Environ Earth Sci (2015) 74:2297–2313
DOI 10.1007/s12665-015-4221-1

ORIGINAL ARTICLE

Thermodynamic calculations for the salt crystallisation damage in porous built heritage using PHREEQC

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Received: 4 July 2014 / Accepted: 20 February 2015 / Published online: 4 March 2015

Abstract This work considers the crystallisation mechanisms of the most common and aggressive salts that generate stress in porous building stones as a result of changing ambient conditions. These mechanisms include the salt crystallisation that result from decreasing relative humidity and changes in temperature and, in hydrated salts, the dissolution of the lower hydrated form and the subsequent precipitation of the hydrated salt. We propose a new methodology for thermodynamic calculations using PHREEQC that includes these crystallisation mechanisms. This approach permits the calculation of the equilibrium relative humidity and the parameterization of the critical relative humidity and crystallisation pressures for the dissolution–precipitation transitions. The influence of other salts on the effectives of salt crystallisation and chemical weathering is also assessed. We review the sodium and magnesium sulphate and sodium chloride systems, in both single and multicomponent solutions, and they are compared to the sodium carbonate and calcium carbonate systems. The variation of crystallisation pressure, the formation of new minerals and the chemical dissolution by the presence of other salts is also evaluated. Results for hydrated salt systems show that high crystallisation pressures are possible as lower hydrated salts dissolve and more hydrated salts precipitate. High stresses may be also produced by decreasing temperature, although it requires that porous materials are wet for long periods of time. The presence of other salts changes the temperature and relative humidity of salt transitions that generates stress rather than reducing the pressure of crystallisation, if any salt has previously precipitated. Several practical conclusions derive from proposed methodology and provide conservators and architects with information on the potential weathering activity of soluble salts. Furthermore, the model calculations might be coupled with projections of future climate to give as improved understanding of the likely changes in the frequency of phase transitions in salts within porous stone.

Keywords Halite · Mirabilite · Salt weathering · Stone conservation · Climate

Introduction

Salt crystallisation is one of the main contributors to weathering of porous stones and other porous materials in both historical and modern buildings. Salt weathering can result both in aesthetic and physical damage. Aesthetic damage relates to disfiguring weathering patterns on architecture, whereas physical damage means decay within the materials. Experimental studies on salt weathering under extreme cyclic environmental conditions of different salts show that certain salts, most notably sodium sulphate, sodium carbonate and magnesium sulphate, generate consistently stress; sodium nitrate is sometimes effective and two of the most common salts in the environment, calcium sulphate and sodium chloride, appear to be relatively ineffective (Goudie and Viles 1997).

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The precipitation of salt crystals occurs through different mechanisms closely related to changes in environmental conditions:

1. Decreasing relative humidity to reach the saturated salt solution. The equilibrium or deliquescence relative humidity, RH_{eq}, of a salt is the relative humidity at which a salt crystallises from an aqueous solution. All soluble salts exhibit a critical relative humidity at any given temperature. Above this point they absorb moisture from the air, and below it they crystallise. Variations of relative humidity lead to salts dissolution and recrystallisation. That implies that climate (outdoors) and microclimate (indoors) exerts a key control on the weathering activity of soluble salts. The mechanism is also a product of evaporation that can lead to supersaturation by decreasing water vapour pressure above the salt solution and/or increasing temperature.
2. Salt crystallisation from a solution by changes in temperature. Some salts rapidly decrease in solubility as temperature falls. This is particularly important for sodium sulphate, sodium carbonate and magnesium sulphate, but to a lesser degree for calcium sulphate and sodium chloride.
3. In hydrated salts, the dissolution of the lower hydrated form and the precipitation of the hydrated salt. Salt deterioration takes place chiefly through repeated crystallisation–dissolution processes that are strongly controlled by the thermodynamic properties of the salt, and the relative humidity and temperature of the environment. More aggressive salts are produced by aqueous solutions of Na_2SO_4, $MgSO_4$ and Na_2CO_3, which include various hydrated forms. The hydrated salts produce high crystallisation pressures during changes in thermohygrometric conditions.

As a consequence, salt weathering cannot be understood without taking into account the interaction between monuments and buildings, local climate and salts. This involves the use of parameters different from those typical in meteorology (e.g. temperature or relative humidity) and focuses on cycles and combinations of meteorological parameters that relate to material damage (Brimblecombe 2010). Thus, in a new building, we will have appropriated criteria for selecting the most adequate stone in terms of local climate. In preventive conservation, we consider environmental control to minimise salt damage. This implies to keeping environmental relative humidity and temperature permanently above or below the critical value for salt transition. These practices are usually applied to indoors and at hypogean sites, where microclimate conditions can be controlled. Heritage climatology has been proposed (Brimblecombe 2010) to account for the particular climate parameters that affect monuments, materials and sites and perhaps allied with the material climatology proposed by Brischke et al. (2008), and the consents also suggest criteria for application in different contexts, including salt decay research (Benavente et al. 2008).

Most studies of salt crystallisation have been carried out on single salts and focus on the behaviour of sodium and magnesium sulphates as these salts are particularly damaging. However, building materials rarely contain one particular type of salt, but rather multicomponent solutions, which means that a multiplicity of solid phases may precipitate (Arnold and Zehnder 1990). In fact, salts are less likely to cause damage in multicomponent systems because of the decreasing of water activity and thus ionic activity coefficients, which are included in the ionic product (Cardell et al. 2008).

Salt weathering is normally attributed to a physical process (crystallisation pressure), but also involves chemical dissolution of the stone. Chemical dissolution can be important in the calcite fractions of the stone. This may generate new pores and fissures and therefore amplify the physical process (Martinez-Martinez 2008; Benavente et al. 2011; Ruiz-Agudo et al. 2011). Moreover, chemical changes in concentration and ions and other minerals can generate stress. Atmospheric CO_2 can also contribute to chemical weathering, mainly in hypogean materials where ventilation may be hindered (Sanchez-Moral et al. 2005; Benavente et al. 2011).

The importance of these processes on stone conservation works has encouraged the development of software for thermodynamic calculations, including specific codes in stone conservation such as the *Jac-Library Chemical Model*, Runsalt or ECOS (Environmental Control of Salts) (Price 2000; Sawdy and Price 2005; Steiger et al. 2008), and geochemical codes, such us the outdated PHRQPITZ (Plummer et al. 1998; Benavente et al. 2004b, 2008, 2011; Cardell et al. 2008). Each code provides complementary results and they run in different formats. The specific codes execute thermodynamic calculations, where salt precipitation is estimated by crossing the equilibrium relative humidity. However, they do not consider the salt crystallisation from a solution by changes in temperature and by dissolution–precipitation mechanisms.

In this paper, we illustrate the use of the PHREEQC code (Parkhurst and Appelo 1999, 2013). While it was widely used in geochemistry for calculating a variety of reactions and processes in natural waters or laboratory experiments, it is less known in the heritage science. PHREEQC presents an extensive list of advantages that provide valuable possibilities for future research in stone conservation, including (1) ease in modelling and incorporation of interactions; (2) works with different ion interaction models [the approach of Pitzer which is based on extensions of the Debye–Huckel—Pitzer (1991)]; (3) ease in modification of the database, which includes the equilibrium constants and their variation with temperature, and parameters of the ion interaction models; (4) ability to model salt crystallisation from aqueous solution and dissolution–precipitation; (5) incorporation of chemical dissolution of the host rock by the presence of salts can also be calculated and (6) applications with attractive potential for stone conservation research such as the introduction of kinetic equations, simulating evaporation (by removing water), mixing of saline solutions, modelling 1D transport processes (advection, dispersion and diffusion), inverse modelling, ion exchange (e.g. in clay-bearing stones) and mineral-gas reactions in the pore solution.

This paper examines different crystallisation mechanisms that generate stress for the most common and aggressive salts through changes in the surrounding climate and to propose a new methodology for thermodynamic calculations that includes crystallisation mechanisms using PHREEQC. For this purpose, we reconsider the sodium and magnesium sulphate and sodium chloride systems, in both single and multicomponent solutions. We briefly compare the sodium carbonate system to other hydrated systems and also examine the benign behaviour of the calcium sulphate system since it is one of the most common salts in building stones. The variation of crystallisation pressure, the formation of new minerals and the chemical dissolution in the presence of other salts are also evaluated. All the calculations, expressions for different phase transitions and diagrams are carried out using PHREEQC and explained in detail in “Appendix 1.”

The thermodynamic calculations and the conceptual model for a single salt should be considered at the beginning of an investigation or conservation work; however, salt mixtures, kinetics of salt crystallisation and physical properties of stones moderate the theoretical estimates of damage from salt crystallisation.

Theory and equations

In this paper, the Correns’ equation is used to estimate the (maximum) crystallisation pressure. Correns (1949) emphasised that crystallisation damage in porous materials originates not only in supersaturation, but also from the energy mismatch between the crystal and the pore wall, which is generally expected in concrete and rocks (Flatt 2002). The equation is applied to calculate crystallisation pressures for supersaturated solutions of aqueous, including the various hydrated forms of soluble salts.

However, depending on the nature of the salt, neglecting non-ideal behaviour may cause considerable error in the calculation of crystallisation pressure (Steiger 2005). The ion interaction approach of Pitzer (1991) is appropriate to calculate water activities and activity coefficients in supersaturated solutions thus describing the non-ideal behaviour. This approach offers additional advantages as temperature dependence of the interaction parameters and can be easily incorporated along with the treatment of multicomponent solutions, which are properly accounted for in the calculation of crystallisation pressures of salts, P_C. The Correns’ equation can be written as follows:

$$P_{\mathrm{C}} = \frac{RT}{v_{\mathrm{C}}} \ln \frac{\mathrm{IAP}}{K} = \frac{RT \cdot \ln 10}{v_{\mathrm{C}}} \phi, \quad (1)$$

where R is the gas constant, T is the temperature in Kelvin degrees, K is the equilibrium constant, IAP is the ionic product, v_{C} is the molar volume of the crystal (Table 1) and ϕ is the saturation index defined as

$$\phi = \log(\mathrm{IAP}/K). \quad (2)$$

Incorporating the ion interaction equations in the crystallisation pressure equation appears to be more convenient for hydrated salts since IAP includes both water activities and activity coefficients. The equilibrium constant and its variation with temperature can change substantially depending on the source. This may introduce important errors in the calculation of crystallisation pressures.

At the equilibrium, water activity, a_{w}, of an aqueous solution is equal to the relative humidity, i.e.

$$a_{\mathrm{w}} = p_{\mathrm{w}}/p_{\mathrm{ow}} = \mathrm{RH}, \quad (3)$$

where p_{w} is the partial vapour pressure above the salt solution and p_{ow} is the saturated vapour pressure of pure water. This relationship is important since it can be used to obtain the equilibrium or deliquescence relative humidity, $\mathrm{RH}_{\mathrm{eq}}$. The equilibrium relative humidities of hydrated sodium carbonate and sodium sulphate are high, whereas those of sodium chloride, sodium nitrate and calcium chloride are lower by comparison (Table 2). The equilibrium relative humid of a salt varies with the temperature and in the presence of other ions in the solution, and it can be obtained by calculating water activity through the ion interaction approach, described above.

At high values of relative humidity (higher than $\mathrm{RH}_{\mathrm{eq}}$), salts can also precipitate from aqueous solution as temperature decreases. The influence of temperature on salt precipitation can be evaluated for the equilibrium constant. For instance, a decreasing in temperature produces a strong decrease of the equilibrium constant of mirabilite ($Na_2SO_4 \cdot 10H_2O$) and natron ($Na_2CO_3 \cdot 10H_2O$) and consequently, an increase in the saturation degree (which explains the aggressive behaviour of the salts) (Table 1).

Salts with various hydrated forms, such as Na_2SO_4, Na_2CO_3 and $MgSO_4$ systems, can also precipitate by

Table 1 Fit parameters of Eq. (6) in the range 273.15–333.15 K and log *K* at 298.15 *K*

Mineral	A_1	A_2	A_5	log *K*	v_C (cm^3/mol)
Mirabilite, $Na_2SO_4 \cdot 10H_2O$	3.02E+00	5.86E−03	−5.33E+05	−1.2358	220
Thenardite, Na_2SO_4	7.05E+00	−1.69E−02	−2.06E+05	−0.307	53
Heptahydrate, $Na_2SO_4 \cdot 7H_2O$	1.01E+01	−1.41E−02	−5.84E+05	−0.703	175
Epsomite, $MgSO_4 \cdot 7H_2O$	2.53E+00	−7.28E−03	−1.97E+05	−1.8514	147
Hexahydrite, $MgSO_4 \cdot 6H_2O$	5.06E+00	−1.53E−02	−1.84E+05	−1.5651	133
Pentahydrite, $MgSO_4 \cdot 5H_2O$	9.95E+00	−2.65E−02	−2.86E+05	−1.1803	111
Starkeyite, $MgSO_4 \cdot 4H_2O$	1.08E+01	−2.96E−02	−2.49E+05	−0.7949	96
Kieserite, $MgSO_4 \cdot H_2O$	1.26E+01	−3.66E−02	−1.50E+05	−0.0324	57
Natron, $Na_2CO_3 \cdot 10H_2O$	−1.90E+01	5.50E−02	1.63E+05	−0.794	199
Thermonatrite, $Na_2CO_3 \cdot H_2O$	3.53E+01	−7.25E−02	−1.18E+06	0.437	55
Halite, NaCl	4.97E+00	−6.77E−03	−1.22E+05	1.5845	28

A_1, A_2 and A_5 mismatch of a correlation coefficient of $R = 1$, and A_3 and A_4 are not required

Molar volume of the crystals, v_C, is calculated from unit cell volume

Table 2 Equilibrium or deliquescence relative humidities for different salts

Mineral	Deliquescence relative humidity		Deliquescence relative humidity variation with temperature	
	Temperature interval (°C)	RH_{eq} (%) [at specific T (°C)]	Rate (%/°C)	Temperature interval (°C)
Mirabilite, $Na_2SO_4 \cdot 10H_2O^a$	0–32.2	93.5 (25)	−0.27	0–32.2, no linear
Thenardite, $Na_2SO_4^a$	32.2–60	88.2 (40)	+0.09	32.2–60
Natron, $Na_2CO_3 \cdot 10H_2O^a$	0–32.5	89.1 (25)	−0.40	0–32.5, no linear
Epsomite, $MgSO_4 \cdot 7H_2O^a$	0–49.3	90.1 (25)	−0.21	0–49.3
Hexahydrite, $MgSO_4 \cdot 6H_2O^a$	49.3–60	84.9 (55)	−0.01	49.3–60
Halite, $NaCl^b$	10–40	75.3 (25)	−0.02	10–40
Silvite, KCl^b	5–25	84.17 (25)	−0.16	5–25
Nitratine, $NaNO_3^b$	10–40	74.18 (25)	−0.25	10–40
Antracticite, $CaCl_2 \cdot H_2O^b$	15–25	28.13 (25)	−0.60	15–25

[a] Calculated from water activity using Eq. (3)

[b] From [27]

hydration through the dissolution of the lower hydrated form (B) and the precipitation of the hydrated salt (A):

$$XY \cdot n_A = XY \cdot n_B + (n_A - n_B) \cdot H_2O, \tag{4}$$

where subscripts *a* and *b* refer to the different hydrated forms of salt *XY*.

The phase transition occurs when the critical relative humidity, RH_{Crit}, is crossed and causes the lower hydrate to change to the hydrated salt. In the equilibrium, the critical humidity can be related to the equilibrium constant (solubility product) through the water activity using Eq. (3):

$$RH_{Crit} = a_w = (K_{n_A}/K_{n_B})^{1/(n_A - n_B)}. \tag{5}$$

Since equilibrium constants depend only on temperature, at constant pressure, the critical relative humidity is not influenced, in an ideal sense, by the presence of other salt species, although the saturation of each mineral phase may be strongly modified by changes in the activity coefficient. Using the variation of equilibrium constants with temperature, the critical relative humidity can be fitted to the analytical expression as discussed below.

Methodology

In this paper, we use the geochemical PHREEQC code to calculate different solution parameters to estimate salt weathering from the different salt crystallisation mechanisms. The most important parameters are water activity (calculation of equilibrium relative humidity) and saturation index (estimation of crystallisation pressure using Eq. 1) and solubility of salt minerals.

We select the original Pitzer database for calculating water activities and activity coefficients in multicomponent aqueous solutions, which include calculations for Na^+–Mg^{+2}–K^+–Li^+–Sr^{+2}–Fe^{+2}–Mn^{+2}–Br^-–CO_3^- –Cl^-–SO_4^{2-} –H_2O systems. Coefficients and the number of ions can be easily modified in the database (see supporting online material pitzer_salts.dat).

In particular, equilibrium constant parameters (A) were revised and adapted according to salt crystallisation literature. Steiger et al. (2011b) point out the important differences found in the literature for the equilibrium constants of minerals and their variation with temperature. PHREEQC uses the Van't Hoff equation, which requires the reaction enthalpy or uses an analytic expression of the type:

$$\log K = A_1 + A_2 \cdot T + A_3/T + A_4 \cdot \log T + A_5/T^2, \qquad (6)$$

where T is the temperature in Kelvin and A_i are fitted parameter. Using the verified data available in the literature, we modify the equilibrium constant and the analytic expression for halite, mirabilite, heptahydrite, epsomite, hexahydrite, petahydrite and kieserite (Steiger et al. 2008, 2011b) and natron (Linke 1965), and introduce more minerals to the database such as thenardite and starkeyite (Steiger et al. 2011b) and thermonatrite (Linke 1965). In Table 1, the fitted parameters are given for the modified and added minerals.

A detailed description of input files for PHREEQC is shown in "Appendix 1," where different options are proposed for modelling salt weathering. In particular, the calculation of crystallisation pressure that arises through dissolution of the lower hydrate and the precipitation of the hydrated salt is carried out in (a) pure water (condensate water and/or rainwater) and (b) in the presence of other salts. Finally, (c) the influence of chemical dissolution of the host rock on mineral speciation precipitation is also evaluated. Salt precipitation from a saturated solution is studied under conditions when (a) air relative humidity is lower than the equilibrium or deliquescence relative humidity and (b) by varying temperature and/or concentration. Finally, brief mention is made of the salt precipitation from the saline pore water. Although the precipitation from saline waters within pores in stone is the focus in the present manuscript, we introduce some guidelines that can be of interest in conservation studies.

Mineral phase diagrams can be created using the equilibrium constant and/or calculated water activity using PHREEQC. These essential diagrams can be modified if more accurate equilibrium constants and interaction coefficients are found. Figures 1 and 4 can easily be plotted using thermodynamic data with our proposed methodology. The solution-mineral line (top line) can be defined by the equilibrium relative humidity (and calculated from the water activity, Eq. 3). The boundary between two minerals can be defined using water activity when two mineral phases are in the equilibrium ($\phi = 0$ for both minerals) or through the equilibrium constants (solubility products) using Eq. (5). In the case of crystallisation of hydrated salts from lower hydrates, the phase transition occurs by crossing this boundary (critical relative humidity, RH_{Crit}). The polynomial expressions for RH_{Crit} for these phase transitions are shown in Table 3. The relative humidity at a given temperature is proportional to water activity (Table 2). Moreover, this property is used to plot Fig. 7 and evaluate the variation of relative humidity by the presence of other salts at different temperatures.

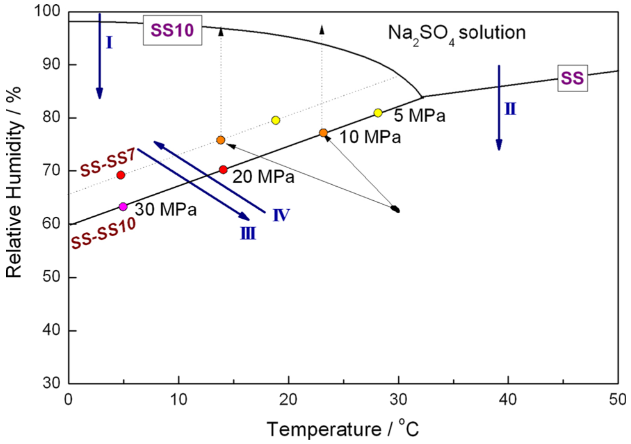

Fig. 1 Phase diagram of sodium sulphate system: *SS10* mirabilire ($Na_2SO_4 \cdot 10H_2O$); *SS* thenardite (Na_2SO_4); *SS7* heptahydrate ($Na_2SO_4 \cdot 7H_2O$). The precipitation of hydrated salts is produced by different pathways that also are deliquescence and critical hydration–dehydration equilibrium humidities. Pathways-I and II correspond to mirabilite and thenardite precipitations from a saturated dissolution (deliquescence humidity). Pathway-III displays mirabilite dehydration and pathway-IV describes mirabilite hydration after thenardite dissolution (SS–SS10 critical hydration–dehydration humidity). *Yellow*, *orange*, *red* and *magenta* points indicate, respectively, a crystallisation pressure of 5, 10, 20 and 30 MPa

Discussion

Estimation of potential salt damage

Na_2SO_4 system

The precipitation of hydrated salts is sensitive to both temperature and relative humidity and it can occur through different pathways. The sodium sulphate-water system has two stable phases: mirabilite ($Na_2SO_4 \cdot 10H_2O$) and thenardite (Na_2SO_4); and a metastable phase ($Na_2SO_4 \cdot 7H_2O$). The heptahydrate is obtained in the laboratory by rapid cooling of a solution saturated at 40 °C (Gans 1978). Figure 1 shows the pathways for the Na_2SO_4–H_2O system, which can be considered equivalent to the Na_2CO_3–H_2O system (although with different transitions values). The estimated damage therefore depends on the pathway. The precipitation of mirabilite (pathway-I) and thenardite (pathway-II) from a saturated dissolution is produced at high values of equilibrium relative humidity (Table 2). Thenardite precipitation via dissolution varies slightly with

Table 3 Polynomial expression for critical relative humidities for different phase transitions

Eq.	Phase transition	Polynomial expression for critical relative humidity	Temperature interval (°C)
1	Mirabilite-thenardite	$\mathrm{RH_{Crit}}\ (\%) = 0.0028 \cdot T\ (°\mathrm{C})^2 + 0.7462 \cdot T\ (°\mathrm{C}) + 60.359$	0.0–32.2
2	Heptahydrate-thenardite	$\mathrm{RH_{Crit}}\ (\%) = 0.0008 \cdot T\ (°\mathrm{C})^2 + 0.8616 \cdot T\ (°\mathrm{C}) + 65.702$	0.0–23.8
3	Epsomite-hexahydrate	$\mathrm{RH_{Crit}}\ (\%) = 0.012 \cdot T\ (°\mathrm{C})^2 + 0.5132 \cdot T\ (°\mathrm{C}) + 31.331$	0.0–50
4	Hexahydrite-Starkeyite	$\mathrm{RH_{Crit}}\ (\%) = 0.0038 \cdot T\ (°\mathrm{C})^2 + 0.2647 \cdot T\ (°\mathrm{C}) + 32.13$	0–60
5	Hexahydrite-Kieserite	$\mathrm{RH_{Crit}}\ (\%) = 0.0029 \cdot T\ (°\mathrm{C})^2 + 0.4048 \cdot T\ (°\mathrm{C}) + 37.438$	20–60

All the polynomial fittings have a $R^2 > 0.999$

the temperature, whereas mirabilite precipitation can become important with decreasing temperature. Thenardite precipitation from solution occurs at $T > 32$ °C and varies slightly with temperature, although it does not produce damage. Espinosa-Marzal et al. (2011) proved experimentally that thenardite precipitates in the pores of a limestone causing the expansion of the stone, but no damage was found under the experimental conditions (where samples were impregnated with sodium sulphate solution and dried at 105 °C). Figure 2 shows the strong variation of the saturation index (Eq. 2) of mirabilite by modifying temperatures and solution concentration. Maximum stress is found when mirabilite precipitates under rapid decreases of temperature. Espinosa-Marzal and Scherer's (2008) experimental measurements showed defects induced in stone from mirabilite crystallisation by cooling to temperatures as low as 0 °C. Pressure crystallisation, using Correns' equation (Eq. (1)), is also plotted in Fig. 2 and illustrates that a fast decrease of temperature from 25 to 15 °C produces a crystallisation pressure of 10 MPa.

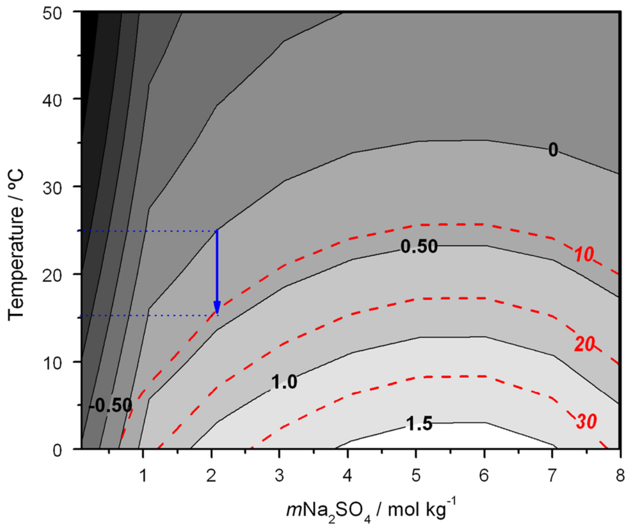

Fig. 2 Isolines of saturation index, ϕ, (*lines*) and crystallisation pressure, P_C (MPa) (*red dotted lines*) for mirabilite crystallisation. *Blue lines* illustrate how a rapid decrease of temperature of 10 °C produces a crystallisation pressure of 10 MPa

Damage by mirabilite precipitation from the pore solutions by decreasing temperature will be important during rainy periods. In these periods, the saturated solution remains for a long time in porosity and allows the dissolution–precipitation by temperature variations. This damage mechanism (pathway-I) will be therefore effective if stone is fully waterlogged with a saturated solution. However, in the built heritage, pores are generally only partially filled with brine, since it can dry and move through the wall by capillary action.

The dehydration process (pathway-III) frequently occurs under ambient conditions of temperature and relative humidity, but does not produce damage.

For temperatures below 32.2 °C, mirabilite hydration (pathway-IV) takes place through thenardite dissolution and mirabilite precipitation (Benavente et al. 1999; Rodríguez-Navarro et al. 2000; Linnow et al. 2006; Espinosa-Marzal et al. 2011; Schiro et al. 2012). These transformations are common and frequent in porous materials as a result of diurnal cycles in climate. Water, from rainfall and/or condensation, dissolves the powdered thenardite crystals and produces highly supersaturated solutions with respect to mirabilite. This precipitation pathway occurs when the phase boundary is crossed and can generate sufficient stress to damage the stone. The critical relative humidity, RH_{Crit}, for the thenardite–mirabilite phase transition can be defined from the equilibrium constants of mirabilite and thenardite (Eq. 5) and fitted through an analytical expression (Table 3). This analytical expression is nearly the same as used in our previous work (Benavente et al. 2008, 2011; Grossi et al. 2011).

Figure 1 shows some examples for mirabilite hydration by thenardite dissolution and mirabilite precipitation (pathway-IV). If the transition occurs at 23.3 °C, the mirabilite yields a stress of 10 MPa. This result is similar to Flatt (2002) who neglected the non-ideal behaviour for the crystallisation pressure calculations. Espinosa-Marzal et al. (2011) derived the crystallisation pressure in limestone from the measured stone deflection by thenardite

Table 4 Linear expression for crystallisation pressure for different mineral transitions salt systems is reflected in Table 4 and can provide a more specific critical temperature

Eq.	Phase transition	Temperature interval [°C] for calculations	Linear expression for crystallisation pressure in pure salt systems
1	Thenardite → mirabilite	0–32.2	$Pc\ (\mathrm{MPa}) = -1.1099\ T\ (^\circ\mathrm{C}) + 35.828$
2	Thenardite → heptahydrate	0–24.0	$Pc(\mathrm{MPa}) = -1.0183\ T\ (^\circ\mathrm{C}) + 24.273$
3	Hexahydrate → epsomite	5.3–49.3	$Pc\ (\mathrm{MPa}) = -0.3309\ T\ (^\circ\mathrm{C}) + 16.578$
4	Starkeyite → hexahydrite	10–45	$Pc(\mathrm{MPa}) = -0.2357\ T\ (^\circ\mathrm{C}) + 26.44$
5	Kieserite → hexahydrite	20–60	$Pc(\mathrm{MPa}) = -0.4348\ T\ (^\circ\mathrm{C}) + 40.374$
6	Thermonatrite → natron	0–25	$Pc\ (\mathrm{MPa}) = -0.7326\ T\ (^\circ\mathrm{C}) + 25.723$

All the polynomial fitting has a $R^2 > 0.999$

dissolution and mirabilite precipitation. This reaches values close to 13 MPa when mirabilite precipitation is produced at 21 °C. Figure 1 displays crystallisation pressures of 5, 10, 20 and 30 MPa for mirabilite precipitation temperatures of 27.8, 23.3, 14.3 and 5.3 °C, calculated using Eq. (1) of Table 4.

Precipitation of the metastable phase (heptahydrate) can also generate stress. As a result of its greater solubility compared to mirabilite, the supersaturation at a given concentration and the crystallisation pressure are significantly lower (Steiger and Asmussen 2008). Therefore, damage caused by growth of the heptahydrate is only expected at very low temperatures (Fig. 1). Crystallisation pressure can be calculated using Eq. (2) of Table 4. Thus, 5 and 10 MPa are reached for precipitation temperatures of 18.9 and 14.0 °C.

The critical relative humidity for the phase transition mirabilite-thenardite is not affected by the presence of other salt species, although the saturation of each mineral phase may be strongly modified. Thus, damage by salt weathering is less effective in multicomponent solutions as a result of decreasing water activity and ionic activity coefficients, which are included in the ion product (Cardell et al. 2008). This can be important in salty environments, such as coast areas or near the roadside through the presence of de-icing salts.

Figure 3 displays the influence of the presence of different ions in pore solution in pressure crystallisation by decreasing the temperature that crystallisation produces a given pressure. Results for mirabilite and heptahydrite are similar to Steiger and Asmussen (2008) who evaluated the crystallisation pressure in the standard test of salt crystallisation. For example, if the thenardite is dissolved in a pore solution that contains 1 mol kg^{-1} $MgCl_2$, the transition point that yields 10 MPa decreases by ~7 °C. This solution contains 0.095 g $MgCl_2$ + 0.384 g Na_2SO_4 per g H_2O and is, at 16.5 °C, supersaturated for mirabilite ($\phi = 0.3958$), saturated in thenardite and subsaturated for all the presented minerals [although close to saturation in bloedite—$Na_2Mg(SO_4)_2 \cdot 4H_2O$]. The 3 mol kg^{-1} NaCl solution, for instance, is composted of 0.175 g NaCl + 0.249 g Na_2SO_4 g^{-1} of H_2O. Such high concentrations sometimes have no practical relevance and may not exist for the most of the studied salts (Steiger et al. 2011a). The maximum concentration to be achieved by evaporation was ~0.8 g per g H_2O in levitated droplets (Tang 1997).

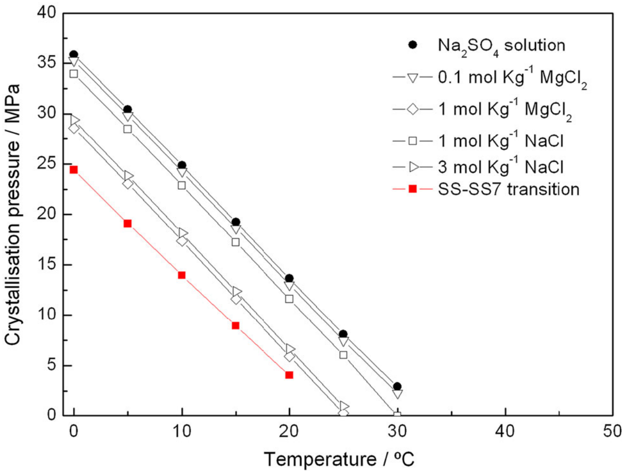

Fig. 3 Variation of crystallisation pressure of mirabilite precipitation after thenardite dissolution in the presence of other salt species ($MgCl_2$). Thernadite-mirabilite transition is compared to thernadite-heptahydrate (SS–SS7) precipitation in pure water

As mentioned above, the temperature which a saturated solution generates stress decreases by the presence of other salt species, although this does not modify the variation of crystallisation pressure with temperature. This ratio is equal to 1.1 MPa/°C for both pure and mixed sodium sulphate solutions. This strong variation of 1.1 MPa/°C makes sodium sulphate an aggressive salt when variations are produced in the temperature cycles. This large ratio indicates that the critical point in the salt crystallisation standard tests is the temperature of the solution in the immersion stage rather than drying stage.

The number of phase transitions can be used as a method for estimating potential salt damage (Price 1978; Benavente et al. 2008; Grossi et al. 2011). For the sodium sulphate system, it can be calculated by considering (1) the number of times the relative humidity crosses the critical relative humidity (Table 3) on two consecutive days, and (2) that thenardite would convert to mirabilite under conditions exerting a pressure greater than 10 MPa, i.e. for $T < 23$ °C for pure sodium sulphate solution. This value has been chosen because it usually exceeds the tensile strength of porous stone. The analytical expression for crystallisation pressure for salt systems is given in Table 4, and provides more specific critical temperature. This methodology was also considered for evaluating salt damage patterns in built heritage monuments by changes in microclimatic conditions in different seasons (Benavente et al. 2011).

The presence of other salts can enhance the dissolution of the host rock, mainly in the calcite fraction. As a result, the chemical pore saline changes in concentration and type of ions. Physical damage by salt weathering is less potent although new minerals can generate stress. For instance, if we consider that condensate and/or rain water dissolves the thenardite found in pores and calcite is also dissolved to achieve equilibrium with atmospheric CO_2, then the resulting solution is supersaturated in mirabilite and is slightly undersaturated in gypsum, which might precipitate after further evaporation (the PHREEQC input file of this example is shown in the "Appendix 1").

$MgSO_4$ system

The major naturally occurring hydrates in the $MgSO_4$-nH2O system are kieserite ($MgSO_4 \cdot H_2O$), hexahydrite ($MgSO_4 \cdot 6H_2O$) and epsomite ($MgSO_4 \cdot 7H_2O$). Other hydrates, pentahydrite ($MgSO_4 \cdot 5H_2O$) and starkeyite ($MgSO_4 \cdot 4H_2O$), exist but are less common. The formation and natural occurrence of lower hydrated forms with 2, 2.5 and 3 mol H_2O is less characteristic of porous stone.

Dissolution–recrystallisation cycles of epsomite and hexahydrite can be triggered by humidity cycling at very high RH and, more likely, by rainfall and subsequent drying. In addition, ambient relative humidity may regularly cross the epsomite–hexahydrite equilibrium curve. Formation of lower hydrated phases can only occur under dry conditions. In general, all dehydration processes have to be considered as potentially damaging, especially the rehydration of the lower hydrated phases under conditions of confinement within a porous material. These processes can produce substantial stress (Steiger et al. 2008). Several authors (Chipera and Vaniman 2007; Steiger et al. 2008; Wang et al. 2009) have shown that the tetrahydrate, starkeyite is much more easily formed than the apparent stable product kieserite by dehydration than either epsomite or hexahydrite. The formation of kieserite is not kinetically favoured, such that starkeyite is the major product of epsomite and hexahydrite dehydration at low and intermediate *RH*. A possible damage mechanism arises through the hydration of kieserite into hexahydrate in confined spaces as shown by Steiger et al. (2008) and fast drying (Balboni et al. 2011).

As discussed in the section above, precipitation of hydrated salts in the $MgSO_4$ system is sensitive to both temperature and relative humidity. Salt precipitation can occur through different pathways (Fig. 4) and the estimated damage depends on the pathway. The precipitation from a saturated dissolution mainly produces epsomite (pathway-I), since hexahydrite requires higher temperature values (pathway-II). Precipitation of epsomite and hexahydrite depends only slightly on temperature, by comparison with mirabilite precipitation and needs a decrease in temperature and/or evaporation (Fig. 4). It is difficult to obtain kieserite by direct crystallisation from solution (von Hodenberg and Kühn 1967) and it is only formed at high temperature and low relative humidity (Steiger et al. 2011b).

Figure 5 shows the variation of the saturation index of epsomite as a function of temperature and solution concentration. Maximum stress is found when epsomite precipitates under fast decreases of temperature (example 1) and also evaporation (example 2 for an isothermal evaporation and 3 for thermal evaporation). Pressure

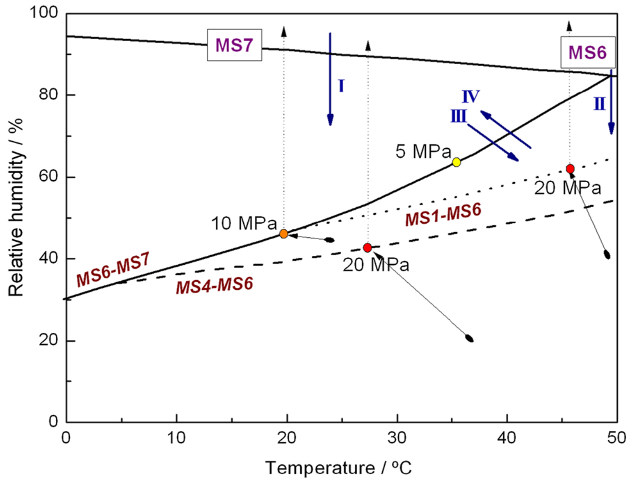

Fig. 4 Phase diagram of magnesium sulphate system: *MS7* epsomite ($MgSO_4 \cdot 7H_2O$); *MS6* hexahydrite ($MgSO_4 \cdot 6H_2O$); *MS4* starkeyite ($MgSO_4 \cdot 4H_2O$) and *MS1* kieserite ($MgSO_4 \cdot H_2O$). Pathways-I and II correspond to epsomite and hexahydrite precipitations from a saturated dissolution (deliquescence humidity). Pathway-III displays epsomite dehydration and pathway-IV describes epsomite hydration after hexahydrite dissolution. Critical hydration–dehydration humidity for MS6–MS7, MS4–MS6 is also displayed MS1–MS6. *Yellow*, *orange* and *red* points correspond, respectively, to a crystallisation pressure of 5, 10 and 20 MPa

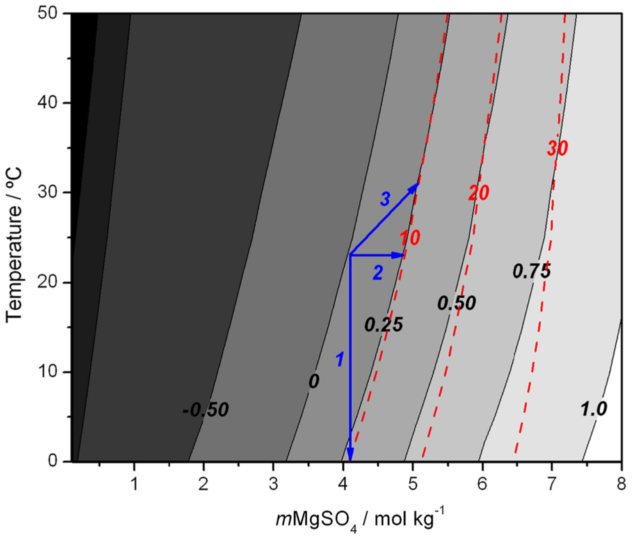

Fig. 5 Isolines of saturation index, ϕ, (*lines*) and crystallisation pressure, P_C (MPa) (*red dotted lines*) for epsomite crystallisation. *Blue lines* illustrate how a fast decrease of temperature (*1*), isothermal (*2*) and thermal (*3*) evaporation produces a crystallisation pressure of 10 MPa

crystallisation, using Correns' equation (Eq. 1), is also plotted in Fig. 5 and shows how a crystallisation pressure of 10 MPa can be reached.

The dehydration process (pathway-III) occurs frequently under typical climatic conditions, but does not produce damage. Epsomite hydration takes place through hexahydrite dissolution and epsomite precipitation (Lopez-Arce et al. 2008; Balboni et al. 2011; Steiger et al. 2011b), which is common in porous materials due to diurnal climate cycles. The transition from hexahydrite to epsomite that yields 10 MPa occurs at 19.9 °C and is not affected by the presence of other salts. Crystallisation pressure can be calculated using Eq. (3) of Table 1. Figure 4 also shows crystallisation pressures of 1 and 5 MPa that correspond to 35 and 44.1 °C, respectively.

Although the critical relative humidity for phase transitions is not greatly influenced by the presence of other salt species, the saturation of each mineral phase may be strongly modified. As explained for the Na_2SO_4 system, damage by salt weathering is less aggressive in multicomponent solutions. Figure 6 displays the temperature at which a saturated solution generates decreased stress in the presence of other salt species. The ratio 0.4 MPa/°C is not modified by the presence of salt species and is ~1/3 the ratio for Na_2SO_4 system. For example, if the hexahydrite is dissolved in a pore solution that contains 3 mol kg^{-1} NaCl decreases the transition that yields 10 MPa by ~2 °C. The resulting multicomponent solution is slightly saturated in bloedite and for temperatures below of 10 °C, solution is supersaturated in mirabilite.

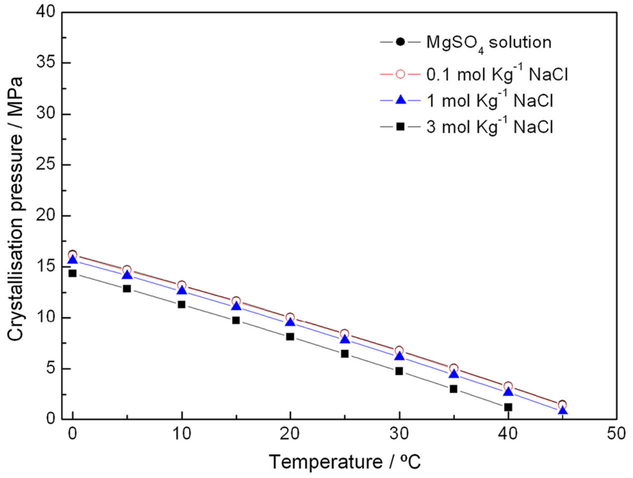

Fig. 6 Variation of crystallisation pressure of epsomite precipitation after hexahidrite dissolution in the presence of other salt species (NaCl)

In extreme dry and hot climates, such as those expected in some areas in a future southern Europe (Brimblecombe 2010; Grossi et al. 2011) or in building stones that are exposed to direct solar radiation, the dissolution of kieserite, or the metastable phase starkeyite, and hexahydrite crystallisation could result in very high stresses. Pressure crystallisation expressions for these transitions are shown in Eqs. (4) and (5) of Table 4. Moreover, Fig. 4 also displays the climatic conditions under which this important stress is produced.

The methodology for estimating potential salt damage from the sodium magnesium system can be calculated by considering (1) the number of times the relative humidity crosses the critical relative humidity (Table 3) on two consecutive days, and (2) that hexahydrite would convert to epsomite under conditions exerting a pressure greater than 10 MPa, i.e. for $T < 49.3$ °C for pure sodium sulphate solution (Table 4). If extreme dry and hot climates are considered, other transitions should be evaluated, such as kieserite → hexahydrite and starkeyite → hexahydrite (see Table 3 for the critical relative humidity transitions).

NaCl system

This system presents two stable mineral phases: halite (NaCl) and hydrohalite ($NaCl{\cdot}2H_2O$). The later crystallises below 0 °C and its effect in built deterioration has been not considered since ice crystallisation tends to be the most important decay mechanism. Halite is a common salt in monuments and is mainly related to sea-salt aerosols and de-icing salts (Arnold and Zehnder 1990; Steiger et al. 2011a).

Halite can crystallise only when the ambient relative humidity is lower than 75.3 %, the equilibrium relative

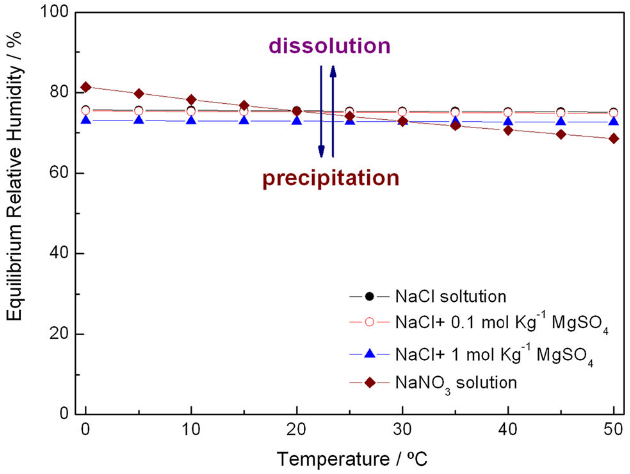

Fig. 7 Unhydrated salts such as halite andnitratite crystallise at a fixed humidity that is nearly independent of temperature and the presence of other salt species

humidity of the saturated salt solution (Table 2). This relative humidity is nearly independent of both temperature (Fig. 7), and the influence of other salt species is slight. Other non-hydrated salts present similar behaviour, including other chlorides (silvite-KCl) and nitrates (niter-KNO_3 or natrite-$NaNO_3$).

Halite has been observed to crystallise readily and not reach high supersaturation ratios before crystallising in porous materials (Rodríguez-Navarro and Doehne 1999), which explains the low level of physical damage by halite in the built heritage. In most of the saline crusts found in the built heritage, halite is presented as cubic crystal aggregates that result from halite precipitation at low supersaturation (Sunagawa 1981). Eswaran et al. (1980) also observed halite as cubic crystal aggregates in most saline crust in soils, reporting that hair-like or acicular halite crystals appeared only where the evaporation rates were extremely high. Therefore, it can be hypothesised (Wely 1959) that under the low supersaturation ratios halite crystals cannot generate enough pressure to produce the breakdown of the stone, and crystal growth should stop or else pressure-induced dissolution would take place.

Several authors consider that halite damage is linked to thermal expansion rather than salt crystallisation. Thus, Scherer et al. (2001) point out that if the pores of a stone become filled with halite, the mismatch in the coefficient of thermal expansion, α, can be destructive, for example, $\alpha = 42$ ppm/ °C for sodium chloride and from 4 to 12 ppm/ °C for the most of stone. Given that the thermal stress is roughly equal to the product $E \cdot \Delta\alpha \cdot \Delta T$, where the elastic modulus is $E \sim 35$ GPa, and the thermal expansion mismatch between stone and salt is $\Delta\alpha \sim 30$ ppm/ °C. This is about 1 MPa per degree change in temperature, so the change in temperature from day to night could generate stress exceeding the tensile strength of stone (<10 MPa), if the pores were full of salt. The methodology for estimating potential salt damage in the sodium chloride system can be calculated by counting the number of times the relative humidity crossed the critical relative humidity (Table 2) on consecutive days.

High supersaturation ratios require a modified methodology for estimating salt damage, so Benavente et al. (2011) considered that the difference between the critical relative humidity and the equilibrium relative humidity is equal to 10 %. Thus, transitions for NaCl were estimated by considering the number of times the relative humidity crossed the critical relative humidity of 65.3 % on two consecutive days. This assumes that evaporation is important.

Na_2CO_3 system

The Na_2CO_3–H_2O system is similar to the Na_2SO_4–H_2O system although it has not often been studied in salt decay literature in as much detail. Sodium carbonate presents two stables mineral phases: natron ($Na_2CO_3 \cdot 10H_2O$) and thermonatrite ($Na_2CO_3 \cdot H_2O$). Geologically, natron is formed when salt lakes rich in sodium carbonate dry up. Here, the alkalinity of the lake is so high, that little bicarbonate is present in solution. In most cases, the mineral natron will form together with some amount of nahcolite (sodium bicarbonate). Otherwise, the minerals trona or thermonatrite and nahcolite are commonly formed (Libowitzky and Giester 2003). These salts are less common in monuments than other salts, so relative few studies are found in the literature (Steiger et al. 2011a).

In the sodium sulphate and carbonate systems, the dissolution of the lower hydrate and the precipitation of the hydrated salt leads to high crystallisation pressures (Table 4). As commented above, the temperature at which a saturated solution generates stress decreases in the presence of other salt species. Thus, the addition of a solution 1 mol kg^{-1} $MgCl_2$ decreases the transition point that yields 10 MPa by ~ 8 °C. The resulting multicomponent solution is supersaturated in natron, and also in brucite, magnesite and nesquehonite in the temperature interval of 0-25 °C. The variation of crystallisation pressure with temperature is equal to 0.9 MPa/ °C for both pure and mixed sodium carbonate solutions, which explains the aggressive character of these salts.

$CaSO_4$ system

Charola et al. (2007) reviewed calcium sulphate and its role in the deterioration of building materials. The deterioration of buildings and monuments by gypsum is the result of crystallisation cycles of this salt. Although gypsum can dehydrate to a hemihydrate (bassanite) and an anhydrate (anhydrite), in nature this reaction occurs slowly, sometimes on a geological time scale, so is unlikely to occur in building materials. Thus, the deterioration caused by gypsum in building stones cannot be attributed to hydration pressures. As in the case of any other non-hydrating salt, it is a result of its crystallisation pressure within the pores. However, given its low solubility, it is not as aggressive as other, more soluble salts such as sodium and magnesium sulphate. The little damage that is produced by gypsum is generated during the growth of gypsum crystals and is less significant than that caused by other, more soluble salts. Gypsum, once deposited in the pore space of a building material, tends to continue accumulating over time, causing aesthetic rather than physical damage. For that reason, we did not estimate stone damage by thermodynamic transition events, as discussed below for the sodium sulphate and chloride salts.

Limitations of the methodology

This work represents a first attempt to calculate salt damage on buildings that results from variations in climate. In this section, we consider the main limitations to the approach and the areas that need further research. The proposed methodology itself presents some limitations as enumerated below:

1. The Pitzer's database does not include for instance nitrates, which are quite often present in building materials. Therefore, some work should be carried out into extend the database to other ions.
2. It does not consider the mineral fractionation (ions of precipitates salt are no retired from solution), as the most programmes occur.
3. The most important limitations of the calculations are the rate of the salt crystallisation and the internal structure and fluid transfer properties of the building stones. In general, porous stone is particularly susceptible to salt decay, and this susceptibility is related to the petrophysical properties on the material: a pore structure permits salt crystallisation stress, capillary rise of solutions and water adsorption and condensation, and results in a very low mechanical strength (Benavente et al. 2004a).
4. The kinetics of the phase transitions may be crucial in determining the magnitude of damage. The salts studied here respond rapidly to changes in ambient humidity and/or temperature (Benavente et al. 1999; Linnow et al. 2006; Espinosa-Marzal and Scherer 2008, 2010; Zehnder and Schoch 2009), so thermodynamics calculation can be used to predict salt crystallisation. In fact, the kinetics of salt precipitation from saturated solutions can be calculated using PHREEQC, if the rate law is known. This is easy to compute due to well-know relation between kinetic and thermodynamic (IAP/*K* ratio) (Lasaga 1998). For instance, the dissolution rate of thenardite and the crystallisation of mirabilite strongly influences each other. A fast crystallisation of mirabilite accelerates the dissolution of thenardite, since the solution quickly becomes significantly undersaturated with respect to thenardite. The mechanism precipitation of mirabilite can be effective in 2–3 h (Espinosa-Marzal and Scherer 2008, 2013). Schiro et al. (2012) showed that the coupled dissolution–precipitation of heptahydrate-mirabilite can also account for significant damage to the porous substrate. This competitive process should consider the rate of dissolution of both metastable and stable phases and interaction salt-pore surface in the precipitation. For instance, calcite enhances nucleation of heptahydrate compared to quartz minerals, so it can be expected that nucleation of the heptahydrate in calcite-stone requires lower supersaturation for nucleation than sandstone (Saidov et al. 2012). The kinetics of crystallisation depends also on the critical supersaturation required for nucleation. These nuclei cannot generate pressure, as they are not yet confined. Salt growth into pore space and against pore wall consumes supersaturation that our calculations do not consider.
5. Kinetics of salt damage may be slower than the precipitation kinetics of salt from the solution. More research is needed to improve the understanding of crystallisation kinetics inside porous materials in terms of each crystallisation mechanisms, e.g. Na_2SO_4 decay by dissolution–crystallisation of thenardite must include the presence of water inside of stone (rain and capillary waters or condensate water) to properly describe the temperature and relative humidity initiating the transition.
6. Capillary flux of the solution from the wet surface towards the interior during uptake of water can occur during rain or capillary transport. Porous building stone usually presents entry pores in the range 0.01–100 μm and a connected porosity higher than 10 %. As a consequence, the capillary transport through the stone is important and is reflected by high values of capillary imbibition coefficients of stones (for standard stones 10–100 g m^{-2} $s^{-0.5}$). For example, in stone with a porosity equal to 15 % and coefficient of 50 g m^{-2} $s^{-0.5}$, water can penetrate 1-cm depth (enough to produce subflorescences) in ∼15 min (for 2 cm, 1 h).
7. Solution transport can reduce by the pore clogging with salt crystals that enhances the tortuosity of the diffusion path (Espinosa-Marzal and Scherer 2013).

Moreover, salts in pores cause a reduction of the volume, which hinders solution transport, a phenomenon called *pore clogging*. Espinosa-Marzal and Scherer (2013) indicated that materials with small pores are more prone to *pore clogging* and the kind of salts can dominate over the pore structure. In case of magnesium sulphate, the resistance to flow is related to the formation of a dense layer of epsomite crystals at the liquid–vapour interface that impedes further drying (as well as subsequent capillary uptake) in materials with different pore size distributions. Mirabilite dehydrates more readily than magnesium salts, which allows partially reopening of blocked pores.

8. The exact point at which the phase transitions occur within the stone pores has yet to be well established, because the relationship between the humidity within pores and that external environment is not yet understood. Neither is the rate of change of this internal humidity. This process depends on the cycles of relative humidity and on the pore fraction active to water condensation. For a porous material at relative humidity values lower than 100 %, water is firstly adsorbed on the pore surface and subsequently condenses. This is particularly important in pores of radius <0.1 μm, where the Kelvin effect dominates. This is intensified by the presence of saline solutions, because water activity decreases and, therefore, the saturated vapour pressure decreases. Moreover, the presence of salt crystals in pores enhances water condensation since they are deliquescent and decrease the effective pore radius. For example, Franzen and Mirwald (2009) measured the moisture uptake of the salt-bearing sandstone material and Lubelli et al. (2004) studied salt-contaminated bricks. They found higher levels of water adsorption in samples with different salts. The results showed that the amount of adsorbed water depends on the chemical composition of the salt mixture and the salt phase precipitated. Air and stone temperatures are also responsible to water condensation; triggered when the partial pressure of vapour in the air exceeds the vapour pressure at the temperature of the rock surface or at the temperature of the water film previously condensed on the rock surface (such a thin-water film will quickly reach thermal equilibrium with the rock surface) (Fernández-Cortes et al. 2013).

The temperature transmission from air to inside of the stone, vapour and water transport through the material, the role of evaporation rate of pore solutions at low humidity and the phase transitions inside of materials should be quantified and included in a kinetic description of the process.

Conclusions

This work examines the crystallisation mechanisms that generate stress in porous building stone from changes in the ambient environment. These mechanisms include the salt crystallisation from decreasing relative humidity and changes in temperature and, in hydrated salts, the dissolution of the lower hydrated form and the subsequent precipitation of the hydrated salt. The crystallisation pressure calculations represent the upper limits of salt damage.

Results for hydrated salt systems show that high crystallisation pressures are possible as lower hydrated salts dissolve and more hydrated salts precipitate. High stresses may be also produced from decreasing temperature, although it requires that porous materials are wet for longer periods of time. Sodium sulphate is a more aggressive salt system relative to the magnesium sulphate and sodium carbonate systems. This is reflected in the variation of pressure crystallisation by temperature, where a ratio of 1.1 MPa/°C is found for mirabilite, whereas epsomite and natron are 0.4 and 0.9 MPa/°C, respectively. Salt damage arising from a solution of a single salt is greater than multicomponent solutions for given thermohygrometric conditions. The presence of other salts changes the temperature and relative humidity of salt transitions that generates stress rather than reduces the pressure of crystallisation, if any salt has previously precipitated. Therefore, the methodology quantifies the effect of other salts on salt crystallisation and predicts the precipitation sequence from multicomponent solutions.

The use of PHREEQC for the thermodynamic calculations of the potential for salt damage offers understanding stone durability relevant to conservation. This approach estimates the equilibrium relative humidity and parameterizes critical relative humidity and crystallisation pressures for dissolution–precipitation transitions. The influence of other salts on salt crystallisation and chemical weathering can be assessed.

In a practical sense, the thermodynamic approach to salt crystallisation mechanisms gives conservators and architects detailed information on the potential weathering activity of soluble salts. We quantify the stress generated in likely crystallisation processes in monuments. Both indoors and outdoors environments undergo daily cycles of temperature and humidity, forced by either the solar cycle or by heating, ventilating and air-conditioning systems. Practical recommendations derive from the proposed methodology and contribute to the control of microclimate conditions to minimise salt damage, mainly indoors and at archaeological hypogean sites, strategies for ventilation, lighting, heating or air-conditioning and desalination treatments. This methodology estimates likely salt damage potential in heritage by changes in microclimatic conditions after building renovation.

It will also allow particularly harmful humidity regimes to be explored. Furthermore, the models might be coupled with projections of future climate to give as improved understanding of the likely changes in the frequency of phase transitions in salts.

Future work might well address the way in which temperature is transmitted from the external environment to the stone interior, vapour and water transport through the material, the role of evaporation rate of pore solutions at low humidity. Phase transitions inside of materials should be quantified along with a kinetic description of the process.

Acknowledgments This study was carried out in the framework of the research projects CGL2011-25162 (Spanish Ministry of Science and Innovation) and IJP 2006/R2 (the Royal Society Joint Project).

Appendix 1: PHREEQC input files calculations

PHREEQC is used for calculating a variety of reactions and processes in natural waters and laboratory experiments. A full description of many alternatives for input and the mathematical background can be found in the manual of the programme by Parkhurst and Appelo (1999, 2013), Appelo and Postman (2005) and at the link: http://www.xs4all.nl/~appt/.

The aim of this Appendix is to show how the calculations were carried out (for the PHREEQC users) and to present this widely used geochemical code to the researchers in the heritage conservation as a new tool to model salt weathering. Of course, there are other ways to structure the input file for modelling salt crystallisation. Here, we try to build up the input an easy and intuitive way. The number of calculations can be increased using the REACTION keyword, by adding or removing chemical, minerals or water; and REACTION_TEMPERATURE, which changing the temperature of the solution. Results can be delivered in a spreadsheet-type format (e.g. EXCEL) using the keyword SELECTED_OUTPUT keyword.

Calculation of pressure crystallisation by dissolution of the lower hydrated form and the precipitation of the hydrated salt

Examples of these transitions are thenardite (Na_2SO_4) → mirabilite ($Na_2SO_4 \cdot 10H_2O$); thenardite (Na_2SO_4) → heptahydrite ($Na_2SO_4 \cdot 7H_2O$); hexahydrite ($MgSO_4 \cdot 6H_2O$) → epsomite ($MgSO_4 \cdot 7H_2O$) and are recorded in Table 4. This calculation considers that water dissolves the lower hydrated form until equilibrium is reached ($\phi = 0$). The resulting solution is then supersaturated in the hydrated salt at a given temperature. The temperature interval in which hydrated phase is more stable than lower hydrated form is reported in Tables 4.

PHREEQC calculates the saturation index and pressure crystallisation using the Current's equation (Eq. 1). This thermodynamic calculation can be carried out considering the following:

Dissolution–precipitation in pure water

This calculation only considers the simple transformation by dissolution–precipitation at a given temperature or changing the temperature of solution using the REACTION_TEMPERATURE keyword. For example, the dissolution of thenardite and mirabilite precipitation at 20 °C can be calculated as:

```
SOLUTION
temp 20
EQUILIBRIUM_PHASES
thenardite
END
```

The output of this simple calculation provides interesting results: composition of solution (or pore water); pH; ionic conductivity (evaluation ionic diffusion); density (necessary to fluid transport studies); ionic strength; distribution of species and the saturation index. The resulting solution is saturated in mirabilite and heptahydrite. Using the Corren's equation (Eq. 1), crystallisation pressure of mirabilite precipitation after thenardite dissolution at 20 °C is then estimated as follows:

$$P_c = \frac{RT \cdot \ln 10}{v_c} \phi = \frac{8.3145 \cdot (20 + 273.15) \cdot \ln 10}{220} 0.53 = 13.56\,\mathrm{MPa}. \quad \text{(A1)}$$

The calculation at different temperatures through the REACTION_TEMPERATURE keyword can be preformed using the following input file:

```
SOLUTION
EQUILIBRIUM_PHASES
thenardite
REACTION_TEMPERATURE
0 5 10 15 20 25 30
SELECTED_OUTPUT
-reset false
-file mirabilite_precipitation_T.xls
-saturation_indices mirabilite heptahydrite thenardite
-temperature
END
```

This example calculates the saturation index of mirabilite at 7 temperatures from 0 to 30 °C at constant intervals. This keyword also permits the user to specify temperatures or as steps, as done below. In this example, we calculate the equilibrium from 0 to 30 °C in 7 steps (0 30 in 7 steps).

The output file contains a large quantity of results. PHREEQC can select some of parameters using the SELECTED_OUPUT keyword in a text or EXCEL file. These parameters include the saturation index, pH, activities, temperature, etc. In the previous example, the excel file contains the saturation index for mirabilite, heptahydrite and thenardite and solution temperature.

Pressure crystallisation is calculated using Corren's equation, the saturation index and a fitted linear function of temperature. Table 4 gives linear expressions for different mineral transitions using the our methodology.

Presence of other salts

The presence of other salts is a common situation buildings. Their influence on mineral transitions and the crystallisation pressure is easy to be evaluated using PHREEQC. The chemical composition of solution is changed, in isothermal conditions, using a given chemical composition of solution or through REACTION keyword. For example, the presence of 1 mol Kg^{-1} NaCl in the hexahydrite → epsomite transition at 20 °C can be computed as follows:

```
_
SOLUTION
temp 20
units mol/kgw
Na 1
Cl 1
EQUILIBRIUM_PHASES
hexahydrite
END
_
```

The input file for calculating this transition by adding 0, 0.1, 0.5, 1, 3, 4 and 5 mol of NaCl at 20 °C presents the following structure:

```
_
SOLUTION
temp    20.0
EQUILIBRIUM_PHASES
hexahydrite
REACTION
NaCl
0.0 0.1 0.5 1 3 4 5
SELECTED_OUTPUT
-reset false
-file   influence_NaCl_epsomite_hexahydrite.xls
-temperature
-molalities Cl-
-saturation_indices epsomite hexahydrite halite mirabilite
END
_
```

In this example, the EXCEL output file contains temperature, Cl^- concentration and the saturation index of epsomite, hexahydrite, halite and mirabilite, although a widely options can be selected for the user at the SELECTED_OUTPUT data block. The presence of other ions in solution generates a multicomponent saline solution and, consequently, other minerals can precipitate and generate stress. Figures 3 and 6 are produced using this method.

Chemical dissolution of the host rock

The dissolution of calcite in the presence of saline solutions increases the concentration of calcium and bicarbonate–carbonate ions. As commented in the previous section, the presence of ions can precipitate other minerals. The input file might include the following information:

```
_
SOLUTION
temp 20
EQUILIBRIUM_PHASES 1
thenardite
calcite
CO2(g) -3.5
END
_
```

This example displays the mirabilite precipitation after thenardite dissolution at 20 °C. As the equilibrium is imposed (thermodynamic approach), thenardite dissolves in pure water with the rock-forming calcite in equilibrium with the atmospheric CO_2 (open system). The resulting solution is supersaturated in mirabilite and is slightly substantiated in gypsum, which might precipitate after some evaporation.

Precipitation from the solution

Equilibrium or deliquescence relative humidity

The equilibrium or deliquescence relative humidity, RH_{eq}, of a salt is the relative humidity in which crystallises in an aqueous solution and varies with the temperature and by the presence of other ions in the solution. RH_{eq} can be obtained by calculating water activity as described above. The input file is similar to other described in "Appendix 1." Water activity is displayed in the "description of solution" in the output file. For example, RH_{eq} for halite at 20 °C can be calculated using the following input file:

```
_
SOLUTION; temp 20; EQUILIBRIUM_PHASES; halite; END
_
```

In this example, halite solubility is 6.088 mol kg^{-1} and the activity of water is 0.755 and therefore $RH_{eq} = 75.5\ \%$. The influence of temperature and other ions can be evaluated using the previous input file or through the REACTION_TEMPERATURE or REACTION keywords. For example:

```
_
SOLUTION
EQUILIBRIUM_PHASES
halite
REACTION_TEMPERATURE
0 60 in 13 steps
SELECTED_OUTPUT
-reset false
-file RH_equilibrium.xls
-activities H2O
-temperature
END
_
```

The EXCEL file contains the log a_w for temperatures in the range of 0–60 °C.

Mineral precipitation by varying temperature and/or concentration

At high values of equilibrium relative humidity (higher than RH_{eq}) salts can also be precipitated from an aqueous solution by decreasing the temperature.

Mineral precipitation from a saturated solution is produced by decreasing temperatures and/or increase concentration. This pathway can be carried out through a simple speciation by calculating a multiple of speciation. A simple speciation includes the chemical composition and temperature of the solution as follows:

```
_
SOLUTION
temp 20
units mol/kgw
Mg 4
S(6) 4
END
_
```

This example calculates the saturation index of minerals of $MgSO_4$ system (epsomite; hexahydrite; Kieserite; Pentahydrite and Starkeyite) in a 4 mol kg^{-1} $MgSO_4$ solution at 20 °C. Pressure crystallisation is calculated using Eq. (1).

However, multiple calculations are recommended since a multiple set of saturation indexes (and crystallisation pressures) are obtained. Moreover, the mineral stability zones can be graphically displayed as in Figs. 2 and 5. The input file requires either the REACTION_TEMPERATURE or REACTION keywords in order to save time in the calculation. Thus, the REACTION_TEMPERATURE keyword is used for an each concentration as follows:

```
_
SOLUTION
temp 20
units mol/kgw
Mg 4
S(6) 4
REACTION_TEMPERATURE
0 60 in 13 steps
SELECTED_OUTPUT
-reset false
-file precip_solution_m.xls
-saturation_indices epsomite hexahydrite
-temperature
END
_
```

whereas the REACTION keyword is considered for each temperature:

```
_
SOLUTION
temp    20.0
REACTION
MgSO4
0.0 0.1 0.5 1 5
SELECTED_OUTPUT
-reset false
-file precip_solution_T.xls
-saturation_indices epsomite hexahydrite
-temperature
END
_
```

Saturation index each mineral is obtained and pressure crystallisation is calculated using Eq. (1).

Precipitation from saline pore water

The analysis of chemical composition of soluble salts within stones is a frequent procedure for conservators and architects. Salt analysis permits to estimate the theoretical mineral precipitation sequence, which has not been considered in the present paper. We here include a sort reference that can illustrate this interesting task.

A simple speciation can be carried out defining the chemical composition, pH and temperature of solution. Calculation of the saturation indexes of minerals provides a good idea of the precipitation sequence that may occur in the stone.

This approach can be improved by the simulation of evaporation, which is accomplished by removing water from the chemical system. Thus, water can be removed by an irreversible reactant with a negative reaction coefficient in the REACTION keyword input. An interesting example that can illustrate this simulation is accessed in the User's Guide to PHREEQC:

http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc.v1/html/phqc_55.html.

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