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ORIGINAL ARTICLE

Evaluating the influence of mixture composition on the kinetics of salt damage in wall paintings using time lapse video imaging with direct data annotation

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Abstract This paper presents an examination of the timescale of phase transition behaviour of a series of salts known to cause damage to wall paintings and other cultural property. The rate of deliquescence and crystallisation of single salts (nitromagnesite and halite) under different RH regimes, and the extent to which this was affected when mixed with other salts (niter, nitratite and gypsum), was investigated. The study was conducted using simple conventional techniques (mass measurements over time) and also using an innovative new method: timelapse video imaging with online data annotation. The results demonstrate the synergy gained from combining video imaging with environmental data in reference to time in the study of salt phase changes: where it revealed new information concerning the kinetics of deliquescence and crystallisation. The implications of these results for the implementation of environmental control measures within historic buildings are discussed.

Keywords Salt damage · Wall paintings · Kinetics · Timelapse video imaging · Environmental control

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Introduction

Soluble salts are a major cause of damage to wall paintings and other porous materials, but their complex behaviour remains insufficiently understood. Among the variables that affect the nature of the deterioration and the possibilities for passive environmental control are the kinetics of phase changes and the influence of salt mixtures on this behaviour. Although there are phase diagrams to predict the behaviour of mixed salt systems, there is a paucity of information available on the kinetics of phase changes. By using time-lapse video imaging—to visibly accelerate motion—it was possible to record these dynamic processes in combination with thermohygrometric data to provide critical information for the characterisation and potential control of these mechanisms. This study is the result of two complementary research projects, the experimental parameters for the salts set by Sawdy (1995) and those for the imaging by Heritage (1995).

Wall paintings and architectural polychromy are particularly susceptible to salt damage. This susceptibility arises from their inherent fragility and location at the interface between the external environment of the building and he internal environment of the wall. Thus the comparatively thin paint layers and their immediate support are the primary site both of evaporation and salt accumulation, and also moisture sorption which in turn mobilises salts as aqueous ions (see Fig. 1). Although this problem is extreme for wall paintings it is also common, and of key importance, for the preservation of a vast range of cultural property. The damage caused by soluble salts is often so severe that remedial measures are required, of which

Fig. 1 **a** Monasterio de San Jerónimo, Granada. Interior view of Church (Capilla del lateral Izquierdo del Crucero). **b** Monasterio de San Jerónimo, Granada. Detail showing salt damage to stonework and wall paintings within church interior

the isolation of the supply of soluble salts to the object is a desirable component. However, this is not always achievable, nor will it necessarily ensure the cessation of deterioration, since those soluble salts that are already present may be activated by their environment. Consequently, in the treatment of this condition there are currently three principal approaches, the choice of which is primarily dependant on the object's material composition and condition, and the salt type, phase (i.e. whether in solid or aqueous solution), and distribution. These treatment methods are: mechanical removal; aqueous extraction typically by poulticing or rarely by electro-osmosis; and conversion (in the case of sulfation, whereby gypsum is converted to calcite and barium carbonate using the so-called 'barium method') (Matteini 1991). Current research into the potential use of crystallisation inhibitors is also underway, in the form of the EU FP6 project 'Saltcontrol' (Prevention of salt damage to the built cultural heritage by the use of crystallisation inhibitors (Saltcontrol) EU FP6 programme priority 8.1B, 3.6, project number SSP1-CT-2003-501571).

However, there are many problems associated with these methods, particularly since salt deteriorated objects are typically very friable and do not readily lend themselves to treatment, during the course of which the risk of causing further mechanical damage is great. Moreover, the use of water as an extraction medium brings with it potential risks, such as the re-distribution of salts and the activation of salt damage processes. Another major problem facing the treatment of monumental objects such as wall paintings, unlike smaller objects where is may be possible to carry out treatment via partial or total immersion, is that current treatments are primarily efficient only at the object's surface, and may not produce any significant effect at depth. In view of these problems, the obvious, and most desirable, alternative to remedial treatment is passive intervention as a preventative measure. To this end, for interior wall paintings and architectural polychromy, environmental control has been proposed as a means to avoid salt damage by limiting the building climate to ranges of relative humidity (RH%) and ambient temperature (T °C) under which phase transitions do not take place (Arnold and Zehnder 1991). The achievement of this stability requires the selection and maintenance of a suitable environment, but determining appropriate ranges for environmental parameters is fraught with difficulties. Much valuable work has been undertaken in recent years in the area of 'environment selection', notable contributions being the work of Price, Brimblecomb, Clegg and Steiger, and the development of the ECOS programme (Price and Brimblecombe 1994; Steiger 1994, 1996a, b, 2003; Steiger et al. 2000; Price 2000; Sawdy and Price 2005). However, such models relate to the ideal case of salt behaviour in bulk solutions, and as such do not necessarily overcome the problems associated with the alteration of salt and moisture behaviour within porous media, and the effects of salt mixture fractionation, and solution supersaturation.

Nevertheless, assuming the appropriate thermohygrometic ranges can be identified, the question of maintaining these conditions remains to be answered. To control the microclimate to within a narrow range may not be feasible in many cases, particularly in respect to historic buildings. Significant and potentially expensive alterations may be required to control the environment: and this may not be considered desirable given the building usage and/or the extent of alterations required. It is therefore imperative to determine

the level of control needed to have an appreciable benefit. In this regard, knowledge of the kinetics of salt phase transitions is clearly of crucial importance. The rate at which a transformation takes place is an important factor governing whether it will occur under specific conditions. For instance, an object contaminated with sodium chloride may be considered at risk of damage if the RH falls below 75%. However, were the RH to drop to 70% for 30 min would damage take place? Or is a significantly longer time (and/or a much lower RH) needed—in which case the requirements for environmental control are much less stringent. It is clear then, that the timescale of salt phase transitions, and the factors that may alter this timescale have to be adequately determined in order to ensure that the level of environmental control that is feasible within historic buildings is in fact effective.

At present, the evidence from phenomenological studies in situ regarding the rate of salt phase transitions is somewhat conflicting: for example, the alteration of efflorescences to an aqueous solution (and vice versa) has been recorded as occurring on a seasonal basis (Arnold and Zehnder 1991; Laue 1996), while other observations show the occurrence of daily cycles of crystallisation and hydration state change (Arnold and Küng 1985). Indeed, in laboratory experiments salt deliquescence has been shown to take place well within this time period (Piqué et al. 1992). This highlights a particular problem hampering in situ studies: the monitoring carried out is intermittent, and therefore the perception of the rate of phase changes is dependant on the time interval of observation, the level of magnification possible on site, and whether the phase transitions are occurring at an exposed surface. Events of partial dissolution or crystallisation may therefore go unnoticed.

Experimental

The aims of the study were to assess the kinetics of crystallisation and deliquescence of a range of salts known to cause damage to wall paintings and other cultural property; and to determine the extent to which this behaviour is moderated in the presence of other salts. The principal experimental variables were (a) RH, and (b) the composition of simple two-salt mixtures. Other factors which could also exert an influence on the rate of phase transitions, such as temperature, air movement, and variation in salt surface area (crystal size and morphology), and the type of phase transition occurring (i.e. crystallisation or hydration state change) were kept constant. Consequently, the experiments were run at a constant temperature of 20 ± 3°C (maintained by means of air conditioning in the laboratory), and the salt crystals were sieved to obtain uniform crystal size. Moreover, care was taken to choose salts that did not undergo hydration state change under the experimental conditions selected, in order to restrict the study to transformations around a single phase boundary for each salt.

The salts selected for the study—nitromagnesite ($Mg(NO_3)_2{\cdot}6H_2O$), halite (NaCl), nitratite ($NaNO_3$), niter (KNO_3) and gypsum ($CaSO_4 2H_2O$)—are representative of those known to cause damage to wall paintings, and cover a wide range of solubilities and equilibrium relative humidities (RHeq). See Table 1 Gypsum was included in this study, although due to its sparingly soluble nature it is not generally considered to be a deliquescent salt. Nevertheless, given the increase in gypsum solubility when in the presence of other salts, and the extensive damage caused by this salt, it was considered worthy of inclusion.

Table 1 Solubility and vapour pressure data of salts selected for study

Name	Formula	Solubility (g/100 g solution) at 25°C[a]	Solubility (moles/l solution) at 25°C	Water vapour pressure over saturated solution at 25°C (RHeq)[b]
Nitromagnesite	$Mg(NO_3)_2{\cdot}6H_2O$	42.5	2.87	52.9
Halite	NaCl	26.43	4.52	75.3
Nitratite	$NaNO_3$	47.8	5.62	74.3
Niter	KNO_3	27.5	2.72	93.6
Gypsum	$CaSO_4{\cdot}2H_2O$	0.208	1.29×10^{-3}	99.96

Although the experiments were conducted at 20 ± 3°C, the values presented here are for systems at 25°C, due to availability of published data at this temperature. Nevertheless, despite this slight temperature difference, the values given are sufficiently representative of the range of solubilities and RHeqs of the salts used under the experimental conditions

[a] From Linke 1958

[b] The data for gypsum is from Price and Brimblecombe 1994, all others from Arnold and Zehnder 1991

Table 2 Salt combinations and experimental RH levels

Mixture composition			Experimental regime		
Primary salt (A)	Secondary salt (B)	Mixture compositions (A:B by weight)	Exposure RH (based on RHeq of salt A at 20°C)		Salts undergoing deliquescence
Nitromagnesite ($Mg(NO_3)_2{\cdot}6H_2O$)	Halite (NaCl)		RHeq-10%	45	
	Nitratite ($NaNO_3$)	A alone	RHeq-5%	50	
	Niter (KNO_3)	2:1	Rheq	55	A
	Gypsum ($CaSO_4{\cdot}2H_2O$)	4:1	RHeq + 5%	60	A
			RHeq + 10%	65	A
Halite (NaCl)	Nitromagnesite ($Mg(NO_3)_2{\cdot}6H_2O$)		RHeq-10%	66	
		A alone	RHeq-5%	71	
	Nitratite ($NaNO_3$)	2:1	RHeq	76	A + nitratite
	Niter (KNO_3)	4:1	RHeq + 5%	81	A + nitratite
	Gypsum ($CaSO_4{\cdot}2H_2O$)		RHeq + 10 %	86	A + nitratite

Methodology

The loss and uptake of moisture by salts and the associated alterations in their appearance were first monitored by mass measurements, and then subsequently using timelapse video imaging with online data annotation. By these techniques, the kinetics of deliquescence and crystallisation of different salt mixture combinations were observed with respect to time and RH change.

Mass measurements: experimental conditions

To assess the influence of the difference between the ambient RH and the RHeq of the salt, the following RH regimes were selected:

- RH = RHeq;
- RH = RHeq + 5% RH;
- RH = RHeq + 10% RH;
- RH = Rheq–5% RH;
- RH = Rheq–10% RH.

Given that niter and gypsum both have RHeq values of over 90%, the experimental design was arranged to follow the moisture sorption and desorption behaviour of halite and nitromagnesite, with the other salts used as secondary salts to combine with these.

Consequently, the rate of moisture adsorption (due to deliquescence) and desorption (due to evaporation) were monitored for the following salt combinations:

- Nitromagnesite ($Mg(NO_3)_2{\cdot}6H_2O$) + second salts (halite; niter; gypsum);
- Halite (NaCl) + second salts (nitratite; niter; gypsum).

Since the differential between the RHeqs for all of these salt combinations apart from halite–nitratite is greater than 10% RH, it was possible to observe the influence of the presence of a second salt without interference due to its deliquescence. This could then be compared to the behaviour of the individual salts, and also to the instance of halite–nitratite combinations where both salts are deliquescing (see Table 2).

Deliquescence

The sample mass of the primary salts was kept constant at 16 g, and the secondary salts added in either of two combinations—1:2 and 1:4 (secondary:primary) by weight. The crystalline salts (previously stored at RH values well below their RHeq) were sieved and weighed to correct proportions, mixed and placed in non-porous glass supports of identical shape and size. The samples were then placed in an environmental chamber conditioned to the correct RH and temperature relevant to each experimental run.[1] Quantitative monitoring was undertaken by recording the mass change of the salt combinations (using a Sartorius toploader LC1200 balance sensitive to 0.001 g placed within the environmental chamber) at 15 min intervals over a 2 h period. By the end of the experiment all samples had undergone some degree of deliquescence, but none of the salts had completely dissolved.

[1] The RH within the climate chamber was controlled using a micro climate technology (MCT) generator (model: 92MCG. TC), and MCG Monitoring Software via a laptop. The climate chamber had its own humidity sensor, however the RH and T data recorded was acquired from a higher quality Vaisala HMP233 transmitter.

Crystallisation

The desorption experiments were conducted on saturated salt solutions (i.e. in the case of the salt mixtures, the solution was saturated with respect to both salts). This was achieved by using the partially deliquesced samples from the previous experiments, which had been conditioned at RH > RHeq of the primary salt, such that the samples had a continuous film of saturated solution over the solid salts. In the case of the salt mixtures, care was taken that neither of the salts completely dissolved, so that the solutions remained saturated with respect to both salts. The sample holder size was kept constant, and thereby also the surface area for evaporation. By the end of the experiment all samples had undergone some degree of re-crystallisation, but none of the solutions had evaporated completely.

Timelapse experiments

Following the experiments described above, a further series of adsorption and desorption experiments were undertaken, this time qualitatively monitored using timelapse video imaging with online data annotation. During these timelapse experiments, the visual alteration of the salts due to deliquescence and crystallisation was recorded together with the RH and temperature conditions of exposure.[2] For the purposes of the timelapse video recording, a four chamber sample holder was constructed to allow simultaneous monitoring of four different salt combinations, and hence direct comparison between the behaviour of the single salt, and that of the mixtures. The temperature during these experiments was again maintained constant, but was slightly higher (averaging around 23°C) than previously by virtue of the laboratory air conditioning. Following each experiment, the re-crystallised salt mixtures were examined using polarising light microscopy, to confirm the identity of the salt species present.

Deliquescence and crystallisation cycles were recorded for:

- Nitromagnesite ($Mg(NO_3)_2{\cdot}6H_2O$) + second salts (niter; halite; nitratite);
- Halite (NaCl) + second salts (niter; nitratite; gypsum).

Deliquescence

The deliquescence experiments were undertaken using dry crystalline salts. The sample preparation for these experiments differed slightly from those of the mass measurements study, in that the salt mixtures were made up in equimolar proportions. Each salt was sieved to a uniform grain size, and the mixtures were ground gently in a pestle and mortar to ensure even mixing. The same mass of each mixture (4 g) was then placed in separate sample chambers, and the surface smoothed. As a preliminary to the deliquescence experiments, the RH in the chamber was initially set to just below the RHeq of the primary salt (Rheq-5% RH). This was maintained for a number of hours to determine whether any alteration of the salt mixtures occurred. Following this, the RH was then raised to levels above the RHeq of the primary salt, and the deliquescence behaviour monitored.

Crystallisation

Following the deliquescence of the salt mixtures (apart from the halite–gypsum combination, in which the gypsum did not completely dissolve), the RH in the chamber was then lowered to below the RHeq of the primary salt, and the evaporation and crystallisation of the salt solutions was monitored.

One of the principal advantages offered by the timelapse experiments was that it was possible to record the behaviour of different salt combinations simultaneously. Thus, while these experiments did not exactly replicate the mass measurements experiments, nevertheless, they provided very useful complimentary information regarding the variation in behaviour of the salt systems under study.

The timelapse video imaging system was developed by Heritage for this study and other research, and is described in Heritage 1995, 1999 and Rodríguez Navarro and Doehne 1999. Two principal aims of the study were to assess the potential of using time-lapse video imaging to record dynamic processes in conservation, and to superimpose data—numerical and text information—on to video images in real-time to allow process monitoring. This method of direct annotation accomplished during the capture process is desirable because it directly synchronises the image and data

[2] While it would have been optimal to undertake the mass measurement and timelapse experiments simultaneously, this was not possible as the mass measurements necessitated the movement of samples on and off the balance, hence precluding the possibility for timelapse imaging. Moreover, the timelapse experiments were able to provide different, but complimentary information through the use of a four chamber sample holder, which allowed simultaneous imaging of four different combinations of salt, thus providing direct visual comparison between the behaviour of each.

components, providing a crucial time reference[3] (see Figs. 2–4).

Results

The results of the experiments recorded using mass measurements are summarised in Fig. 5–6.[4]

In general, it can be seen that all samples underwent some degree of deliquescence and crystallisation during the 2 h period, however, the extent to which this took place was strongly dependent on the conditions of exposure (RH), and also the salt mixture composition. Once the deliquescence of one salt species commenced (and so a solution was present), the rate of moisture uptake and loss was seen to vary between the different sample mixtures.

Deliquescence

It is clear that the presence of a second salt affected the rate of deliquescence, though the relative humidity at which the primary salt began to deliquesce did not appear to be altered.[5]

This observation can be explained as the result of a combined deliquescence–dissolution process: the deliquescence of one salt providing an aqueous solution into which the other can then dissolve. While the presence of two salts sharing a common ion may experience a mutual decrease in solubility, nevertheless, the overall ionic concentration of the resulting solution is increased. Since the reduction of the solution vapour pressure below that of pure water is a colligative property dependent on the number of salt ions present, it therefore follows that higher ion concentrations lower the vapour pressure of the solution to a greater extent. The magnitude of this effect can be predicted using the ECOS programme, but was demonstrated empirically during this study by measuring the RH over the saturated mixed salt solutions (saturated with respect to both salts), all of which had a lower vapour pressure than the RHeq of the component salts—some more so than others (see Table 3). Consequently, the difference between the ambient RH and the solution RHeq was greater for the mixed salt solutions than for the single salts. The experimental results indicate that this increase in RH interval had a marked influence on the rate of deliquescence, causing a corresponding rise in the rate of moisture uptake by the salt mixture.

[3] The time lapse system comprised of an Infinivar™ Video Inspection Microscope attached to a Sony DX–930 video camera. Build around a multitasking Apple Macintosh computer, the system was required to automate procedures and fulfil the technical requirement of obtaining images at time intervals and mixing computer video with computer graphics. Thereby, adding to the captured images the environmental and time data that was simultaneously being received. Hardware included a Truevision NuVista + framegrabber for digitisation and overlaying graphics and video. Software for data acquisition, manipulation, and presentation included the following: ZTerm (a communication software for modems. It runs in the background and was used to log data readings to file independently of LabVIEW); LabVIEW for Macintosh (National Instruments) using VIs (Virtual Instruments: these software-created modules can be assembled to perform the same operations as physical instruments) for direct processing of the data; O'Clock (to provide an analogue clock face). Software for macro programming: Quickeys. Software for VCR and digital capture control: Video Online; Animaq. The Sony UVW-1800 Betacam edit/recorder was a compromise at the time in lieu of an affordable, practical digital solution. Nonetheless, together with the animation controller board it was capable of sequential recording of single or multiple frames, and frame-accurate retrieval and editing. The Sony UVW-1800 was computer-controlled via an RS-422 9-pin interface by the DiaQuest DQ-Animaq edit controller board and software. The NuVista + board handled all video imaging aspects, while LabVIEW's role was to run in the background, updating data in real-time or at regulated intervals on to a computer graphics display. Precise live video overlay with computer graphics is only possible using genlock circuitry. Therefore the camera, VTR controller, frame buffer card, transcoder, VTR, and monitors need to be driven (or regulated) from a single source of sync.

[4] During the mass measurement experiments it was found that while the rate of moisture uptake and loss of the samples differed dependent on the salt mixture composition, nevertheless, this rate did not vary throughout the course of the 2 h monitoring period (i.e. all plots of adsorption and desorption over time were linear). Consequently, the results of these experiments are presented here in terms of the total moisture exchange that took place over 2 h.

[5] The results for the behaviour of the salts at the RHeq of the primary salt (see Figs. 5, 6) do indicate that some degree of adsorption takes place. However, the accuracy of RH control within the chamber was ±2.5% RH, and so this slight degree of moisture uptake could be attributed to temporary and slight fluctuations of RH above the RHeq, and therefore cannot be conclusively attributed to deliquescence behaviour below the RHeq. Indeed, it is important to note that in the case of the salt mixtures here described, once deliquescence has started the mixed salt solution formed will have a lower RHeq than that of the pure salt. Consequently, moisture uptake may proceed even if the RH once again falls below the RHeq of the single salt. As a preliminary to the timelapse experiments, the salt mixtures were held at RH values close to, but slightly below the RHeq of the primary salt (RHeq–5% RH). For the nitromagnesite mixtures, some slight degree of moisture deliquescence was observed for the nitromagnesite–halite combination after a period of about three and half hours. However, again, this might have been to temporary RH fluctuations above the RHeq of nitromagnesite. For the halite mixtures, no apparent deliquescence was observed. Consequently, the evidence indicates that deliquescence commences only when the RHeq of the primary salt is exceeded—albeit temporarily.

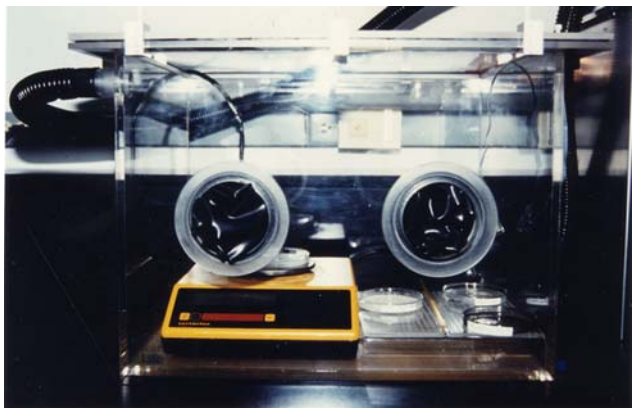

Fig. 2 Equipment set-up for monitoring salt moisture sorption by mass measurements. Detail showing environmental chamber (with controlled RH air supply), mass balance and salt samples

Fig. 3 Timelapse video imaging system

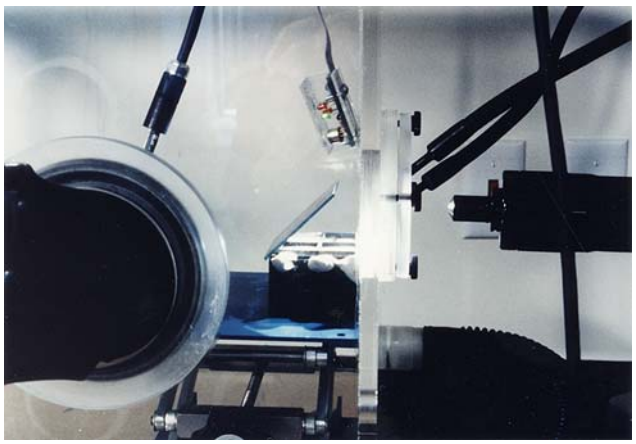

Fig. 4 Detail of Fig. 3 showing four chambered sample holder, environmental monitoring sensors (RH and temperature), and microscope

Crystallisation

It appeared from the experimental results that in comparison to single salt solutions, those formed by the salt mixtures had a reduced rate of moisture loss. Again, this may be explained by the reduction in solution vapour pressure due to the presence of additional salts. Consequently, under the conditions for evaporation, the interval between the ambient RH and the solution vapour pressure is reduced, and as such the rate of moisture loss is less.

The degree to which additional salts affect the rate of moisture sorption and desorption is thus clearly related to the RHeq of the mixed salt solution. Indeed, on closer inspection of the results given in Fig. 5, it can be seen that the rate of moisture uptake and loss of nitromagnesite is most strongly affected by the presence of halite, but that the presence of niter and nitratite produce a much smaller effect. This reflects the degree to which the RHeq is reduced by the presence of these salts: halite–nitromagnesite mixture having a RHeq of around 35% RH, in comparison to the nitromagnesite–niter and nitromagnesite–nitratite combinations which both have a RHeq of about 52%RH. A similar pattern of behaviour can be observed for the halite (see Fig. 6), such that the rate of moisture uptake and loss is most strongly affected by the presence of nitratite (RHeq halite–nitratite = 67% RH), followed by niter (RHeq halite–niter = 68% RH), while almost no effect is observed for the presence of gypsum (RHeq halite–gypsum = 75% RH) (see Table 3).

Timelapse video imaging

The benefits afforded by imaging multiple samples mixtures simultaneously allowing comparative visual interpretation are evident. The recordings made using the timelapse video imaging system proved extremely informative: clarifying the order in which the phase transitions of the four sample mixtures progressed, and also providing a dramatic visualisation of their relative rates of deliquescence/dissolution and crystallisation. This technique was therefore both illustrative and illuminating, since it was possible, for example, to determine the actual onset and rate of crystallisation (see Figs. 7–10).

For the nitromagnesite combinations, it was observed that the deliquescence of the nitromagnesite–halite commenced first, while the other mixtures all started to deliquesce at about the same time, some 10 h later. Conversely during the desorption experiment, nitromagnesite was the first salt of this series to start to re-crystallise (after approximately 1 h at RH < RHeq

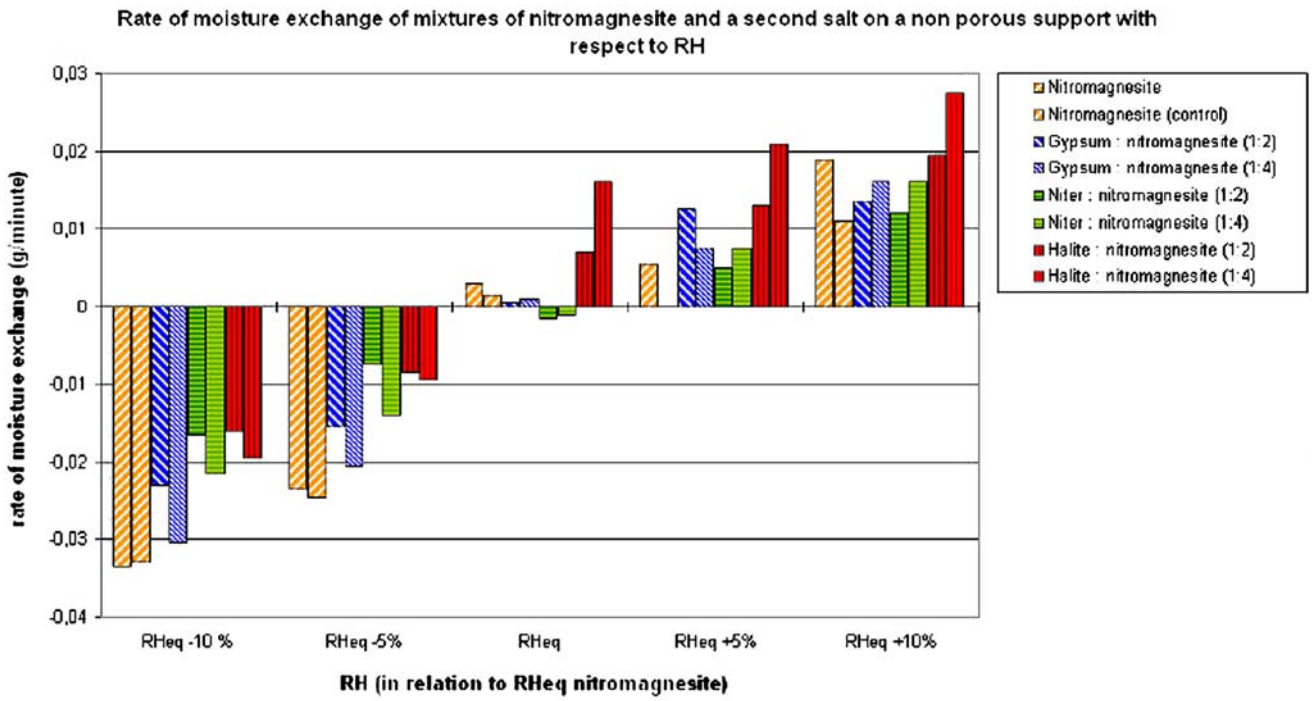

Fig. 5 Moisture sorption of nitromagnesite with and without additional salts

nitromagnesite); followed by nitromagnesite–niter (at 4 h), then nitromagesite–nitratite (at 5 h), while the nitromagnesite–halite combination remained in solution throughout (the ambient RH being 40%, while the RHeq of saturated solution of nitromagnesite–halite is 35%).

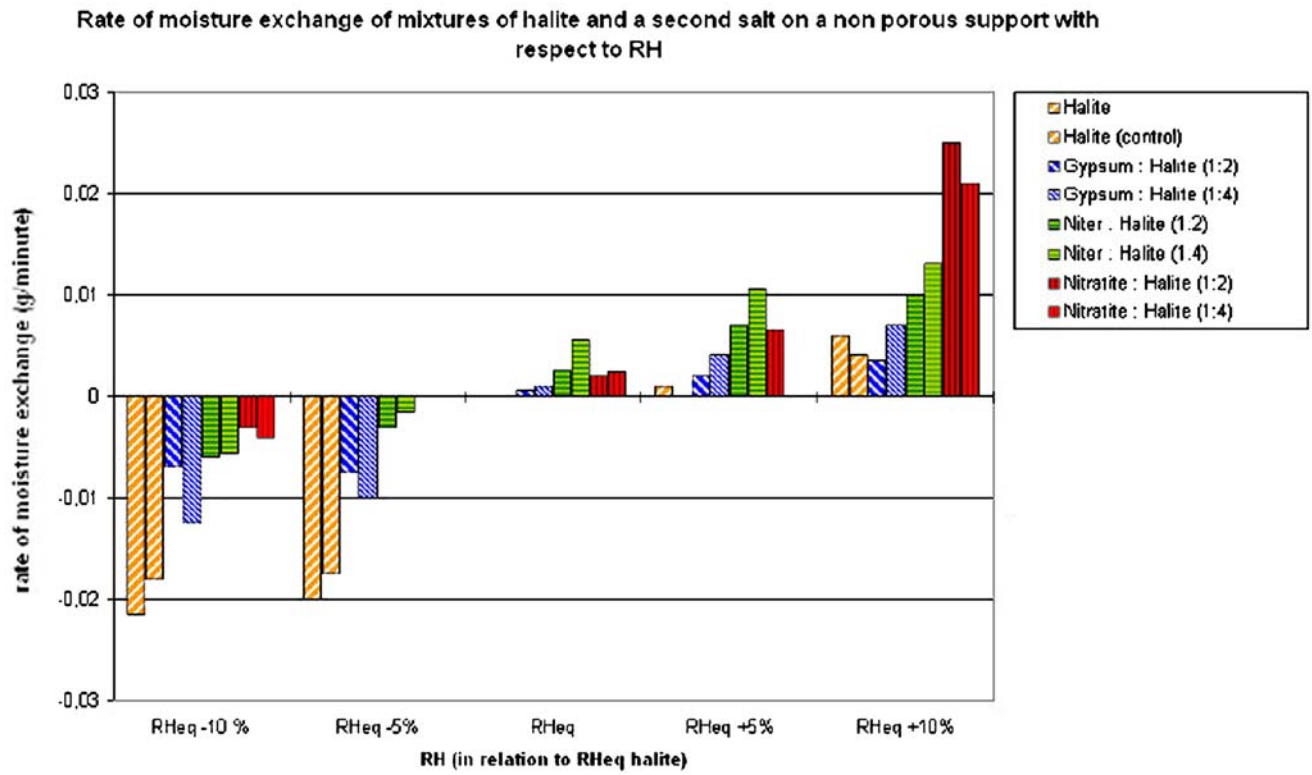

Fig. 6 Moisture sorption of halite with and without additional salts

Table 3 RHeq (measured and calculated) for solutions saturated with respect to two salts in comparison to single salts

Solid salts present	RHeq measured at 20°C (%RH)	RHeq at 20°C calculated using ECOS (%RH)	Reduction in vapour pressure due to presence of second salt (%RH) calculated using ECOS values
Halite	75	75	
Halite + gypsum	77	75	0
Halite + niter	70	68	7
Halite + nitratite	68	67	8
Nitromagnesite	55	56	
Nitromagnesite + nitratite	52	52	4
Nitromagnesite + niter	52	53	3
Nitromagnesite + halite	34	35	21

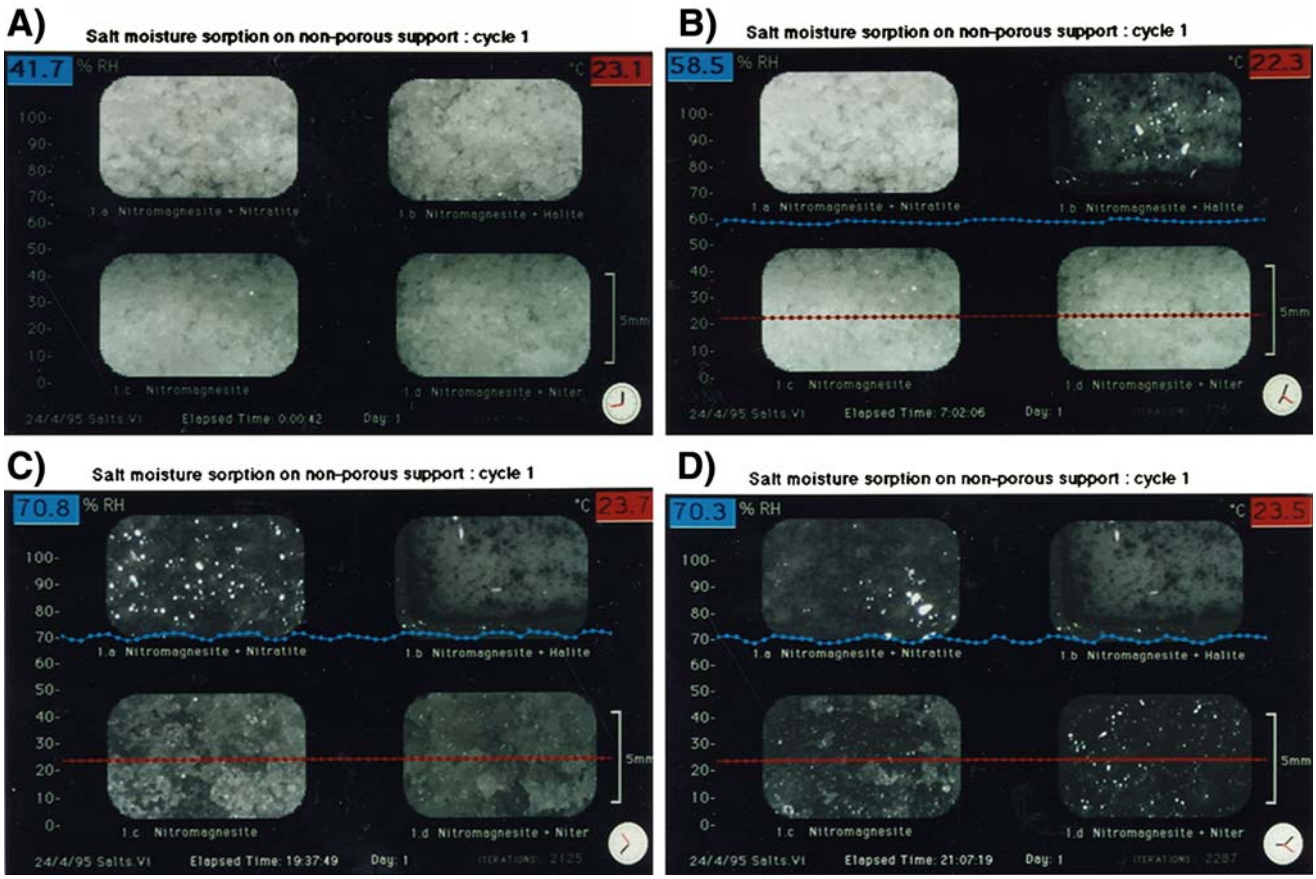

Fig. 7 Timelapse video recordings of moisture uptake by nitromagnesite (with and without additional salts). **a** At start of experiment, **b** after 30 min exposure above the RHeq of nitromagnesite at 60 ± 2% RH (7 h from the beginning of the experiment): the nitromagnesite–halite sample has begun to show signs of moisture uptake, **c** after 13 h exposure at RH > RHeq of nitromagnesite: dissolution of the nitromagnesite–halite sample is well progressed, that of the nitromagnesite–nitratite has commenced, while the other samples are only just beginning to deliquesce, **d** after fourteen and a half hours exposure at RH > RHeq of nitromagnesite: solution is visible in all four samples. It can be seen in this video series that the deliquescence and dissolution of the nitromagnesite–halite mixture takes place much more rapidly than the other samples. The sequence in which solution formation is observed is as follows: *1* nitromagnesite–halite, *2* nitromagnesite–nitratite, *3* nitromagnesite–niter and *4* nitromagnesite

For the halite combinations, the deliquescence of the halite–nitratite and halite–niter mixtures starts at about the same time (after approximately seven and a half hours of exposure at RH > RHeq), well ahead of halite and the halite–gypsum mixture (some 10 h later). The reverse sequence is then observed during the evaporation experiment, during which halite and the halite–gypsum mixture are the first to show signs of crystallisation (after five and a half hours at RH < RHeq halite), followed by the halite–niter

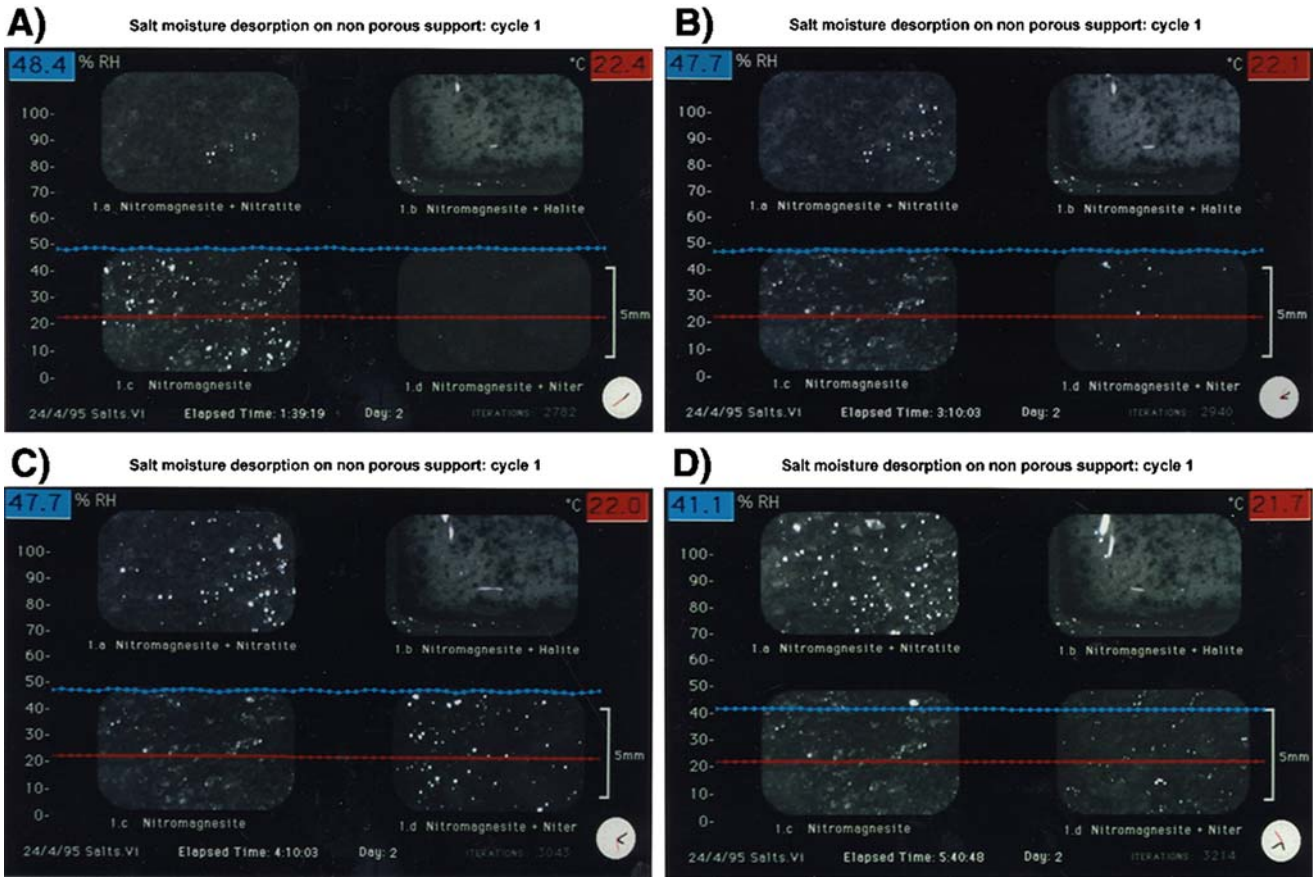

Fig. 8 Timelapse video recordings of evaporation by nitromagnesite solutions (with and without additional salts). **a** After 45 min exposure at RH < RHeq of nitromagnesite: sample has started to crystallise, **b** after 2 h and 15 min at RH < RHeq of nitromagnesite: the nitromagnesite–nitratite sample has started to crystallise, **c** after 3 h and 15 min at RH < RHeq of nitromagnesite: crystallisation has commenced in all samples except the nitromagnesite–halite, **d** after four and a half hours at RH < RHeq of nitromagnesite: the nitromagnesite–halite sample still shows no sign of crystallisation. In this video series it can be seen that the sequence of crystallisation for the samples is the reverse of their dissolution: *1* nitromagnesite, *2* nitromagnesite–niter, *3* nitromagnesite–nitratite (nitromagnesite–halite remains in solution)

combination (at 7 h), and finally the halite–nitratite mixture (at 9 h).

Conclusions

The results of this study demonstrate that the composition of a salt mixture has a significant effect on the kinetics of the deliquescence and crystallisation behaviour of its components. This is most likely due to the lower vapour pressure of a mixed salt solution, in comparison to that of single salts. The most salient consequences of these observations were:

- in general the rate of deliquescence/dissolution of the salt mixtures increased;
- deliquescence only began when the RH was above the lowest individual RHeq of the salts in the mixture;
- the rate of evaporation from mixed salt solutions was reduced, thus delaying the onset of crystallisation.

The implication of these results for the deterioration of wall paintings and other cultural property affected by soluble salts is that generally, the presence of additional salts promotes the formation of an aqueous solution. This effect is achieved both thermodynamically (the lower vapour pressure of the mixed salt solution thus extending the range of RH under which the salts are in the aqueous phase) and also kinetically (by increasing the rate at which moisture sorption takes place, and reducing the rate of moisture desorption). Consequently, when more than one salt is present (as is most typically the case) and the climate fluctuates around the RHeqs of the individual salts present; it is more likely that the salts will form a saline solution than if only one salt were present. For

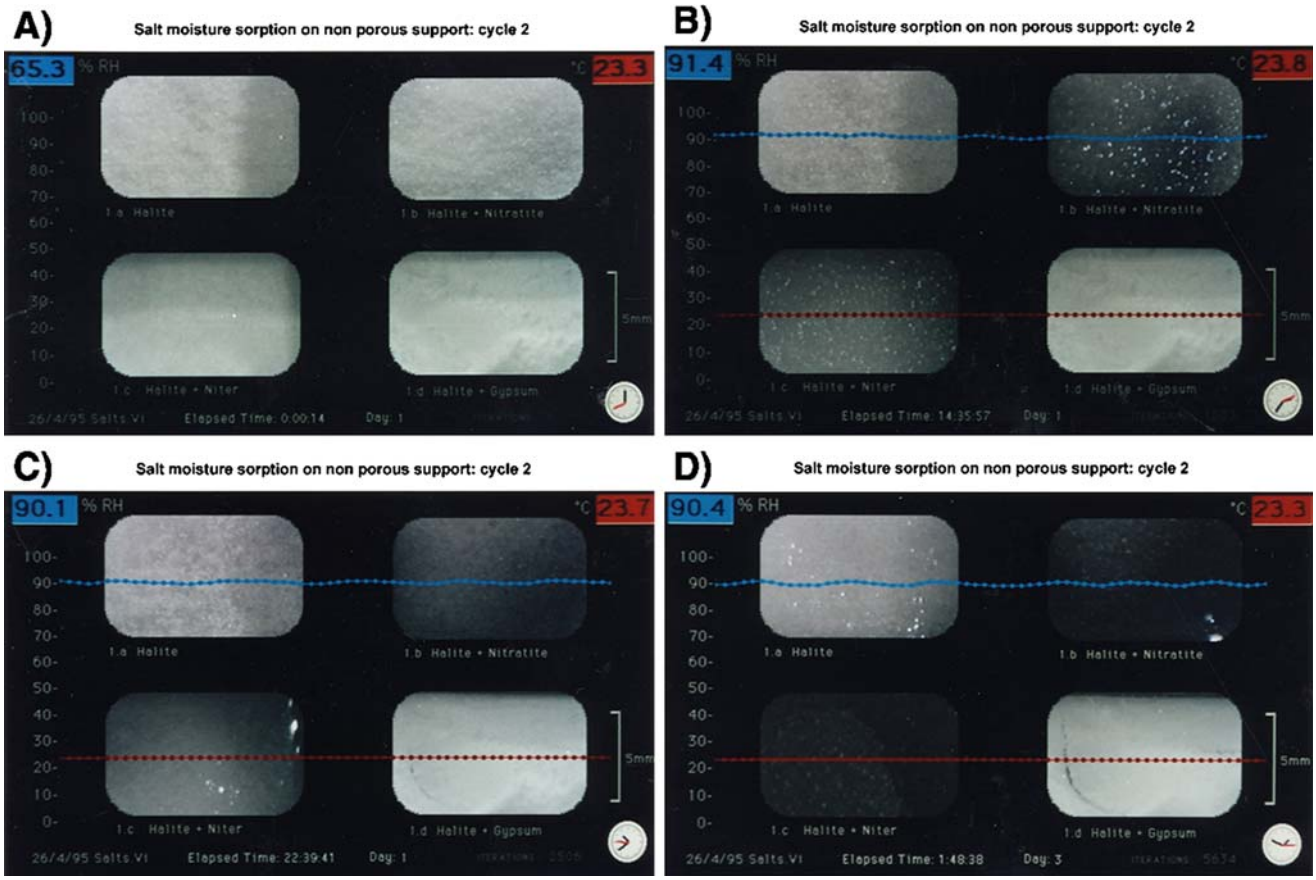

Fig. 9 Timelapse video recordings of moisture uptake by halite (with and without additional salts). **a** At the start of the experiment, **b** after 9 h at RH > RHeq of halite (fourteen and a half hours from the beginning of the experiment): the halite–nitratite and halite–niter samples have started to deliquesce, **c** after 17 h at RH > RHeq of halite: the halite sample is just beginning to appear damp, **d** after 44 h at RH > RHeq of halite: aqueous solution is visible in all four samples. In this video series the sequence in which solution formation is observed is as follows: *1* halite–nitratite, *2* halite–niter, *3* halite–gypsum and halite

crystalline salt mixtures, deliquescence may occur rapidly if the RH rises temporarily above the lowest RHeq of the salts present. However, should the RH subsequently fall to a similar degree below the RHeq for an equivalent time period, a reciprocal crystallisation may not necessarily result.

The influence of the degree of RH change was particularly notable: the results indicate that short but large swings in RH can have a greater impact than longer but smaller RH shifts. In particular, a 10% RH alteration from the RHeq was seen to produce phase transitions within hours.

These experiments were conducted on nonporous supports, however it is certain that the porous support itself will also exert a significant effect on salt phase transition behaviour. Indeed, recent NMR studies have demonstrated that salt solution solubility is potentially strongly affected by pore size: such that within microporous regions, the solubility of sodium carbonate solutions is enhanced (Rijniers 2004). This, combined with the incidence of capillary condensation, infers that the promotion of salt solution formation observed during the current study is likely to be further enhanced within porous media. Furthermore, other research has demonstrated the role of the porous support and other factors including temperature and air movement as significant factors in determining the rate of moisture sorption by salts (Sawdy 2003).

In general, therefore, it can be surmised that in a northern European context, if environmental control is to be implemented, given the normal ambient conditions in historic buildings (i.e. there are periods when the RH rises to levels greater than 70%) and the types of salts typically found, it may be somewhat more feasible to maintain the salts as an aqueous solution than in their crystalline state. This however has clear implications should the object suffer from other types of moisture-related damage such as biodeterioration.

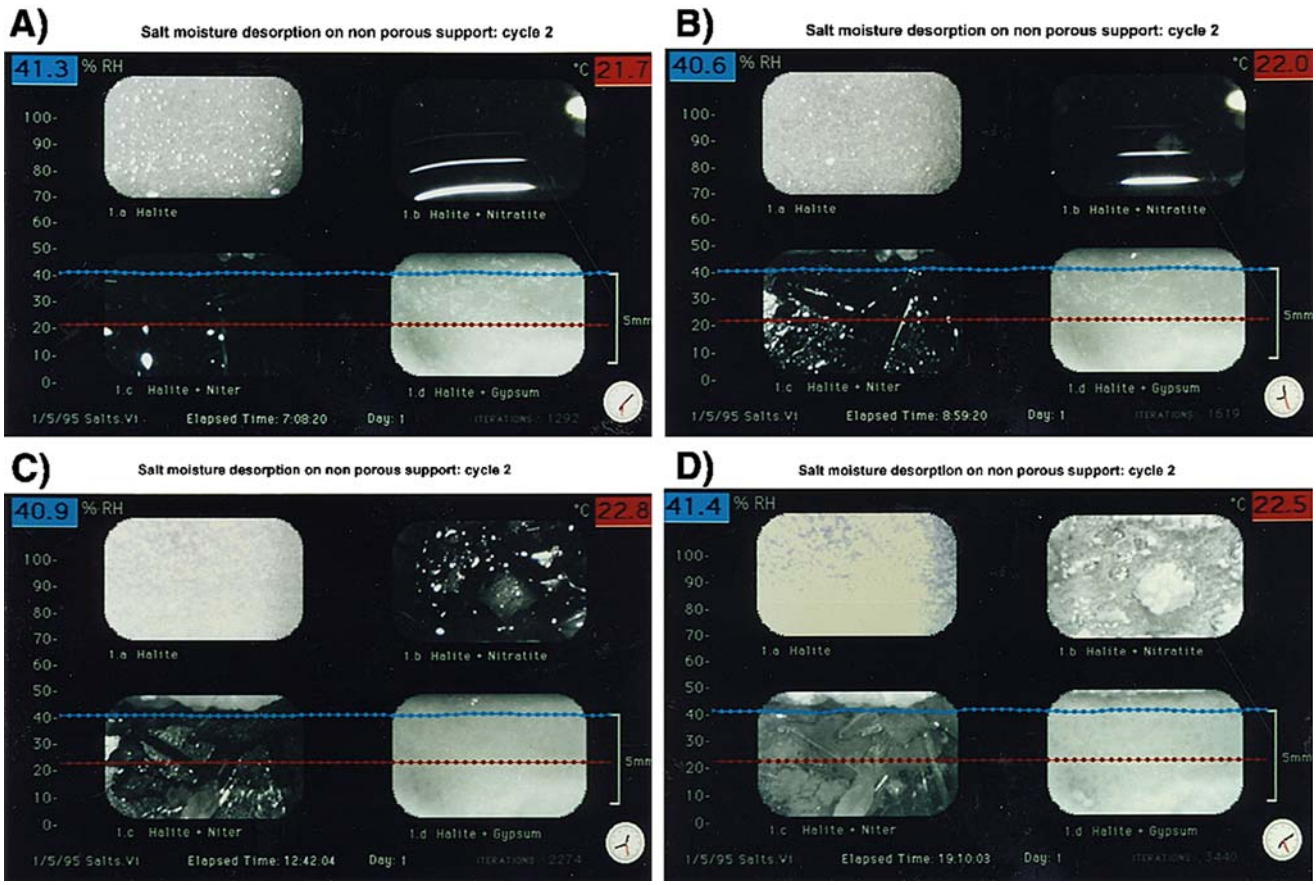

Fig. 10 Timelapse video recordings of evaporation by halite solutions (with and without additional salts). **a** After 7 h at RH < RHeq of halite: the halite–gypsum and halite samples have started to recrystallise, **b** after 9 h at RH < RHeq of halite: crystallisation is beginning to commence in the halite–niter and halite–nitratite samples, **c** after 12 h and 40 min at RH < RHeq of halite, **d** after 19 h at RH < RHeq of halite. The sequence of crystallisation observed is as follows: *1* halite–gypsum and halite *2* halite–niter, *3* halite–nitratite

Moreover, the results of this study suggest that salt phase transitions are capable of occurring within extremely short time periods, and are therefore likely to be affected by diurnal fluctuations in RH, especially when more than one salt type is present. However, should high RH conditions be permissible, the formation of an aqueous solution of the salts present may reduce the possible incidence of damage associated with their transitions, as crystallisation is less likely to occur in a mixed salt solution than in a single salt solution should the RH temporarily fall below the RHeq for a given time period.

This study explored the potential contribution of timelapse video recording with on-line data annotation for the study of salt behaviour in relation to environmental conditions, the results of which were highly rewarding in revealing information relating to the sequence, timescale and nature of salt phase transitions. The value and complexity of phenomenological studies of salt deterioration in situ have already been demonstrated, however, site investigations are typically hampered by the intermittent nature of observations.

The advantages afforded by scientific visualisation are only beginning to be realised in the field of conservation (Heritage 2000). Timelapse video recording should provide an extremely valuable tool for recording new information on the dynamics and manner of salt deterioration that have not previously been observed. The work carried out during this study was a preliminary, but necessary, step towards wide-ranging applications in the laboratory and with the eventual goal of in situ remote time-lapse monitoring.

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