Tracing back the origins of sodium sulfate formation on limestone as a consequence of a cleaning campaign: the case study on Charité and Espérance sculptures of Chartres cathedral

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Abstract

In 2012, five years after cleaning by Mora paste, sodium sulfate related deterioration was noticed on two XVIIIth century limestone sculptures of Chartres cathedral. This paper presents the results of the diagnostic study and of the conservation intervention performed on these sculptures, with a focus on trials to determine the salt phases responsible for their deterioration. The methodology chosen includes mineralogical and chemical analyses of samples collected on the sculptures during the diagnostic phase and after kaolin-based poultice desalination (XRD, quantification of soluble salts, SEM-EDS), but also mineralogical analyses of the salts extracted from the poultices.

Mora paste chemicals (and in particular EDTA disodium salt) are probably responsible for the quick deterioration of the sculptures through complex and unidentified chemical pathways : at least two of the mineral phases found in this case study are not present in the JCPDS data base on mineral phases. It is proposed to set up an inventory of unidentified phases found in case studies similar to this one, in order to gather the knowledge spread in different institutions, and later to build scientific projects on the topic of EDTA-related deterioration.

Keywords: thenardite, EDTA, Mora, AB57, cleaning, desalination, limestone

1. Introduction

At Chartres cathedral, four limestone sculptures representing the virtues allegories Charity, Esperance, Faith and Humility and originating from its last Jube built between 1765 and 1770, are displayed on the ground floor of the southern Tower. The statues were separated into two groups after the dismantling of the rood-screen in 1866. Charity and Esperance were fixed to a wall located on the ground floor at Chartres Musée des Beaux Arts, in a situation sheltered from rain but exposed to outdoor environment, and probably in contact with the ground *(Figure 1)*. Faith and Humility were placed outdoors, some meters above the ground, against a monumental doorway at Hotel Dieu and later at Chambre de Commerce. No restoration is documented between 1866 and the 2000's.

In 2007, the four sculptures reintegrated the cathedral, where they were placed on pedestals ca.1 m height, back to the walls but without any contact with the masonries *(Figure 1)*. Before being reinstalled, Charity and Esperance were cleaned using "Mora" paste, while Faith and Humility did not undergo any intervention, apart the application of a limewash, clearly visible to the naked eye on their surface. It is believed that this intervention was performed to give the two sculptures an homogeneous colour, as this paint layer covers pollution black crusts.

In 2012, five years after their restoration, strong scaling, granular disintegration and salt efflorescence were noticed on Charity and Esperance sculptures *(Figure 2)*. This led Irène Jourd'heuil, the curator responsible for their preservation to ask for a condition survey, aiming at understanding the reasons for their quick degradation, and at setting up a conservation project.

This paper presents the results of the diagnostic study and conservation of these sculptures, with a focus on trials to determine the salt phases responsible for their deterioration.[1, 2]

2. Analytical methodology

The nature and quarry area of the stone were identified through macroscopic in situ observations and observation, under binocular lens, of centimetric samples which were compared with samples from the LRMH collection of 6000 stone samples originating from 700 French quarries and 500 monuments. The pore size distribution was determined with a Micromeritics mercury intrusion porosimeter. Scales and efflorescence collected on the sculptures were characterized with a powder diffractometer Brucker D8 advance, fitted with a copper anticathode. Some surface samples were analyzed on a JEOL JSM T30, fitted with an Oxford energy dispersive spectrometer (SEM-EDS). A fragment of the poultice relicts

Figure 1: Charity and Esperance sculptures: presentation at Chartres Musée des beaux Arts in 1998 (left), and into the cathedral in 2012 (right)

Figure 2: Face of the statue Espérance: blackening in 1998 (detail of figure 1), scaling and granular disintegration in 2012.

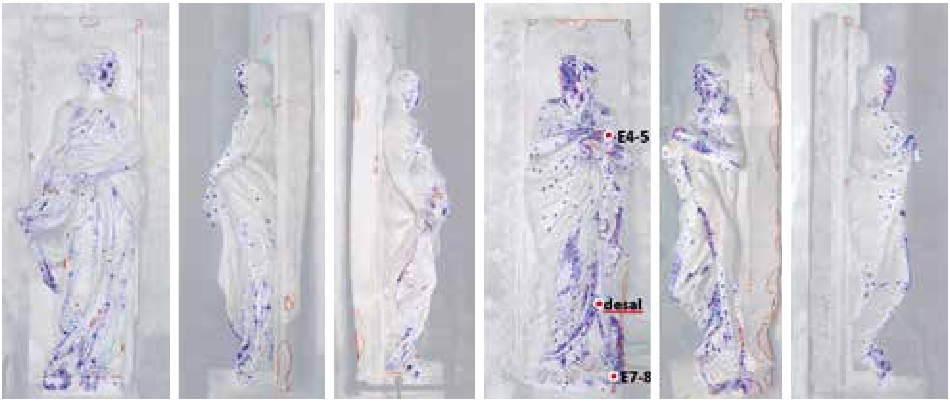

Figure 3: Charity (three images on the left) and Esperance (three images on the right): distribution of stone losses due to granular disintegration + scaling (blue spots), and to mechanical impacts (red lines). Sampling locations are shown as red spots.

found on the sculpture Esperance was analyzed in ATR mode with a Perkin-Elmer SP 100 IRTF spectrometer fitted with a SPOTLIGHT 400 microscope.

The conservation intervention consisted essentially into five successive applications of poultices based on 0.5 – 1 mm sand (Aqua gravel from Aquasand), kaolin (Speswhite from Imerys Mineral) and micron-size calcite (SoCal31 from Solvay). The first set of poultices removed from each sculpture was collected and put in distilled water (6 to 9 Kg / 12.5 L). After setting of the poultice material, the supernatant was collected, filtered and left to evaporate, using a fan to accelerate the process. Pizza-like light brown evaporates were obtained after one month. Crystals of different shapes were collected in the evaporates and characterized by X-ray diffraction

3. Condition survey and analytical results

The sculptures are 1.5 life size and are made of a fined grained light beige and very homogeneous oo-pelletoïdal and micritic limestone originating from quarries near Tonnerre, France. Mercury intrusion porosimetry (MIP) revealed that the stone has a unimodal pore size distribution, centered on 1µm. Its porosity, as measured by MIP, is equal to 20%.

Many millimetric relicts of a paint layer and of a clayish material were found on the sculptures. SEM-EDS analyses performed on the paint relicts revealed that barium sulfate is present locally, suggesting that the paint layer might contain barite as a pigment.

The mineralogical characterization of the clayish material by X-ray diffraction revealed the presence of palygorskite ($Mg_5Si_8O_20(OH).2,8H_2O$) as the main phase, quartz (SiO_2) and calcite ($CaCO_3$). This suggests that the material is an attapulgite poultice, most probably relictual from the 2007 cleaning campaign. These data do not seem at a first sight in line with the testimony of the conservator who worked on the sculptures. He indicated that he had applied "MORA" pads to clean them, after "many unsuccessful trials". He indicated that he had applied "MORA paste" to clean them, after "many unsuccessful trials". The original MORA paste recipe, also known as "AB 57 paste", was proposed in 1972 by Pr. Paulo Mora and his wife Laura Mora from Instituto central per il Restauro, Rome, for cleaning stone buildings. It comprised Water cc.1000; Sodium Bicarbonate g.50; EDTA (disodium salt) g.25; Desogen, a quaternary ammonium salt, cc.10; and carboxymethylcellulose (CMC) g.60. No clay component entered in the original recipe. However, its formulation has considerably changed in France since the original publication by Mora.[3] For instance on Amiens cathedral in 1995, cellulose powder (instead of CMC) impregnated with a water solution of biammonium carbonate was used as a first step of sculptures cleaning. CMC gels are quite difficult to remove from carved substrates; the operation often necessitates much water to be performed. This is probably the reason why other water retentive agents such as cellulose powder or clays, have replaced CMC gels in a number of workshops in France. It is thus possible that the conservator in 2007 considered using a modified MORA paste based on clay to clean the sculptures.

The sculptures were strongly deteriorated: salt efflorescence, granular disintegration and scaling developed on a high proportion of Esperance and Charity surface *(Figure 3)*.

All surface samples collected in deteriorated parts of the sculptures contained calcite ($CaCO_3$) and sodium sulfate crystallized as thenardite (Na_2SO_4) *(Figure 4)*. Some samples contained also gypsum as a minor phase. Another crystallized phase was put in evidence on the diffractograms, but unfortunately it could not be identified *(Figure 4 and Table 2)*. Stone powder samples were collected at different depths through drilling, and their anionic and cationic contents were measured after salt extraction[4], following the recommendation of the Italian Standard Normal 13/83 : dosaggio dei Sali solubili *(Table 1)*.

Excessive sodium and sulfate quantities are put in evidence in the water extracts of the samples collected at 0-0,5 cm depth *(Table 1)*. This analytical result is in compliance with mineralogical data (pre-

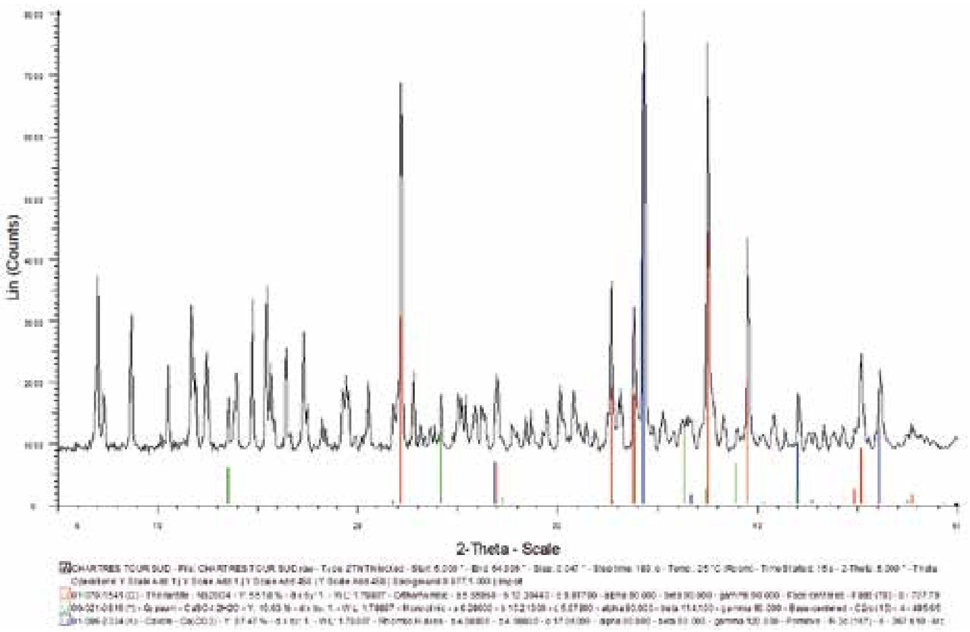

Figure 4: Diffractogram of a typical efflorescence sample collected on the sculpture Esperance. Thenardite (red), gypsum (green) and calcite (blue) are present; most peaks cannot be attributed to an identified mineral phase.

Location	Sample	Depth (cm)	Chloride (%)	Nitrate (%)	Sulfate (%)	Sodium (%)	Potas-sium (%)	Calcium (%)
Left arm	E4	0.0-0.5	0,07	0.06	0,50	0,59	0,01	0,69
	E5	4.0-5.0	0,01	0,01	0,08	0,04	0,01	0,72
Left foot	E7	0.0-0.5	0,09	0,24	0,22	0,64	0,03	0,83
	E8	4.0-5.0	0,06	0,15	0,06	0,08	0,02	0,73

Table 1: Results of the soluble salts quantification at two places of the sculpture "Esperance" Excessive ionic contents are indicated by bold letters. See Figure 3 for samples location.

sence of thenardite). At 4-5 cm depth, sulfates quantities are below 0.1% on both sampling locations, suggesting that the bulk of the sculpture may be considered as not contaminated by this ionic species.[4] Nitrates contents are rather high both close to the surface and in depth in the sampling location located close to the foot of the sculpture (E7-E8).

The same tendency, to a lower extent, is observed for chlorides contents. Calcium contents cannot be interpreted with confidence as some of the calcium carbonate of the substrate most probably got into solution together with salt related sources of calcium during water extraction. These results suggest, considering the location of the sample where nitrates and chlorides were found, that during its stay on the ground at Chartres Musée des Beaux Arts from 1866 to 2006, the sculpture has been contaminated by ground salts through capillary rise. The most probable kick-off event that determined the strong thenardite related decay seems to be the 2007 cleaning campaign, since no heavy stone loss can be observed on the picture taken before

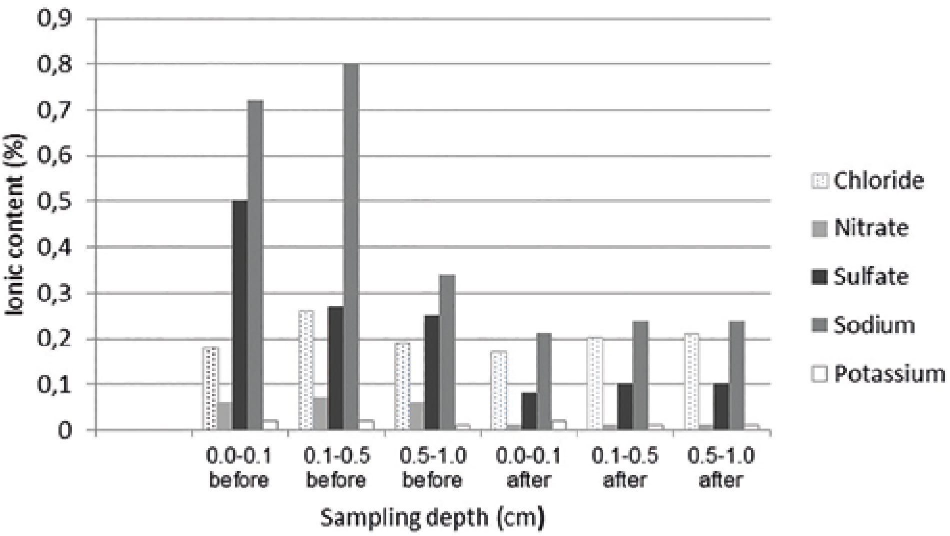

Figure 5: Results of the soluble salts quantification on the sculpture "Esperance. Location of sampling to be found on Figure 3 (ref. "desal")

the 2007 restoration. Interestingly scaling and granular disintegration have appeared preferentially on areas where blackening was present before 2006 *(Figure 3)*, suggesting that some of the chemicals used for cleaning purposes may be responsible for the salt decay. This may be put in relation with the comments of the conservator in 2007: "MORA paste" was used to clean the sculptures, after "many unsuccessful trials".

Considering the nature and depth of the contamination on the one hand, and the pore size distribution of the substrate on the other hand, it was considered a reasonable solution to desalinate the sculptures with kaolin-based poultices.[5, 6]

4. Poultice desalination

After preliminary trials with poultices containing mixtures of various proportions of kaolin, cellulose powder, micron-sized calcite and sand, the following recipes were selected: Charity received five applications of a kaolin:sand:water 1:5:1,5 (vol) poultice. Esperance received one application of a mixture kaolin:nanocalcite:sand:water 0,7:0,3:5:1,5 (vol), followed by four applications of the mixture kaolin:sand:water 1:5:1,5 (vol) on the body parts of the sculpture, while its face received five applications of the mixture kaolin:nanocalcite:sand:water 0,7:0,3:5:1,5 (vol). The reason for a limited application of the mixture containing nanocalcite was that this poultice disintegrated too easily on removal, inducing a strong dust production (health issues and dust deposition on artworks around), while the kaolin/sand mixtures detached more easily into big and coherent pieces. The addition of nanocalcite was a trial to reduce the stone stripping problems during the removal of dried poultices.

Kaolin based poultices being much adhesive, a number of millimetric scales were stripped from the substrate on poultice removal, but the overall results were considered positive, as salt contamination was strongly reduced by the conservation intervention *(Figure 4)*. Kaolin relicts adhering to the surface were gently removed from the surface using a soft brush. Tonnerre limestone having a very light creamy colour, the slight and local whitening due to the presence of minute proportions of kaolin left after brushing did not impair the overall aspect of the sculptures.

The poultice desalination was evaluated on the basis of quantification of soluble ions from zero to 1 cm depth.[7] It appears that the main ions sodium and sulfates have clearly decreased while chlorides contents, relatively high before desalination, remained unchanged as a result of poulticing.

5. Salts extracted from the sculptures

The salts extracted from the two sculptures looked pretty much the same *(Figure 6)*: a light brown colour, and a ring shape sequence of crystals. Samples collected from the outer to the inner ring were characterized by X-ray diffraction *(Table 2)*.

The evaporates contain mainly thenardite. The other major phase is an unidentified phase (ref "unident phase b"), different from the unidentified phase (ref unident phase "a") found on surface samples collected on the sculptures before the desalination intervention. Three other phases are locally abundant: gypsum and halite, and the unidentified phase "a". Calcic EDTA is found in four samples. Interestingly, the sample containing the higher amount of calcic EDTA also contains high amounts of the two unidentified phases. The sample Charity 3 was collected on big flat quadrangular white crystals visible in the two evaporates, suggesting that they are thenardite (or rather mirabilite dehydrated into

Figure 6: General aspect of the evaporates, and overview of the sampling.

Sample	Phases					
	thenardite Na_2SO_4	gypsum $CaSO_4.2H_2O$	calcic EDTA	unident. phase b	halite NaCl	unident. phase a
Charity 1	++++	+	+	++	(+)	++
Charity 2	++	++	tr	++++	++	tr
Charity 3	++++	-	-	-	-	-
Charity 4a	+++	++	tr	++	+	-
Charity 4b	++	++	-	+++	+	-
Charity 5	++	+	++	+++	(+)	+++
Esperance 1	++++	-	-	+	+++	-
Esperance 2	+++	++	-	++++	+++	-
Esperance 3	++++	+	?	++	+	-
Esperance 4	+++	++	-	++	++	+
Esperance 5	++++	+	?	++	++	+
Esperance efflorescence	+++	-	?	-	(+)	+++

Table 2 : Overview of the phases found in the evaporates.

thenardite). Other crystal shapes cannot be attributed clearly to a single phase, although it is clear that the cauliflower-like brown crystals (ref. Charity 2 and Esperance 2) in both evaporates are essentially made of the unidentified phase "b".

Halite and gypsum were probably present in the sculptures before the 2007 cleaning campaign: halite often originates from capillary rise in places where bodies have been buried[1], which is generally the case around churches. Gypsum contaminates very often limestone sculptures which have been exposed to industrial pollution, but can also originate from repairs: in France, plaster of Paris (calcium hemihydrate) has been used a lot for this kind of use. In the present case study, gypsum more probably originates from SO_2 atmospheric pollution, as plaster of Paris repairs are quite localized and absent close to the places where samples were taken.

Sodium sulfate formation is for us related to the 2007 cleaning campaign, in particular the use of a modified Mora paste. Sodium is present in the Mora formula as di-sodium EDTA salt, and as sodium bicarbonate. Sulfates were present as gypsum. Although we are not able to determine the exact sequence of reactions that took place into the stone as a result of Mora paste application, we think that its chemical cocktail is responsible for the formation of thenardite on the artworks. The strong deterioration

	d(nm)	
	Unidentified phase b	Unidentified phase a
14.	-	75287
	-	10283
12.	77839	-
11.	-	87934
10.	-	12769
09.	-	76787
08.	-	80737
	-	66869
07.	59332	39003
06.	-	98898
	36658	67528
	05857	58439
	-	52884
	-	26473
05.	-	95659
	-	66108
	42659	60388
	-	35667
	-	31276
	-	26957
	-	01822
04.	-	53432
	-	45963
	17940	37221
	-	33351
	-	17657
	-	12826
	-	10238
	-	06840
03.	-	92234
	87233	73648
	54945	65018
	50377	61350
	41063	54237

Unidentified phase a: found in samples collected on the sculptures before desalination and in the salt mixture extracted from the desalination poultices

Unidentified phase b: found in the salt mixture extracted from the desalination poultices

Table 3: Inter-reticular distances of unidentified phases

is also most probably linked to the fact that the chemicals could penetrate the stone down to 1cm instead of staying at its very surface: In the original Mora formula the chemicals were kept by CMC, while in this case study attapulgite was used instead of CMC. Attapulgite ability to retain water is far lower: this clay easily changes from non-plastic to fluid over water addition, and in its fluid state, it cannot hold water. We believe that in such a condition, the Mora paste chemicals solubilized in water may have more easily penetrated the stone.

The unidentified phase "a" found in efflorescence may also have played a role in the deterioration process. The unidentified phase b has not been detected in efflorescence, but appears to be a major phase in the salts extracted by the poultice: this phase either was already present in the sculptures and could not be identified because absent in the deteriorated parts we sampled, or was formed via some chemical reaction between the salts present in the sculptures, the relicts of Mora components and the kaolin-based desalination poultice.

6. Conclusion

This case study of a sodium sulfate related deterioration following the application of chemical products is interesting as it points out one of the sources of a quite frequent secondary effect of stone cleaning: the formation of secondary salts, i.e. salts not present originally nor applied during conservation, and far more noxious than the original ones. The newly formed salts may modify the equilibrium relative humidity of the salts present in the substrate, or simply be more dangerous that the original ones (gypsum trapping soiling particles). Here the worst of all has formed: sodium sulfate.

Mora paste chemicals (and in particular EDTA disodium salt) are probably responsible for the quick deterioration of the sculptures through complex and still unidentified chemical pathways: at least two of the mineral phases found in this case study are not present in the JCPDS data base on mineral phases. The literature on stone conservation being very poor with that respect, we propose to build an international data base on mineral phases formed as a result of stone cleaning, and due to the use of EDTA. As a first step, an inventory of stone conservation issues related to the use of EDTA is to be completed.

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