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# Salt deterioration and microclimate in historical buildings
## intermediary report of the project "Sustained care of sensitive historical monuments"

**Report**

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**Salt deterioration and microclimate in historical buildings**
Intermediary report of the project "Sustained Care of Sensitive Historical Monuments"

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## Introduction

Salt deterioration is one of the most important contributors to the weathering of porous materials in historical buildings and the works of art they may enclose. These damages and many others are closely linked with the environmental conditions (Figs. 1-5). Salt deterioration takes place chiefly by repeated crystallization-dissolution or hydration-dehydration cycles, processes that are strongly controlled by the relative humidity (RH) and the temperature of the environment. Environmental control has been proposed as a way for avoiding or limiting the damage (Arnold and Zehnder 1991). This means finding the best-suited environmental conditions for the preservation of a given object. Its practice is compatible with the fragility and the value of many historical buildings, imposing the application of minimal invasive methods for their preventive conservation. However, because of the variety of materials often found in historical monuments, the correct application of microclimate control is not always straightforward: environmental conditions appropriate for avoiding a certain kind of damage (e.g. high RH for preventing salt crystallization on wall paintings) can in turn promote others (growth of bioorganisms on wood). Even in the case where salt deterioration is the only damage process taking place, complex mixtures of salts can render its application very complicate.

In order to limit the damage caused by microclimatic impact on historical monuments, it is necessary to optimize the methods of preventive conservation and improve the understanding of the complex interactions between the materials and the surrounding environment. A reasonable starting point is the study of those deterioration processes that are most widespread. Because of the importance of microclimate and salts as decaying factors in historical buildings, a deep understanding of their workings and their relationships is an essential step. The concept of salt system and microclimate modelling are applied to a pilot study object (church S. Pietro Martire, Gnosca, Switzerland) and presented below. The basic steps involved include: a) Assessment and characterization of the active damage processes. b) Microclimate monitoring. c) Assessment of the building / structural parameters. d) Modelling. e) Comparison of the results with the observations.

## On-site diagnosis and monitoring

Salt deterioration can be a highly dynamic process: many common soluble salts can quickly undergo phase transitions at environmental conditions found in historical buildings. For this reason, a continuous record of temperature and relative humidity, as well as simultaneous inspection of salt-affected areas is fundamental for recognizing the processes.

A number of temperature and RH sensors (Testo testostor 171) were placed at selected locations in the study object. The interval between each measurement was set to 1 hour, providing an accuracy sufficient to document variations relevant for salt crystallization processes. The recorded data serve for finding relationships with the observed salts and for the validation of the microclimate model. The principal salt-affected areas and their distribution were identified and mapped in detail, along with the different types of damage encountered (Fig. 6). These areas are then periodically surveyed and documented.

Figure 1 (top left): Flaking of the paint layer from a wall due to epsomite ($MgSO_4 \cdot 7H_2O$) crystallization. Width of view 20 cm approx.

Figure 2 (top right): Sanding and crumbling of plaster through mirabilite/thenardite ($Na_2SO_4 \cdot 10H_2O$/$Na_2SO_4$) crystallization. Width of view 30 cm approx.

Figure 3 (center left): Flaking of the paint layer occurring after drying of a surface that was exposed for about 1 month to wetting by condensation. Width of view 100 cm approx.

Figure 4 (center right): Mould growth on wooden bench. Width of view 60 cm approx.

Figure 5 (bottom left): Cracking and spalling of mortar from wood on a gilded altarpiece. The damage is caused by swelling and shrinking of materials with different water sorption capacity. Width of view 5 cm approx.

Salt samples are collected and analyzed both optically with a polarizing light microscope and microchemically, according to Arnold (1984) and Bläuer Böhm (1994). Where necessary, an additional X-ray diffraction analysis is performed. The identification of the salt minerals is an indispensable step. Every salt species has a characteristic equilibrium relative humidity ($Rh_{eq}$), above which it dissolves by absorbing moisture from the air and below which it

crystallises, and which, ultimately, determines the potential phase-transitions that can take place at a specific temperature and RH.

Fig. 7 summarizes the localization of the principal salt-affected areas in the case study and the predominant salt species identified. Most salt damage is concentrated in the lower part of the walls, from a few centimeters above floor to about 1 meter height, in the zone of rising damp. A more detailed description can be found in Bionda (2004).
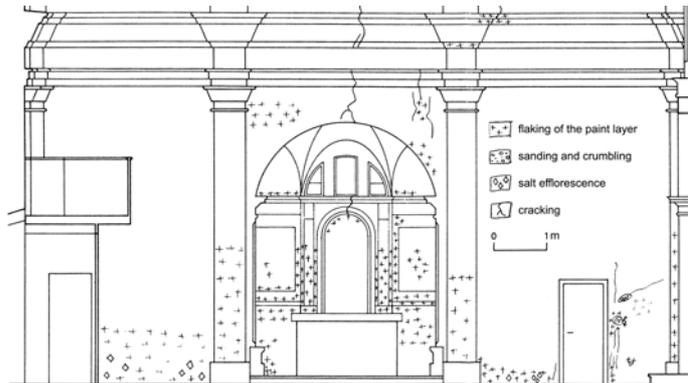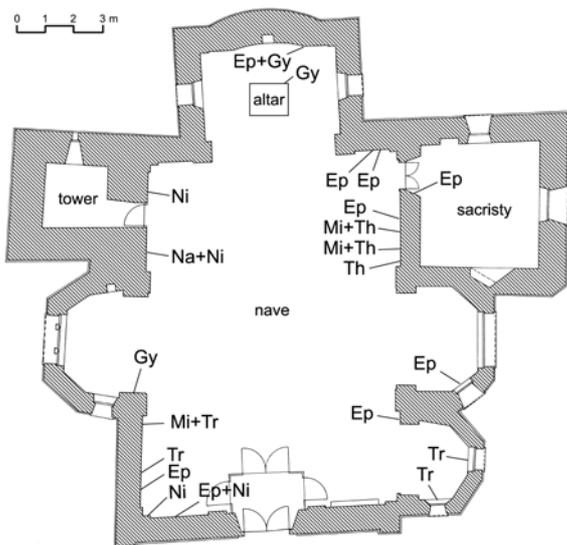


Figure 6: Example of damage map.



Figure 7: Plan of the church and localization of the predominant salt species.

Ep=epsomite
Mi=mirabilie
Th=thenardite
Ni=niter
Tr=trona
Na=patron
Gy=gypsum.

**Salt system modelling**

Sodium sulfate, with its hydrated (mirabilite, $Na_2SO_4 \cdot 10H_2O$) and anhydrous (thenardite, $Na_2SO_4$) phases is considered one of the most damaging salts, especially when transitions from one form to the other persist. The exact mechanism of how damage is produced is not yet fully understood and is still object of studies (e.g. Rodriguez-Navarro and Doehne 1999, Rodriguez-Navarro et al. 2000, Flatt 2002, Tsui et al. 2003).

In the study object, sodium sulfate salts are crystallizing on the youngest repair mortars, mainly at the base of the walls. The theoretical behaviour of sodium sulfate under the environmental conditions actually measured in the building is deduced from a pure phase

stability diagram. For comparison, the simulation of its behaviour with a more complex model for salt mixtures is also shown.

*Pure salt*

The critical relative humidity for the phase transition mirabilite-thenardite is not influenced by the presence of other salt species (Steiger 2003). At 25 °C it lies at about 80% RH. If we are only interested in that specific transition, we can simplify the system by assuming a pure sodium sulfate phase. By plotting all the climatic values recorded during the monitoring period in the phase diagram of sodium sulfate (Fig. 8), it is apparent that both mirabilite and thenardite must have been in turn the stable phase and, hence, that phase transitions must have occurred. Mirabilite stability prevails during winter, while thenardite during summer (Fig. 9).
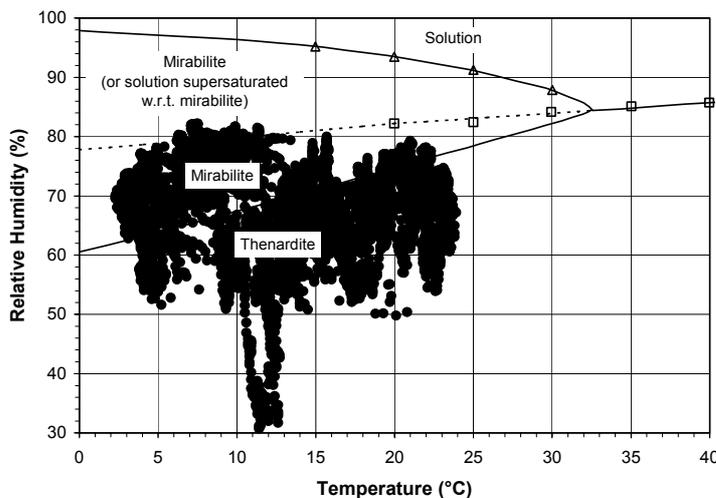


Figure 8: Phase diagram for sodium sulfate and superimposed measured hourly indoor temperature and relative humidity (black circles) for the period April 2002 – March 2003. Phase boundaries constructed according to Flatt (2002) with experimental data from Kracek (1928).
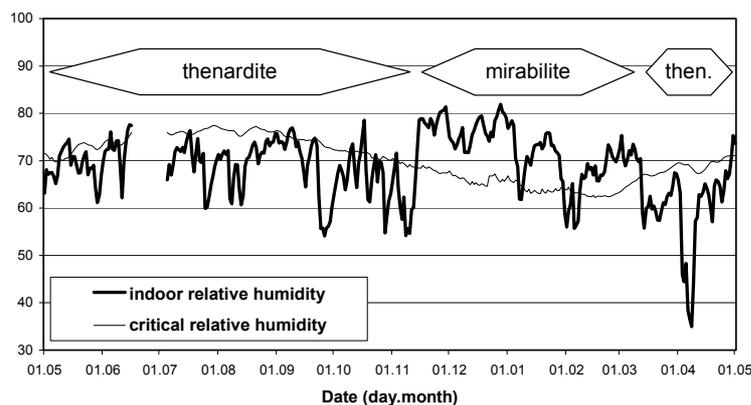


Figure 9: Comparison of the indoor relative humidity daily averages and the calculated temperature-corrected critical relative humidity for the transition mirabilite-thenardite. Mirabilite was the prevailing stable phase from the mid of November to the mid of March, when the indoor RH was mainly above the critical relative humidity, while thenardite stability prevailed for the rest of the year.

*Salt mixture*

In the case of salt mixtures, which are commonplace in salt-contaminated porous historic materials, the determination of the stability field of every component is very complex (see for example Steiger & Zeunert 1996). The $Rh_{eq}$ of pure phases no longer apply and the salts generally start to deliquesce at lower values.

The behaviour of salt mixtures under changing microclimate conditions has been modelled with the ECOS code (Price 2000). ECOS is a thermodynamic model based on the Pitzer theory of electrolyte solutions (Pitzer 1973). It determines the salt species, and their respective

4

amount, present under equilibrium conditions at any given temperature and RH for a specific ion mixture. It thus requires as input the ion analysis ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ $Cl^-$, $NO_3^-$ and $SO_4^{2-}$) of the salt mixture. To conveniently use ECOS, a specific software was developed (Bionda 2002). Further examples of the application of ECOS can be found in Bionda and Storemyr (2002) and Sawdy (2001).

In the case of salt-contaminated mortars, the procedure used was the following: plaster samples of the upper 2 cm were taken from the major salt-affected areas inside the building, dried at 40 °C until the weight was constant and crushed to grain size < 1 mm. Soluble salts were then brought into solution by adding 100 ml deionised water to 1 g of the sample and by shaking vigorously for 2 minutes. The filtered solution was then analyzed with a ion chromatograph (Metrohm 690). Figs. 10 and 11 show the output of ECOS in the form of cumulative plots for a water extract from a plaster sample where sodium sulfate is the observed efflorescing salt. The lines in the plot indicate the solid salt minerals present in the mixture against the RH at the given constant temperature. The exact amount of a particular mineral at a specific RH can be read by the difference between the corresponding line and the next underlying line. For example, in Fig. 11, thenardite goes into solution at about 78 %. From this solution, mirabilite and a minor amount of aphthitalite crystallize. By further increasing the RH, both salts start to dissolve. Above 90% RH all salts are in solution.

In winter (T=4 °C, Fig. 10), the transition mirabilite-thenardite lies at about 63% RH, while in summer (T=22 °C, Fig. 11) it is at about 78% RH. As expected, these values are in agreement with those for pure sodium sulfate (Fig. 8). In addition, this model gives insight into the behavior of other salts that can form from the ion mixture.
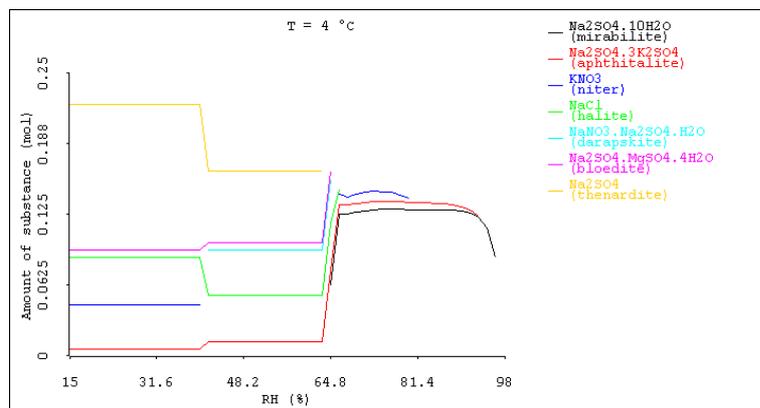


Figure 10: ECOS simulation at T=4°C. Input ion amounts (mol/Kg sample): Na=0.325, K=0.076, Mg=0.007, Ca=0.083, Cl=0.040, $NO_3$=0.038, $SO_4$=0.242. 0.1 mol $Na_2SO_4$ were added to the ion analysis in order to account for the sodium and sulfate ions "trapped" in the salt efflorescence. The transition mirabilite-thenardite is at about 63% RH.
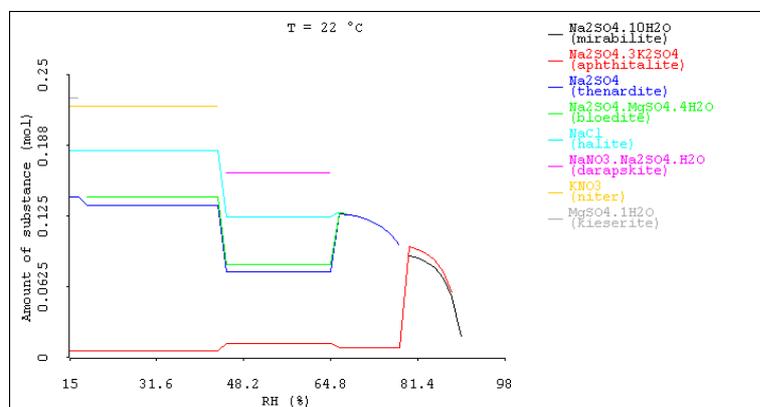


Figure 11: ECOS simulation at T=22°C. Input ion amounts as for Fig. 10. The transition mirabilite-thenardite is at about 78% RH.

*Implications from the conservation point of view*
Salt deterioration can be limited by setting the environment RH and temperature to values that lie within "safe ranges", that is ranges where the present salts are stable and no dissolution/precipitation or phase transitions occur. For the specific ion mixture considered, if we were to choose a safe RH for the whole year, that would imply avoiding the range between 63 and 78% (Figs. 8, 9, 10 and 11), by keeping the ambient RH constantly above or below the critical RH line indicated in Fig. 9. On the other hand, the RH should not be too high (bioorganism growth might become a concern), or too low (other salts might become active, Figs. 10 and 11).


## Microclimate modelling

The ability to accurately simulate the temperature and humidity inside historical buildings can be very useful for their preventive conservation. Two main fields of applications can be expected: *microclimate forecast* and *past microclimate reconstruction.*

*Microclimate forecast*
The prediction of the microclimate evolution inside a building without having to resort to continuous or long-term environmental monitoring can be of good practical use. The consequences of extreme weather conditions, of heating, of the presence of people, of building interventions (for example the replacement of old windows with better-insulated ones) can be simulated in advance, thus facilitating the estimation and allowing the recognition of the risk of damage by microclimate impact.

*Past climate reconstruction*
This is probably the most interesting application of microclimate modelling in connection with damage interpretation. Very often, when conservation studies are started, the damage is already present and the microclimate conditions under which it developed are unknown, as no climatic measurements have yet been done. In many cases, and especially in the case of salt deterioration, it is however necessary to know what climate reigned inside the building in order to understand the dynamic and frequency of the salt phase transitions that produced the observed damage.

Both microclimate forecast and past microclimate reconstruction assume a reliable model, which suits the building in question. Using HELIOS (Frank 1982) and HYGRO (Simmler et al. 1996) a microclimate simulation can be performed on the base of an accurate characterisation of the study object and of regional climatological data from a nearby meteorological station. The results of the ongoing parameterisation and validation of the simulation on the church S. Pietro Martire in Gnosca are summarized in the following chapters.

*Temperature model*
The HELIOS model is used to simulate the indoor air temperature and the temperature of the enclosing surfaces. HELIOS is a one-zone model that explicitly calculates the heat flux for one room taking into account short and long-wave radiation processes.
Several building and climatological parameters are needed in order to perform the simulation. For this purpose, the building envelope is characterized in terms of materials, construction and orientation of the structural elements. Hourly climatological data required by the model are taken from the next meteorological station (ANETZ station of Locarno-Monti). The fit of the

model with the measurements has been improved by using the temperature measured locally by a data logger placed outside the building.

The overall trend of the simulated values (Fig. 12) is in good agreement with the measurements. The systematic discrepancy of about 1-2°C observed during the fall-spring period is probably connected with an imperfect parameterization of the heating episodes. Daily fluctuations of the simulated values closely follow the trend of the measurements with slightly greater amplitude (Fig. 13).
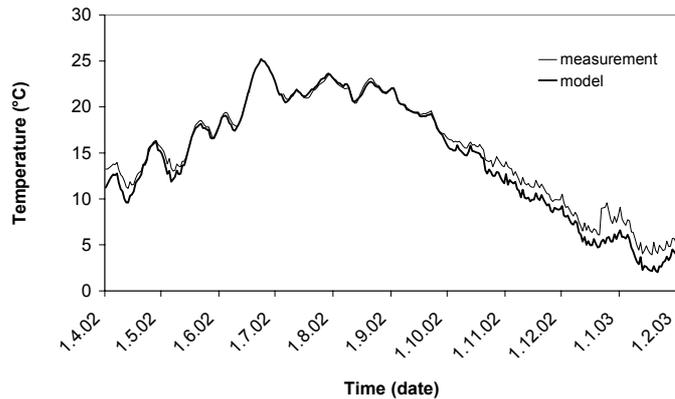


Figure 12. Comparison of modelled and measured indoor temperature. Daily averages over the period April 2002 – January 2003.
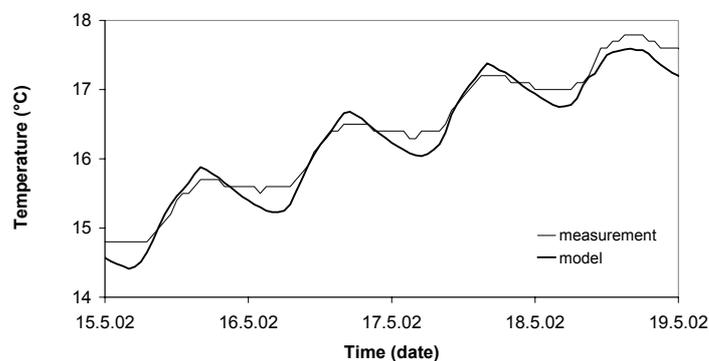


Figure 13. Comparison of modelled and measured indoor temperature. Hourly values over a four days period.

*Humidity model*

The indoor air humidity is simulated with the HYGRO model on the basis of the indoor air and surface temperatures calculated by HELIOS and the outdoor RH and temperature. The required dynamic water sorption capacity of the principal materials present in the church (e.g. plasters, floor tiles, wood) was determined experimentally in a climatic chamber at EMPA: the RH was varied from 45 to 70% and then back to 45%, while T was kept constant at 20°C. Moisture sources such as human vapour production through respiration and perspiration during ceremonies were also considered.

Preliminary results (Fig. 14) show a good agreement of the overall trend and amplitude of the fluctuations of the daily averages of measured and simulated absolute humidity. The discrepancy between measurement and model is generally less than 1-1.5 g/m$^3$. In order to improve the accuracy of the simulation, other materials important for their moisture-storage potential are being characterized in more detail.
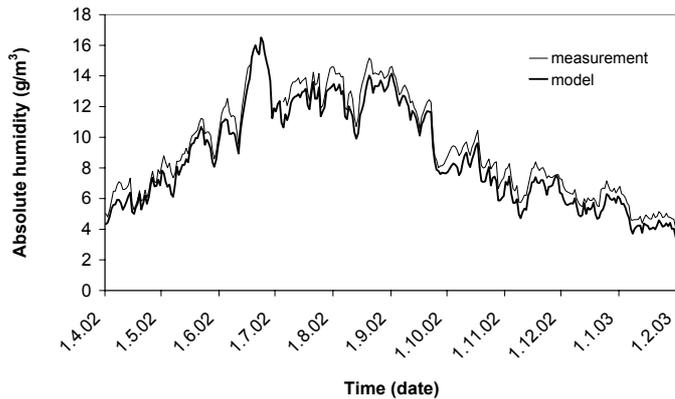
Figure 14. Comparison of modelled and measured indoor absolute humidity. Daily averages over the period April 2002 – January 2003.

**Discussion of models in relation to reality**

Models for the behaviour of salts and the microclimate can be an invaluable aid for the preventive conservation of historical monuments:
- They facilitate the understanding of deterioration processes ("how many times does a specific salt crystallize within a given time span?")
- They can fill gaps in available data or provide educated estimates in situations where continuous investigation and/or monitoring are not practicable.
- They can assist in decision-making (i.e. "how should we set the temperature and RH in the building in order to minimize salt damage?")
- More generally, they can be used as a tool for damage risk assessment.

The concept of modelling as applied here is complementary to a basically phenomenological and analytical approach. The validity of a model and its applicability to a specific situation are verified by on-site observations and measurements and, if necessary, by additional laboratory investigations.

The prediction of the behaviour of salts in response to the environmental conditions is not yet straightforward. In the case of salt efflorescence, i.e. crystal growth on the surface of a support material, the environmental conditions under which the process is occurring roughly correspond to the microclimate in the room and are therefore easily quantifiable. Available models like ECOS, apart from current limitations (Price 2000, Bionda 2004), can be used with success in many such instances. In the case of salt subflorescence, i.e. crystal growth below the surface, in the pores of the support material, the environmental conditions are largely unknown and don't necessarily match the microclimate in the building. In such circumstances, the prediction of the behaviour of the salts is extremely difficult. This is a major drawback, since salt subflorescence is usually more damaging than efflorescence (Cooling 1930, Rodriguez-Navarro and Doehne 1999). The rate at which phase transitions take place is another crucial parameter determining the magnitude of the damage occurring. A salt or salt mixture with a fast response to changes in ambient humidity and/or temperature will be more damaging than a slow one. Thermodynamic models can tell if a specific equilibrium is going to be attained (e.g. if a salt is going to dissolve or precipitate) but won't give any indication about the kinetics of the reaction.

The microclimate models HELIOS and HYGRO are giving promising results and demonstrate their applicability in the field of the preventive conservation of historical monuments. Work is being done in order to further improve the precision of their results.

8

## Outlook

From the discussion above, the following areas needing further investigation emerge:
- On-site determination of the moisture content and the humidity of the air in the pores of the material. This information, together with the temperature, will allow an insight into the behaviour of salts within the pore system of materials.
- On-site determination through monitoring of the kinetics of salt phase transitions and the related damage processes.
- Determination of other material parameters that might be relevant for the development and the magnitude of salt damage (type of porosity, mineralogy of the substrate, etc.)

## Acknowledgements

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