipitated. Clearly these models only roughly approximate the conditions within a building stone, not replicating flow for example, or change of ion exchange properties with ionic strength, or the very high ionic strengths associated with the precipitation of the more damaging highly soluble minerals, but they do illustrate that ion exchange can, in principle, affect precipitation significantly.
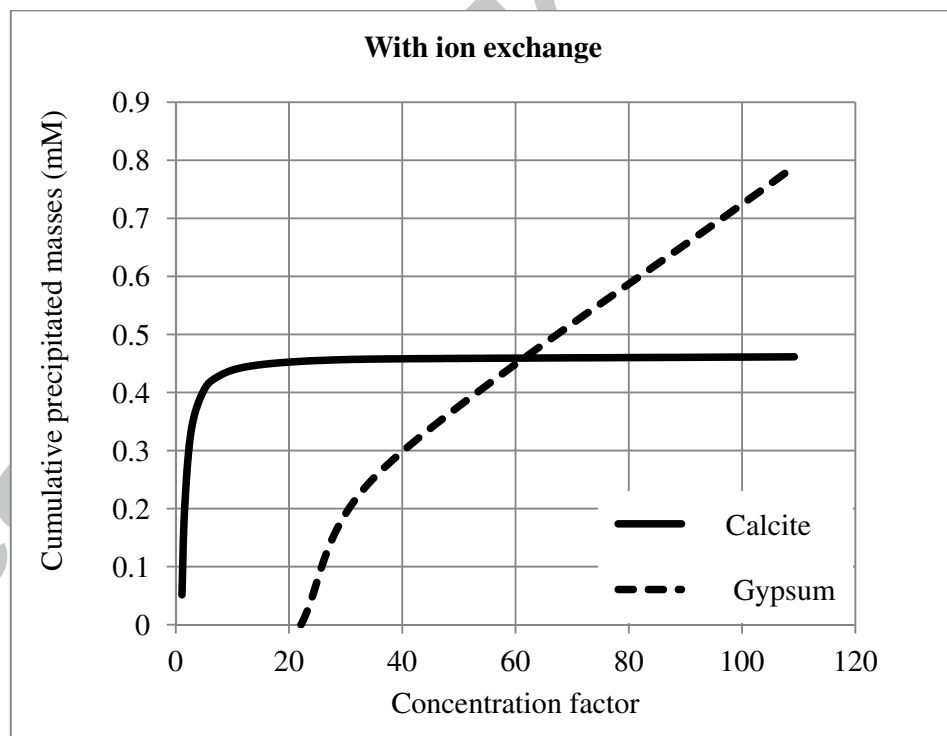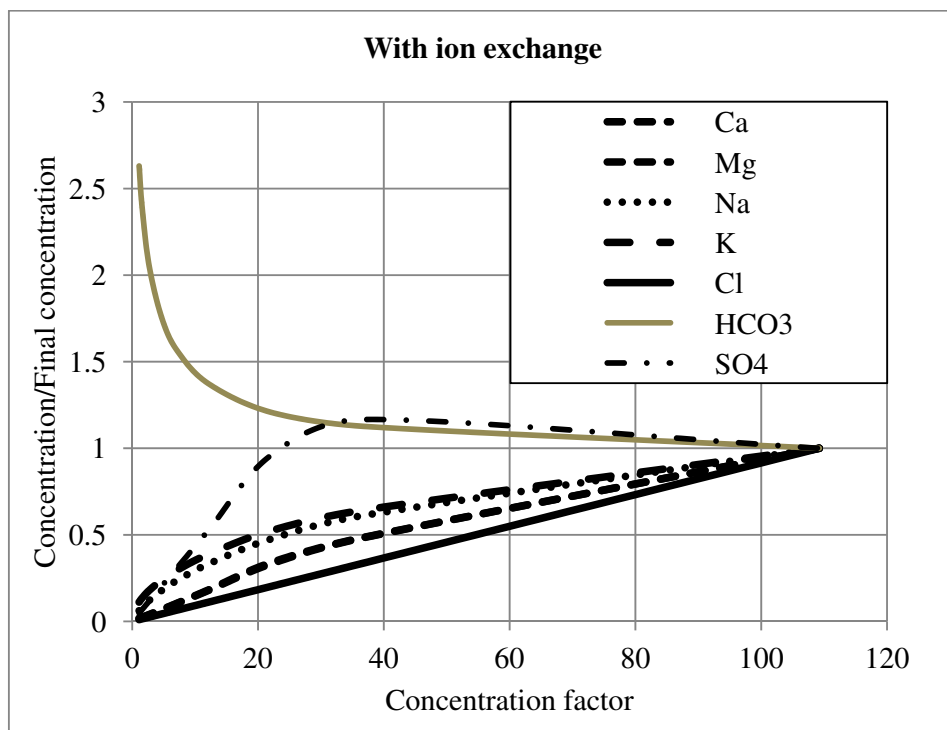
a

b

c

d
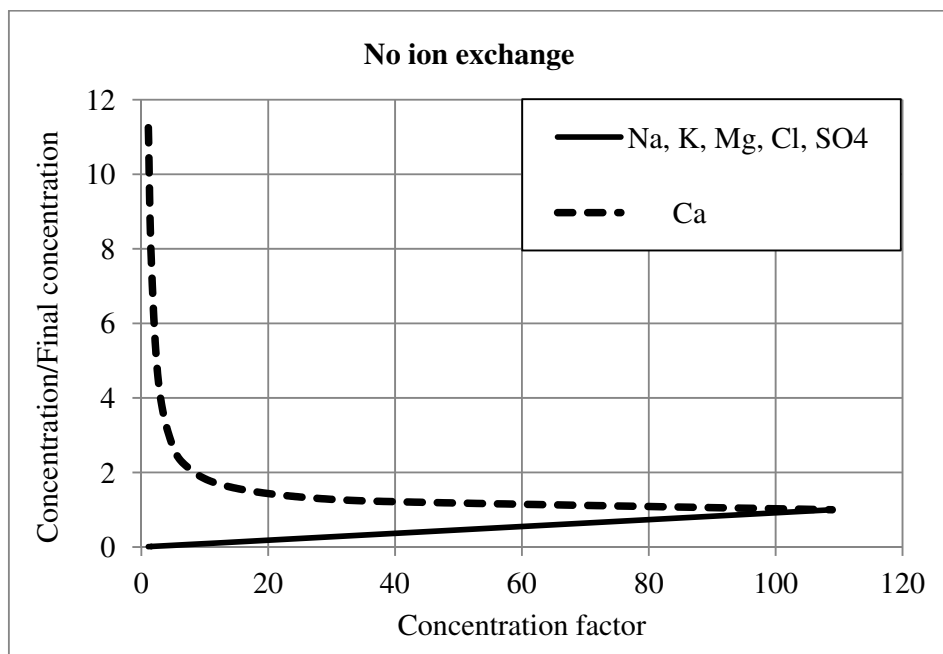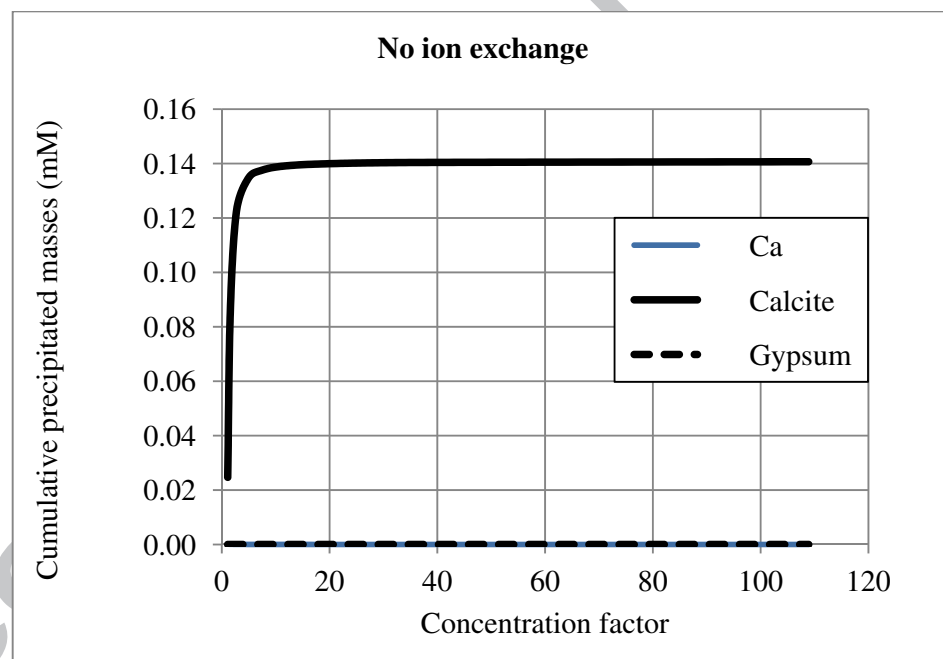
Figure 7. PHREEQC experiment results for the case where no ion exchange (a and b) is
occurring and for the case where it is occurring (c and d). Final concentrations are the
concentrations when the groundwater has been evaporated from 1 to 0.009 kg. Concentration
factor = initial mass of water/final mass of water. In (c) Ca and Mg lines overlie each other.

Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO4 (mg/L)	HCO3 (mg/L)	pH	CEC meq/100g
100	60	23	3.9	65	96	439	7.5	0.4

Table 3: Initial groundwater chemistry and rock properties used in the numerical experiments the results of which are summarized in Figure 7. Selectivity coefficients were set as estimated for the Locharbriggs samples.

The models so far considered are static. However, the chromatographic effect of ion exchange may have a particular influence on efflorescence and subflorescence occurrence. Chromatographic effects can be seen in Figures 2, 4, 5, and 6 above. The salts with lower affinity to exchange sites will have higher probability to form efflorescence whereas the slower transport of salts with higher exchange affinity will be more likely to display subflorescence crystallization, though the ionic proportions of the invading and background pore waters also will influence precipitation distributions.

It can be argued that since there is a fixed amount of ion exchange related to a particular volume of stone, it may reach a saturation point (as observed in the flow-through experiments discussed above) after which exchange phenomena should have less impact on transport and distribution. This will be the case in some systems, though as the calculations above imply, the timing of precipitation may be significantly affected. However, depending on local conditions, groundwater chemistry can be subject to change due to various environmental and geochemical processes on both long and short time-scales (rock weathering, dissolution, precipitation, leaching of evaporitic deposits and dilution of groundwater concentration from rainwater infiltration, and contamination from various sources). Since ion exchange is a readily reversible process, any change in the input concentration and/or chemistry of groundwater would upset the equilibrium, making ion exchange a continuous phenomenon.

Ion exchange may also alter the physical properties of the clays within the stone, causing expansion or contraction especially in the context of sodium uptake on smectites which causes expansion and reduction of permeability. A related phenomenon is change in ionic strength affecting flocculation, either releasing clay particles or causing them to aggregate, again potentially having a significant effect on permeability and thus on salt transport.

Much, therefore, remains to be done in quantifying the impact of ion exchange on precipitation of salts in building stones. This should include examination of the unsaturated porewater movement subject to evaporation and gas phase and solid phase controls, and include impacts of chemical changes on the hydraulic properties of stones. However, we conclude that ion exchange reactions cannot be ignored in this context.

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Highlights

- A geochemical approach was used to study transport & distribution of salt in stone.
- Ion exchange processes significantly control transport of ionic species in stone.
- Sandstones act like chromatographic column during the capillary transport of salts.
- Ion exchange can significantly influence mineral precipitation during evaporation.