

## ASSESSING THE RISK OF SALT DECAY FOR WALL PAINTINGS IN HISTORIC BUILDINGS. THERMO-DYNAMIC MODELING AND TRANSITION CYCLES COUNT

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### *Abstract*

*Salt crystallisation is a major cause of deterioration of porous building materials, strongly related to the fluctuation of the environmental parameters. This paper explores the application of different methodologies to assess the potential damage caused by soluble salts to a series of sixteenth century frescoes with the thermo-hygrometric variations. The method of counting the transition cycles for six crystalline systems, the thermodynamic model ECOS for mixed salt solutions and a combination of both methodologies were used, in order to evaluate and compare these different approaches and to determine the risk of salt decay for this particularly sensitive case study. To this end, the temperature and relative humidity in the churches housing the wall paintings were monitored during a year and the salt content of the frescoes analysed. The seasonality of the salt crystallisation was studied and the range of relative humidity at which the transitions occurred determined. All methods identified a significant risk of salt decay, mainly related to the crystallisation of chlorides and nitrates, which corresponds well with the observations in situ. Finally, the advantages and inconveniences of each method were discussed, along with the results obtained in other published works, and the combined method was suggested as the most efficient*

**Keywords:** Salt weathering; Risk assessment; Environmental monitoring; Wall paintings; ECOS; Transition cycles count

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### **Introduction**

Risk assessment is a useful tool for the conservation of cultural heritage, as it identifies the risks which affect artworks and estimates their magnitude, so that strategies to reduce effectively the potential damage may be developed. This fulfils the principles of preventive conservation, which seeks to identify the deterioration causes affecting cultural heritage, understand the phenomena they originate and control them by means of acting on the environment/building instead of directly on the objects, in order to guarantee the survival of the collections [1]. The need for methodologies for an objective, accurate and reproducible risk assessment of cultural heritage has encouraged the development of two types of tools: comprehensive models for the assessment of all risks [2-4] and methods to evaluate the potential damage caused by certain environmental parameters to a specific material. An example of the latter are the different damage functions available in the literature, such as the effect of RH and T on the mould growth on organic materials [5-7], on the dimensional change

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[8] and moisture movement in wood [9], on the lifespan of paper [10] and the damage caused by pollutants to limestone [11]. The present work focuses on the investigation of different methodologies for the risk assessment of mechanical damage caused by salt crystallisation to porous materials [12-15], specifically to wall paintings.

Soluble salts are one of the most common and serious agents of deterioration for built heritage. They may have different sources, such as marine aerosols, groundwater or the building materials. When dissolved, salts can enter and circulate through the porous materials and, under certain environmental conditions, crystallise leading to deterioration phenomena [16-17]. The damage can be either aesthetic, when salt crystallisation occurs on the surface of the materials (efflorescences) and disturbs the perception of the artwork, or mechanical, if the crystals are formed below the surface (subflorescence), causing pressure within the structure of the material and, after repeated cycles of dissolution-recrystallisation or hydration, provoking the weakening, detachment and loss of the surface layers [18].

Wall paintings are particularly vulnerable to damage by soluble salts, as they have a layered structure and the painted surface is precisely the main area of water evaporation, salt accumulation and atmospheric moisture absorption. The veils or crusts of salts on the murals, in addition to the aesthetic disturbance already mentioned, maintain humid micro-environments in contact with the pictorial layer, increasing the risk of biological colonisation and pigment alteration [19]. The main alterations related to subflorescence are powdering, peeling, scaling, flaking, bulges, cavities and lacunae [20]. Very often, the only feasible option to prevent or reduce damage caused by salts in murals is climatic control, as salt extraction can originate a greater damage in the already weakened material or trigger other deterioration mechanisms related to the use of water. Therefore, monitoring the environmental parameters and assessing the effects that their fluctuations may have on the salts present in the murals is of vital importance.

The main objective of the present work was to compare and evaluate the two main methodologies that have been proposed to assess the mechanical risk due to salt crystallisation in porous materials: the counting of the number of crystallisation-dissolution cycles for certain salt systems depending on the environmental conditions [12-13] and the application of thermodynamic models which aim to predict the behaviour of mixed salt solutions [14-15], as well as their combined use.

These methods were used to determine the risk of salt decay of a particularly sensitive case study: the 16<sup>th</sup> Century wall paintings in the churches from the Ribeira Sacra (Galicia, NW Spain) (Fig. 1), a region known for its invaluable natural and cultural heritage. The Ribeira Sacra spreads along the valley of the rivers Miño and Sil and its steep slopes are dotted with numerous churches and monasteries built during the Middle Ages by religious communities in search of the peace and isolation of the area. Frequently, the walls of these churches and cloisters were decorated with murals of religious subjects, as a means of meditation for the monks and as a *Biblia pauperum* for a mostly illiterate congregation. During the Middle Ages, the pictorial cycles were periodically renewed when their condition was poor. However, by the end of the sixteenth century the murals were systematically destroyed or concealed. This was due to a change in the aesthetic taste, which favoured Baroque altarpieces to decorate the churches, as well as to the common practice of applying limewash to the walls, as a preventive measure against the frequent plagues that devastated Europe at the time [21-22]. Therefore, these paintings had remained forgotten for centuries, until recently, when numerous examples of murals have been discovered beneath the plaster of the churches and efforts are being made to study, investigate and preserve this heritage, also in relation with the application to be recognised as World Heritage by UNESCO.



**Fig. 1.** Location of A Ribeira Sacra within Europe and Galicia (top, left). Sil Valley of the Ribeira Sacra (top, right). Romanesque church of Santo Estevo de Ribas de Miño (bottom, left). Renaissance fresco in the church of Santa María de Proendos (Lugo) (bottom, right).

## Experimental

### *Selected murals and sampling*

The research focuses on a selection of twelve wall paintings, located in countryside churches of the Ribeira Sacra. The reasons for choosing these murals for the present study are, thus, the importance of the natural and cultural heritage of the region, the peculiarity of its continental climate with cold winters and warm and dry summers within the much damper Atlantic context of Galicia and the presence of deterioration signs related to salt crystallisation in certain murals such as veils, cavities and lacunae.

A total of nineteen samples of original plaster, limewash, paint layers and salt efflorescences were taken (table 1). The number and size of the samples were kept to the minimum (1-3 samples per mural, generally of less than 1g) and they were taken in areas of low visual impact, to preserve the integrity of the paintings. As the content of salts is not constant in space or time, the sampling was carried out under the following conditions: during spring/summer, when the relative humidity is lower which favours the migration of the salts to the surface of the murals; at the first external millimetre of the mural where salts accumulate [23]; at approximately the same height from the ground level (1-1.5m); and in areas of the paintings where there was already evidence of salt weathering.

### *Analysis of salts*

The soluble salts were extracted from the samples of plaster and paint with 30mL of deionised water per 0.5g of sample, during 24 hours. The extracts were filtered (0.45 $\mu$ m) and

the ions present were analysed by means of the following techniques. Chlorides and nitrates by conductivity with ion selective electrodes (ISE) (9617BNWP for  $\text{Cl}^-$  and 9707BNWP for  $\text{NO}_3^-$ ), with a ISEmeter *Orion Dual Star* (Thermo Scientific). Sulphates were determined by turbidimetry, making them precipitate with barium chloride and measuring absorbance at 650 nm with a UV-Vis spectrometer Cary100conc. Details of the method can be found elsewhere [24]. The cations (calcium, magnesium, sodium and potassium) were analysed by atomic absorption/emission spectroscopy with an instrument Varian espectralAA 220FS [25]. A fraction of the biggest samples of plaster and efflorescences was ground, sieved and analysed by X-ray diffraction (XRD), with an instrument Philips PW1710, operating at 40kV and 30mA. The diffractograms were obtained in the angular range  $2\theta$  from 2 to  $65^\circ$ , with a step of  $0.02^\circ$  and a time per step of 2s.

### ***Environmental monitoring***

Temperature and relative humidity were monitored in three of the painted churches of the Ribeira Sacra: San Lourenzo de Fión (F), Santa María de Marrube (M) and Santa María de Nogueira de Miño (N). Built in Romanesque style in granite masonry, these examples are representative of the architectonic characteristics and the pattern of use of the churches in the region. They were selected as representatives of different locations in the valley: N is on the west bank of the Miño river and F and M on the east bank, the former very close to the river and the latter further away.

A climatic station was installed in each of the three churches, close to the wall paintings in the presbytery, at approximately 1.5m from the ground level. The stations consist of a Nemom datalogger (Microcom) with probes STHA-10 (BacotA Control Systems). The probes have a platinum thermoresistance Pt-100, measuring temperature in the range  $-10$  to  $50^\circ\text{C}$  with an accuracy of  $\pm 0.2^\circ\text{C}$ , and a capacitive humidity sensor of lineal integration, covering the range 1-100% with an accuracy of  $\pm 3\%$ . The thermo-hygrometric data were recorded hourly during one year (June 2010 - May 2011).

### ***Methods for the risk assessment of salt decay***

#### ***Counting of the transition cycles***

The number of crystallisation-dissolution cycles of a series of salt systems commonly found in monuments [18] was calculated by counting the number of times the daily relative humidity monitored in the churches of a Ribeira Sacra varied across the point of deliquescence or equilibrium relative humidity ( $\text{RH}_{\text{eq}}$ ) of each salt under consideration. This was done following the method of Benavente *et al.* [12] for the thenardite-mirabilite transition ( $\text{NaSO}_4 - \text{NaSO}_4 \cdot 10\text{H}_2\text{O}$ ), hydrated system sensitive to both humidity and temperature, according to the equation  $\text{RH}_{\text{eq}} = 59.11 + 0.87549T$ . The method can be extended to other salt systems by calculating their correspondent  $\text{RH}_{\text{eq}}$  [13]. This was done for halite ( $\text{NaCl}$ ), anhydrous salt with a phase transition at 75.3% RH regardless of the temperature, as well as for nitratine ( $\text{NaNO}_3$ ) and niter ( $\text{KNO}_3$ ), using equations  $\text{RH}_{\text{eq}} = 79.72 - 0.21829T$  and  $\text{RH}_{\text{eq}} = 96.32381 + 0.01429T - 0.00495T^2$ , respectively, calculated by means of linear ( $R = 0.99967$ ) and polynomial ( $R = 0.99973$ ) fit of the values of  $\text{RH}_{\text{eq}}$  for these salts at different temperatures [26].

#### ***Thermodynamic model ECOS***

The following stage involved studying the behaviour of mixed salt solutions in porous materials depending on the thermo-hygrometric conditions, by means of the application of the thermodynamic model Environmental Control of Salts (ECOS) [15]. To this end the software RUNSALT was used [27].

As input data, the ion concentration detected in 19 samples of plaster and paint (namely:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , as moles of ion per gram of sample), as well as the average annual temperature and relative humidity range monitored during the year of study in the churches of a Ribeira Sacra were introduced in the RUNSALT interface. The same

calculations were done using the seasonal environmental data, to investigate whether the seasonal temperature variations would have an influence in the results. Slight charge adjustments were made where there was an imbalance and gypsum was eliminated from the system as, due to its low solubility, it cannot be processed by ECOS.

Then ECOS estimated which crystalline phases were present in the equilibrium and the changes in the total volume of crystals due to RH variations. The output data were graphs representing accumulated volume of solids versus relative humidity, at the average temperature.

#### *Combined method*

Finally, the RH at which ECOS predicted that the crystallisation sequence would start was considered an estimation of the RHeq for the particular salt mixture present in the samples. In consequence, the phase transitions could be counted as a function of the number of times the monitored RH in the churches of the Ribeira Sacra crossed over these RHeq, combining both methods [28].

## Results and discussion

### *Environmental conditions in the churches*

The environmental conditions monitored in the three churches resulted to be very similar, and the data from Marrube will be used as an example. The annual average temperature was 11°C, with a minimum of -1°C in February and a maximum of 24°C in August, and for the relative humidity, the annual average was 71%, with extremes ranging between 50% in October and 84% in May and December. The seasonal average and extreme T and RH were as follows: summer 18°C (13-24°C) and 67% (57-73%); autumn 14°C (6-22°C) and 68% (50-79%); winter 3°C, (-1-8°C) and 78% (70-84%) and spring 9°C (4-17°C) and 71% (55-84%). The RH fluctuations often exceeded 7% within 24 hours, but T used to be quite stable, with an average daily fluctuation of 3°C.

### *Salt analysis: ions and concentration*

The results of the salt analysis of 19 samples of plaster (P), limewash (L) and paint layer (PA) from 12 churches from the Ribeira Sacra are shown in Table 1.

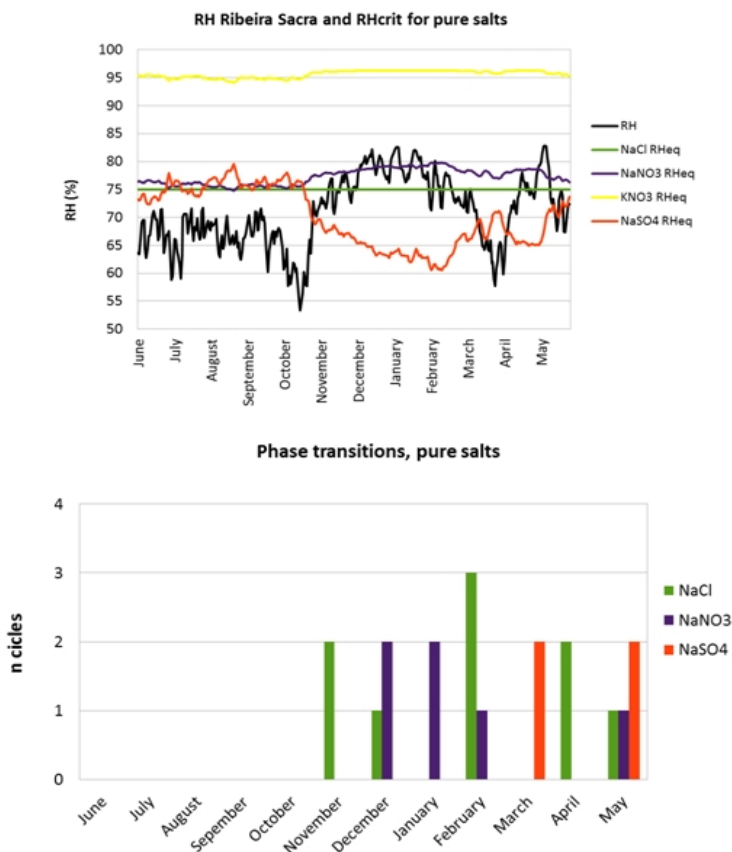
**Table 1.** Concentration of ions in the samples from murals of the Ribeira Sacra

Church	Sample	moles ion/g sample							Total ion content
		Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	
1-Santo Estevo de Ribas de Miño	1P	12.98	5.94	0.00	15.46	3.96	0.25	1.11	38.59
	1PA	0.95	0.84	2.51	0.92	0.23	0.18	3.65	9.28
	1L	11.11	0.83	3.70	14.71	2.48	0.21	35.97	69.01
2-Sta. M <sup>a</sup> de Piñeira	2P	5.21	3.76	0.00	1.79	0.94	0.59	6.70	18.99
	2L	10.04	2.17	0.00	8.57	4.21	0.26	0.35	25.6
3-San Salvador de Ínsua	2L'	9.59	2.56	0.00	7.83	4.06	0.03	0.93	25
	3P	1.19	0.98	0.00	0.26	0.17	0.77	0.85	4.22
4-Santo Estevo de Ribas de Sil	4P	3.95	2.37	0.58	3.24	1.41	0.24	3.29	15.08
	4P'	3.22	2.15	0.00	0.20	0.73	0.16	3.49	9.95
5-San Miguel de Eiré	5P	1.11	0.81	0.00	6.79	0.37	0.20	1.25	10.53
6-Sta. M <sup>a</sup> de Marrube	6P	1.69	1.49	0.00	0.53	0.41	0.28	0.02	4.42
7-San Pedro Fiz de Cangas	7P	2.07	6.47	0.00	1.25	0.82	0.64	0.02	11.27
8-San Pedro de Rocas	8P	1.06	1.20	0.00	0.27	0.44	0.41	3.78	7.16
	8P'	2.79	3.88	0.00	0.15	1.06	1.33	13.28	22.49
9-San Lourenzo de Fión	9P	1.74	2.31	0.00	0.73	0.33	0.59	2.97	8.67
10-San Xulián do Campo	10P	4.45	5.52	0.00	2.60	0.60	0.82	5.13	19.12
11-San Pedro de Bembibre	11P	3.17	3.49	0.00	0.11	0.20	1.21	3.40	11.58
	11P'	6.69	2.31	0.00	4.96	1.09	0.50	1.89	17.44
12-San Mamede da Torre	12P	2.02	1.77	0.00	0.74	0.32	0.96	1.58	7.39

Fundamentally, chlorides and nitrates were detected and, in some cases, also sulphates. In the mural with the highest salt concentration, Santo Estevo de Ribas de Miño, chloride and sodium predominate in the plaster and sulphate and calcium in the paint layer.

**Number and seasonality of crystallisation cycles**

The results of counting the transition phases using the environmental data were very similar for the three monitored churches. As a reference, the figure 2 (above) shows the annual evolution of the monitored RH in Marrube, along with the equilibrium RH for halite, nitratine, niter and thenardite-mirabillite. It can be noted that niter remained in solid state at the conditions monitored over the whole year of study, as the environmental RH is below their equilibrium values. The same applies from June to October to the remaining salt systems. However, from November the RH in the churches started to increase, exceeding the equilibrium RH for halite, nitratine and thenardite, and consequently these salts dissolved. During the months of winter and spring the RH underwent brief fluctuations above and below the equilibrium RH of these three crystalline systems, favouring the occurrence of repeated crystallisation-dissolution cycles, which might involve risk of physical damage to the paintings. The transition cycles calculated for the studied year (June 2010 - May 2011) using Marrube environmental data, are shown in figure 2 (below): 9 cycles were counted for halite, 6 for nitratine and 4 for the transition thenardite to mirabillite. No transition cycles occurred for niter ( $KNO_3$ ).



**Fig. 2.** Annual evolution of the monitored relative humidity (RH) in the church of Marrube, along with the equilibrium RH for halite, nitratine and thenardite-mirabillite (top). Monthly distribution of the number of transition cycles for the considered systems during the studied year (June 2010-May 2011) (bottom).

***ECOS estimations of crystalline phases and changes in volume***

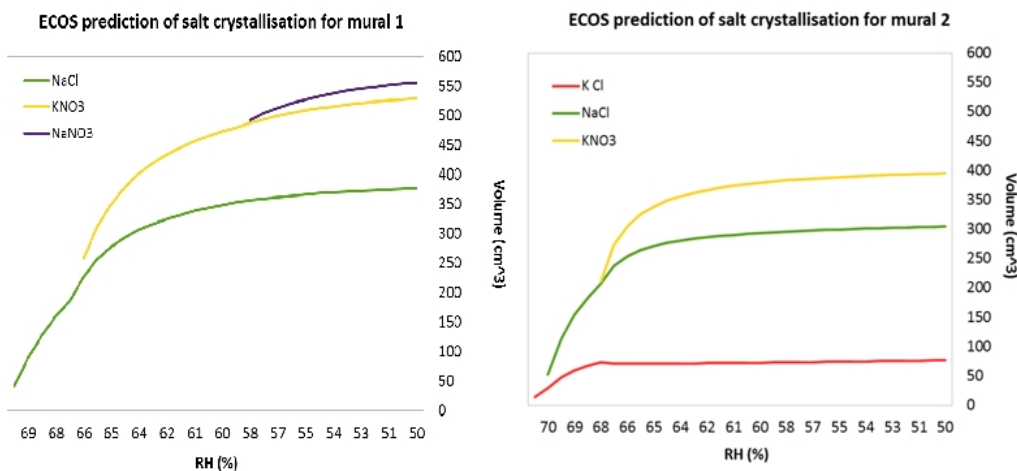
Based on the concentration of ions in the samples, the thermodynamic model ECOS informed on the phases that would crystallise under the environmental conditions monitored in the churches and the volume changes that the salt crystals would undergo with the RH variations. According to the results obtained, three risk categories of salt damage were established:

-*No risk*: no crystallisation possible under the T and RH conditions monitored for the samples 3P, 4P', 8P, 8P', 9P and 11P.

-*Moderate risk*: the model determined that either a relatively small volume of halite (less than 20 cm<sup>3</sup>) would crystallise or that it would happen very sporadically during the year. This is the category for the samples 1PA, 2P, 4P, 6P, 10P, 12P.

-*High risk*: several salt species would crystallise (halite as well as sylvite (KCl), niter and/or nitratine), and/or they would undergo serious volume changes with the RH variations, reaching a maximum total volume of crystalline solids higher than 100cm<sup>3</sup>. This would be the case for the samples 1P, 1L, 2L, 2L', 5P, 7P and 11P'.

The results for the murals showing the highest risk of salt damage (mural 1: Santo Estevo de Ribas the Miño and mural 2: Santa María de Piñeira) are presented in the graphics of figure 3, which show the accumulated volume of crystals (the diverse salt species are represented in different colours and superimposed) versus the RH range monitored during the year of study, at the annual average T.

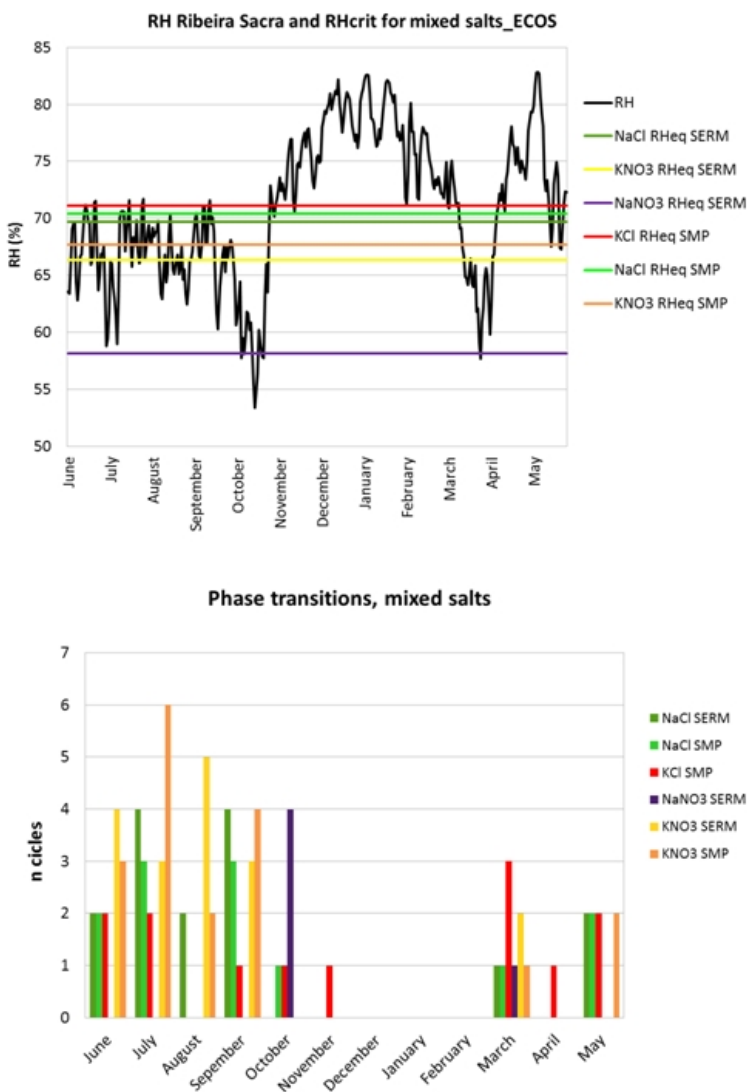


**Fig. 3.** ECOS output for murals 1 (Santo Estevo de Ribas the Miño) (top) and 2 (Santa María de Piñeira) (bottom), showing the accumulated volume of crystals versus the monitored RH range at the annual average T (11°C).

For the plaster of mural 1 (sample 1P, figure 3 top), ECOS suggests that for values of RH above 70% the salts remained in solution. The crystallisation of halite started when RH descended under 70%, that of niter when the RH descended under 66% and of nitratine under 58% RH. As precipitation occurred and the volume of solid crystals increased, the remaining solution got more and more concentrated and in consequence the RHeq drifted towards lower values of RH. The volume of crystals would reach a maximum of 557 cm<sup>3</sup> when dropped down to 50% in the summer. For the limewash of mural 2 (sample 2L, figure 3 bottom), sylvite would have crystallised when the RH descended below 71%, halite 70% and niter under 68%, reaching a total volume of accumulated crystals of 394 cm<sup>3</sup> when RH reached the annual minimum of 50%.

**Combined method: calculation of the  $RH_{eq}$  for salt mixtures and number of transitions**

Using the RH at which the crystallisation sequence would start according to ECOS as the  $RH_{eq}$  for the mixture of salts, the following crystallisation-dissolution cycles were counted for the two cases showing the highest risk of salt crystallisation during the year of study. For mural one: 15 cycles for NaCl, 17 for  $KNO_3$  and 5 for  $NaNO_3$  and for mural two: 13 cycles for KCl, 12 for NaCl and 18 for  $KNO_3$ . Therefore, when a mixed salt solution is considered instead of single salts, it can be noted that the  $RH_{eq}$  are strongly reduced and the number of predicted phase transitions is higher than those calculated in section 3.3. The estimated annual distribution of the salt transitions is also very different, taking place predominantly in the warm and dry summer and autumn months. Figure 4 shows the  $RH_{eq}$  calculated for the salt mixture along with the monitored RH (above) and seasonal distribution of the transitions (below).



**Fig. 4.** Annual evolution of the monitored relative humidity (RH) in the church of Marrube, along with the equilibrium RH for the crystallised salts predicted by ECOS (top). Monthly distribution of the number of transition cycles for the predicted salts during the studied year (June 2010-May 2011) (bottom).



## Discussion

The count of phase transitions for different salt systems proved to be a simple method to roughly estimate the risk of damage due to salt crystallisation, as it only requires the monitored environmental parameters and the equations of the equilibrium RH for each salt system. In the present work, the number of phase transitions estimated for the different salts under the monitored environmental conditions could pose a moderate risk for the wall paintings of the Ribeira Sacra, as 19 dissolution-crystallisation cycles were counted during the year of study. This would be especially worrying in the case of the transition thenardite-mirabilite, because the related increase of the volume of crystals implies a pressure exceeding 10 MPa, sufficient to disrupt porous building materials [12].

However the accuracy of the method is limited due to several factors: 1) it assesses each salt individually, while monuments are affected by complex salt mixtures, in which the different ions would affect each other solubility [29-30]. Our research proved how different the estimation of the frequency and seasonality of phase transitions could be when either single salts or mixed systems are considered. 2) The kinetics of the transitions is not considered in the method, although it can influence the patterns and pressure of salt crystallisation within porous materials [13]. In this sense, *K. Zehnder and O. Schoch* [30] investigated the thermodynamics and kinetics of salt transitions with a custom-built system for continuous real time monitoring of efflorescences on-site, using digital cameras and T/RH sensors, and found out that crystallisation-dissolution events may be triggered by very small RH variations (2-5%) and were very pronounced and rapid for some salts, such as mirabilite. 3) The internal structure of the material and the fluid transfer properties are overlooked as well, so the exact point at which the phase transitions occur within the pores is not defined, and the RH can vary widely between the environment and the interior of the porous material [13]. 4) The number of yearly transitions that could start to be considered a risk for the materials is not clearly defined, and therefore further research is needed [31]. The transition thenardite-mirabilite is an exception, because the RHeq for this system can be considered as a damage function, as the pressure generated by the crystallisation would disrupt porous materials [12].

Even so, the phase transitions count may be useful as a rough estimation of the risk of salt weathering in general studies, for example to compare regions or periods of time, as proved by a number of published works. *C.M. Grossi et al.* [13] introduced the notion of climatology of salt transitions, relating the estimated salt damage to the local climate types. The number of dissolution-crystallisation events for hydrated and non-hydrated salt systems were calculated for the environmental parameters recorded in diverse regions of the Iberian Peninsula. The different climate types presented characteristic patterns of salt transition frequency and seasonality, suggesting that the local climate type can be used as a crude indicator of the risk of salt damage when daily environmental data are not available. In agreement with this, the frequency and annual distribution of the crystallisation-dissolution cycles obtained in our work in the Ribeira Sacra correspond well with the clusters of salt transitions determined by *C.M. Grossi et al.* [13] for the climatic particularities of this region. Other researchers [12, 31] used the count of transition cycles to predict how climate change will affect the salt weathering of European cultural heritage. Their results suggest that an increase in the number of transitions is to be expected over the next century in many European regions, including northern Spain, therefore the risk of damage due to salt crystallisation in the Ribeira Sacra might tend to increase in the future.

Regarding the ECOS thermodynamic model, it can be considered an improvement with respect to the cycles count method in certain aspects. Firstly, ECOS identifies the specific salts that would crystallise considering, not only the monitored environmental conditions, but also

the actual ion concentrations determined in the samples. In addition, it investigates the behaviour of salts in complex mixed solutions, as they are in monuments, and how this affects their solubility. For example for the Ribeira Sacra murals, ECOS predicted the crystallisation of niter at the monitored environmental conditions, while the cycles count method did not. This is due to the strong reduction in the equilibrium RH of niter when in mixture compared to the pure salt, which drops from around 95% to below 68% RH. Other authors [26, 30] also observed a reduction of the RHeq in mixtures of salts and an influence in the kinetics was reported [32]: in salt mixtures generally the rate of deliquescence increases and the rate of evaporation decreases, in comparison with single salts.

The results predicted by ECOS in the present research correspond well with the observations made *in situ* in the churches of the Ribeira Sacra: those murals for which ECOS estimated a higher risk of salt weathering, actually present efflorescences and signs of deterioration related to subflorescence (flaking, detachments, cavities, *lacunae*). Additionally, the XRD analysis of the samples of mortar revealed the presence of some of the predicted salts, such as halite in 1P and 2L. Other published works also confirm the coincidence of ECOS predictions with the actual situation in monuments, although some inconsistencies were found. *Storemyr* [33] investigated the salt crystallisation phenomena on the Renaissance mural paintings in the Regalia Room of the Archbishop's Palace in Trondheim (Norway). The ECOS calculations predicted crystallisation when the RH descends below 66-71%, predominantly in the summer, which corresponded quite well with the author's observations on site, although the actual RHeq of the mixture in the summer seemed to be slightly lower than predicted. *A. Sawdy and C.A. Price* [34] used the ECOS program to provide an insight into the salt deterioration problems affecting the C13th wall paintings in the Sacristy at Cleeve Abbey in Somerset (England). The resulting thermodynamic calculations correlated well with the *in situ* observations and recordings, but only after incorporating to the calculations the salt species identified in the efflorescences, which were not included in the material sampled by drilling, yielding unrealistic predictions at first. This supports the sampling strategy adopted in the present study in the Ribeira Sacra, which included both efflorescences and subflorescences from the murals. *K. Zehnder and O. Schoch* [30] observations using their live digital monitoring system were generally in agreement with ECOS predictions regarding the crystalline species that would crystallise and the RHeq at which the sequence would start.

But ECOS has also some limitations. a) The calculations are made for a fixed temperature, generally the annual average, when the equilibrium constant (and therefore salt precipitation) can be influenced by temperature in different ways [12]. A possible solution is to calculate the volume of crystallised salts seasonally. In the present case, the seasonal T variations have only a small influence in ECOS output, lower temperatures causing a slight increase in the RHeq, therefore the use of the annual average temperature in our study seems appropriate. A similar effect of the T on the solubility of the mixture was observed in other published works [28, 33, 34]. b) It does not inform about the phase transition events at the monitored RH. c) The unbalance of the sum of the ions charge may sometimes be remarkable, possibly due to the presence of carbonates and bicarbonates that are not taken into account by the model, which makes ECOS prediction of the salt species that would crystallise less reliable. d) The model does not include gypsum in the calculations. However, according to *C.A. Price* [15] in most cases this is not a problem due to the low solubility of this salt, which would remain in solid state in most environmental conditions under 99% RH, and therefore it would not contribute to the mechanical damage of the material due to volume changes. The author acknowledges in a later work [34] that the solubility of gypsum increases in the presence of other dissolved salts, but not enough to experience deliquescence and recrystallisation due to the changes in T and RH. The observations made by *K. Zehnder and O. Schoch* [30] with digital

cameras on site seem to confirm this: they have observed rhythmic crystallisation of gypsum at moderate relative humidity between 65 and 75%, as a consequence of mixed salt solutions, but no dissolution-recrystallisation events were registered, likely because the solution remains saturated with calcium and sulphate ions, abundantly present in adjacent materials. However the existence of dissolution-recrystallisation cycles cannot be completely excluded, as it could easily have been overlooked due to the limits of image resolution and sharpness.

Combining both methodologies to assess salt crystallisation is an efficient approach to overcome their individual limitations and reflect more precisely the real situation, as shown in our work. *S. Godts et al.* [28] used this strategy to assess the risks of a salt laden limestone C16th mausoleum in Boussu (Belgium), being able to determine frequent transitions in certain locations of the mausoleum, and eventually explain the damage observed and the source of soluble salts in the building.

## Conclusions

The present work demonstrated that the methodologies investigated are easy to apply, low cost and useful for the assessment of the risk of salt decay in wall paintings. The results obtained correspond well with observations *in situ*, as those murals for which ECOS identifies a higher risk of crystallisation already show symptoms of salt weathering and some of the salts that the model predicts will crystallise at the monitored environmental conditions were actually identified in the samples of efflorescences from the murals.

The combination of both methodologies to assess salt crystallisation proved to be the best strategy to overcome their individual limitations: The deliquescence point is calculated for the salt mixture predicted by ECOS considering the ion concentration in the samples, and then the number of phase transitions at the monitored environmental conditions is counted, which allows the determination of the frequency and seasonality of the transitions and the estimation of the risk of salt weathering. The results obtained considering a complex mixture of ions differ strongly from the calculations for the individual salts, sometimes showing a strong reduction of the equilibrium RH.

The salts present in the murals and the environmental conditions monitored in the churches of the Ribeira Sacra pose a risk of physical damage due to salt activity. Remarkable increases of volume of the crystallised salts were estimated, mainly for the murals in Santo Estevo de Ribas de Miño and Santa María de Piñeira. The higher risk of phase transitions is related with the RH fluctuation around 60-70%, therefore the salt crystallisation-dissolution and hydration cycles are expected preferentially in the summer and autumn, remaining in solution in the winter due to the high RH during this season.

These results will be useful to design a plan of conservation of the paintings and environmental control, within a preventive conservation strategy, as they make possible, on the one hand, to assess the risk of physical damage for the paintings due to salt crystallisation depending on the environmental conditions and, on the other hand, to establish the safe ranges of T and RH for conservation within which salt transitions would be kept to a minimum.

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