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Case study

Damage mechanism in Tournai limestone – The case of the tomb of Admiral Tromp in the Old Church of Delft (The Netherlands)

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ABSTRACT

The funeral monument of Maarten Tromp, in the Old Church of Delft (the Netherlands), is partially built with Tournai stone, a grey-blackish limestone from the Wallonia region (Belgium). This stone is suffering a severe delamination and scaling, which has, in the course of the centuries, led to a considerable material loss from the surface of some of the stone elements. In order to identify the damage process and define a sound basis for the conservation of the monument, a research plan was set-up including, next to the tests and analyses on the stone, a 1-year monitoring of the microclimate in the church and the investigation of the structure of the monument as well as its connections to the adjacent walls. First of all, the stone type was identified by macroscopic features and by thin section microscopy. The moisture distribution in the monument and in the adjacent walls was gravimetrically determined on samples taken at different height and depths. The content and type of salt in the Tournai stone from the monument were determined by X-ray diffraction and ion chromatography, and the results compared to those obtained for the fresh stone. The analyses showed the presence of considerable amount of gypsum, together with a low content of soluble salts (chlorides and nitrates). The SEM-EDS observations showed that gypsum is mainly crystallizing in cracks between the layers of the material. The damage mechanism and the influence of salt on the decay were further investigated by combining hygroscopic moisture uptake, hygric dilation (RH cycles between 50% and 95% RH) measurements and SEM-EDS observations; all measurements were performed both on stone sampled from the monument and, as comparison, on fresh stone specimens. The results show that gypsum is the main salt present, but its role in the damage is not significant. The naturally thin laminated structure of the stone together with the considerable hygric dilation seem to be the main causes of the delamination observed in this stone.

1. Research aims

This research aimed at assessing the causes of the severe delamination affecting the Tournai limestone of the mausoleum of admiral Maarten Tromp in the Old Church in Delft (The Netherlands). The determination of the cause of the damage is the first necessary step when defining a conservation intervention. In this particular case, questions regarding the cause of the damage, the role of soluble salts in the decay, the risk of further damage and the necessity of any conservation intervention (e.g. desalination) needed to be answered. These answers were obtained by a research approach combining on-site and laboratory measurements, on damaged and undamaged stone samples from the monument as well as on fresh stone from the quarry.

2. Experimental

2.1. Introduction

The monument of Tromp (Fig. 1), completed in 1658, combines different stones of very contrasting colours: white Carrara marble of the sculpture, embossing and decoration, red/grey marble, most probably Rouge Royal, of the columns and a grey-black marble, identified in this research as Tournai (also named Doornik) limestone. A survey of the monument, carried out in 2009, showed the presence of severe structural and material damage. Structural damage consisted in displacements of the pillars and of the entablature and in cracking of the red marble columns. This was considered sufficiently important to warrant the dismantling of the monument. During dismantling it became clear that rusting, and consequent increase of volume, of the anchors connecting the monument to

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Fig. 1. The funeral monument of Maarten Tromp in the Old Church in Delft (The Netherlands).

the wall was the main cause of the observed structural damage.

The white and red marbles suffer only loss of gloss of the polished surfaces. Differently, the Tournai stone shows damage in the form of scaling and delamination of the surface; this has resulted, during the centuries, in material loss up to few centimeter depth.

2.2. Materials and methods

2.2.1. Environmental monitoring

In a first phase of the research, previous to dismantling of the monument, an environmental monitoring of the climate in the church was carried out for a period of 1 year. Relative humidity (RH_{air}) and temperature (T_{air}) of the air were measured by means of sensors for RH_{air} and T_{air} (type EJ HS by ESCORT) at 30 minutes intervals; at the same time, the surface temperature (T_{surf}) on three locations on the monument was measured by thermistors connected to a data logger (type Squirrel data logger Series 2010 by GRANT). The RH at the surface (RH_{surf}) was calculated, according to Castenmiller et al. [1], to check the occurrence of surface condensation. Besides, the data were used to assess the possibility of hygroscopic adsorption and consequent dissolution/crystallization cycles of soluble salts eventually present in the stone of the monument.

2.2.2. Sampling

Sampling was carried out in three campaigns, that took place before (first campaign) and during (second and third campaigns) dismantling of the monument. In total about 150 samples were collected from different materials, at different heights and depths in the monument and the adjacent walls. Samples from the monument were taken both from the surface of the monument (fragments which were already detached) as well from the back of the blocks after dismantling (powder drilled at different depths).

2.2.3. Identification of the stone type

The black limestone of the monument of Maarten Tromp was identified by macroscopic and microscopic petrographic investigations. Additionally to petrographic investigation, the calcite content in the stone was measured by dissolving a sample of limestone from the monument in 2.8 M HNO_3 (nitric acid): the soluble part gives a good indication of the calcite amount.

2.2.4. Measurement of the actual and hygroscopic moisture content of the samples

The moisture content of all the samples was determined gravimetrically, after drying the samples in the oven at 40 °C until constant weight, according to the following formula:

MC (%) = 100 × (initial weight of sample – dry weight of sample)/dry weight of sample.

The dry samples were then stored at 23 °C 96% RH for a period of four weeks, their weight measured again and their hygroscopic moisture content (HMC_{96}) calculated as it follows:

HMC_{96} (%) = 100 × (dry weight of sample – weight of sample after four weeks at 96% RH)/dry weight of sample.

The HMC gives a reliable indication of the presence of hygroscopic salts [2]. The HMC values were used as criteria for the selection of samples for further chemical analyses.

2.2.5. Determination of the salt type and content

The presence of salt was checked by ion chromatography (IC) (Dionex ICS 90) and X-ray diffraction analyses (CRD) (Bruker D8 Advance diffractometer) on a selection of samples. Special attention was given to the study of the salt content in the Tournai stone.

2.2.6. Study of the effect of RH changes on hygroscopic moisture uptake and hygric dilation of Tournai limestone

The effect of RH changes on hygroscopic moisture uptake and hygric dilation of Tournai limestone was studied on two samples from the monument and on three fresh samples from the quarry. The samples were subjected to five RH cycles; each cycle consisted of two weeks at 20 °C/50% RH, followed by two weeks at 20 °C/96 ± 1% RH. After each two-week period the samples were weighed and their hygric dilation/shrinkage (perpendicular to the natural layering of the stone) measured. The change in length of the samples was measured by the Electronic Outside Micrometer, opportunely modified.

2.2.7. Optical microscopy and SEM-EDS observations

The samples of Tournai stone subjected to RH cycles were observed under an optical microscope, before and after the execution of the test (maximum magnification 66x). The main aim of this study was the evaluation of the effect of the RH cycles on the width of the cracks present in between layers of the stone.

Next to optical microscope, Scanning Electron Microscope equipped with Energy dispersive X-ray Spectroscopy (SEM-EDS) (FEI NovaNanoSEM650) was used to study the damage. Two stone samples from the mausoleum and one from the quarry were observed making use of the gaseous analytical detector (GAD); this provides a very short beam gas path length able to minimize spurious signals from scattered electrons during X-ray analysis.

2.3. Results

2.3.1. Environmental monitoring

The environmental monitoring showed that the temperature in the church can be very low during the winter period (the church is not heated). The RH_{air} and RH_{surf} during the winter period can be very high, with the occurrence of surface condensation. The RH is lower in the summer period, with the lowest value measured in July 2010 (47%). There are little differences between the RH_{air} and RH_{surf}, since the temperature of the surface of the monument is very similar to that of the air.

2.3.2. Identification of the stone type

The number of types of black marble used for funeral monuments and other purposes in the Netherlands prior to the 19th

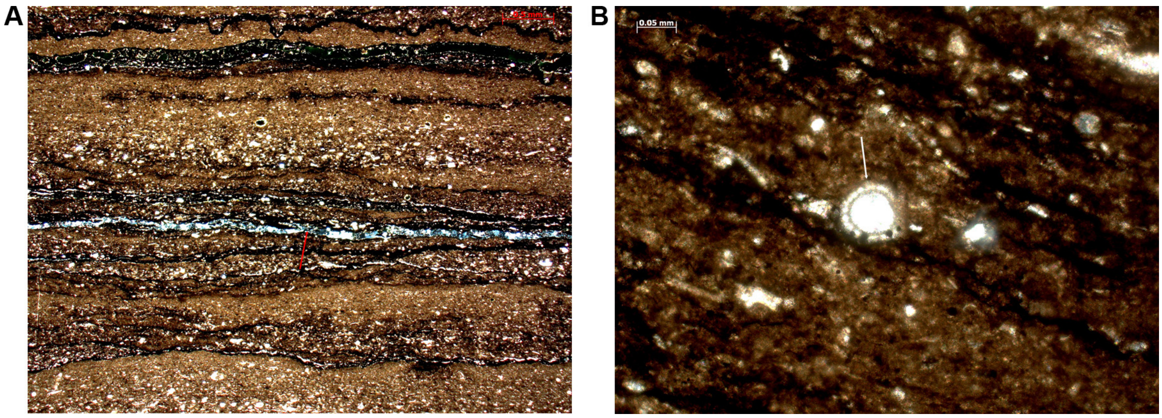

Fig. 2. Microphotographs illustrating the thin laminations and quartz layer (A) and crinoid fragments (B) typical for Tournai limestone, in a sample from the monument of Maarten Tromp.

century is rather limited, most of them being derived from Belgium (for example [3]). One of these, the Tournai limestone, stands out from the others by both mineral composition and microstructure (i.e. thin sedimentary laminations). The Tournai (Doornik) limestone is a limestone from the geological stage Tournaisien (359.2–318.1 Ma), outcropping around the town of Tournai (Doornik), from which both the name of the geological stage and the stone are derived. The Tournai limestone or Calcaire de Tournai is a thin- to medium-bedded, bluish black crinoidal siliceous limestones, with local argillaceous and marl beds and layers with up to 20 cm black chert nodules. This limestone is siliceous, generally consisting of ca. 75–90% carbonate (calcite with occasional dolomite), the remainder being made up by quartz and clay minerals, with minor organic compounds/graphite, pyrite and other opaque phases. Crinoid fossil remains are common [4,5].

The petrographic features of the black marble of the monument of Maarten Tromp (Fig. 2) correspond very closely to those of the Tournai limestone.

Besides, the calcite content determined by chemical analyses (82.3 wt %) is in agreement with that expected for the Tournai limestone [5,6], and it allows to differentiate this stone from the black limestone of the region of Dinant, which has a much higher calcite content.

On the basis of the petrographic investigation and the chemical analyses, the black limestone from the monument has been identified as Tournai limestone.

2.3.3. *Actual and hygroscopic moisture content*

The actual moisture content (MC) in the masonry walls adjacent and behind the monument is generally low (maximum value 2 wt %) and mainly determined by the presence of hygroscopic salts. Exception is constituted by samples collected at 20 cm from the ground level where the presence of rising damp was assessed.

During sampling and dismantling of the monument, it became clear that the upper part of the monument was not in contact with the masonry behind (but only connected by means of anchors) and that the stone blocks of the lower part of the monument constituted the structure of the tomb and not just a cover of a masonry structure. These findings, together with low moisture content in the adjacent walls, excluded the possibility of moisture transport from the masonry to the stones of the monument.

The moisture content in the Tournai limestone varied between 0.3–0.6 wt%, measured in samples from the surface of the tomb, and much lower values, measured in samples drilled from the back of the stone blocks. Values of 0.3–0.6 wt% corresponds, when considering the low porosity of the stone (e.g. 0.54% vol for the Tournai stone from the Lemay quarry in Vaux [7]) to a high degree of water saturation. Surface condensation, the presence of hygroscopic salts and, possibly, the clay content of about 8% on average, mainly illite, of the stone [6], contribute to the measured moisture content. The HMC_{96} in the stone samples from the surface of the monument indicates the presence of hygroscopic salts: in fact, the measured HMC_{96} (up to 1.6 wt%) is higher than the expected equilibrium moisture content of the stone at 96% RH. The last can be estimated, on the basis of the HMC_{96} of the fresh stone and of the samples drilled from the back of the stone blocks, in about 0.5–0.6 wt%.

2.3.4. *Salt type and content*

The type and amount of salts present were determined by the combined use of X-ray diffraction (XRD) analyses and ion chromatography (IC) measurements on powder samples.

The XRD analyses on scales of Tournai limestone from the surface show the presence of gypsum: the gypsum amount is higher at the surface than at the interface between the detached scale and the sound stone beneath. This suggests that crystallization of gypsum is not the main cause of the delamination, otherwise accumulation under the detached layer would be expected. Next to gypsum, calcite and a minor amount of quartz have been detected, both constituents of the stone. No hygroscopic salts could be detected by XRD, indicating that, if present, their amount is below the detection limit of the XRD (3–5 wt%).

The IC results on the Tournai stone clearly indicate the presence of large amount of sulfate, and calcium, and, in some sample from the outer surface, of chloride, nitrate, magnesium and sodium ions (Table 1). It can be supposed, at the light of the XRD results and of the molar ratio between calcium and sulfate, that gypsum is the main salt present in the stone, next to lower quantity of sodium and magnesium salts. As already observed in the case of the XRD results, samples from the outer surface show a higher Ca^{++} and SO_4^{--} content than samples collected in depth at the same location. Besides, the sample from the fresh stone (sample 33-3) show a low SO_4 content. These results suggest that gypsum is most probably the product of a transformation reaction, occurring near the surface of the stone, between calcite and sulfur in the presence of water (probably due to surface condensation and/or hygroscopic adsorption). The hypothesis of migration of gypsum from the gypsum containing mortars used for assembling the stone blocks is not probable, considered the distance between the collected stone samples and the nearest mortar joint and the slow moisture transport expected for this stone. Next to sulfates, some chlorides and nitrates are present in the Tournai limestone from the surface, but their amount can be considered low according to literature [8–10].

Table 1
Ion content as determined by ion chromatography.

Sample	Depth from surface (mm)	Ion content (μmol/g) Cl^-	NO_3^-	SO_4^{--}	Na^+	K^+	Mg^{++}	Ca^{++}
6s-1	0–1	4.90	5.48	81.87	13.86	7.12	28.75	98.41
6d-1	5–7	6.10	6.53	23.56	15.54	10.34	22.01	45.86
53s-1	0–1	2.22	2.57	21.68	6.23	2.99	1.23	37.88
9b-2	2–10	1.01	1.44	45.26	3.62	1.28	1.29	51.79
19-2	0–10	8.36	2.36	24.84	12.26	5.36	3.83	30.32
21-2	20–50	5.96	1.80	9.41	9.06	4.90	3.38	18.05
6-3	0–1	3.13	3.85	27.40	8.56	2.04	3.09	39.56
10s-3	0–0.2	6.83	8.81	116.94	12.34	11.38	29.87	134.77
10m-3	0.2–1.5	2.92	4.48	20.28	5.79	2.26	4.03	32.86
10d-3	2–4	2.86	4.33	7.16	5.46	2.30	3.68	20.51
18-3	0–1	8.46	6.48	36.00	16.51	4.76	3.18	51.14
25s-3[a]	0–10	0.90	0.50	37.81	1.49	0.91	2.88	51.16
25d-3[a]	20–50	0.83	0.44	1.90	1.23	0.71	1.68	15.52
33-3[b]	0–2	2.48	–	1.41	2.67	2.28	2.33	15.37

[a] Sampled from backside monument.
[b] Stone from quarry.

2.3.5. *Effect of RH changes on hygroscopic moisture uptake and hygric dilation*

Fig. 3 reports the hygroscopic moisture uptake of Tournai limestone from the monument (samples 12A-B) and from the quarry (33A-B-C): the weight increase of the stone from the monument at high RH is about five times that of the fresh stone. This is due to the presence of hygroscopic salts (low amount of chlorides and nitrates) and gypsum (the RH of equilibrium of gypsum is about 98%, but this can be lower in the presence of NaCl [11]).

Fig. 3 reports also the corresponding dilation/shrinkage of the samples in direction perpendicular to the lamination of the stone.

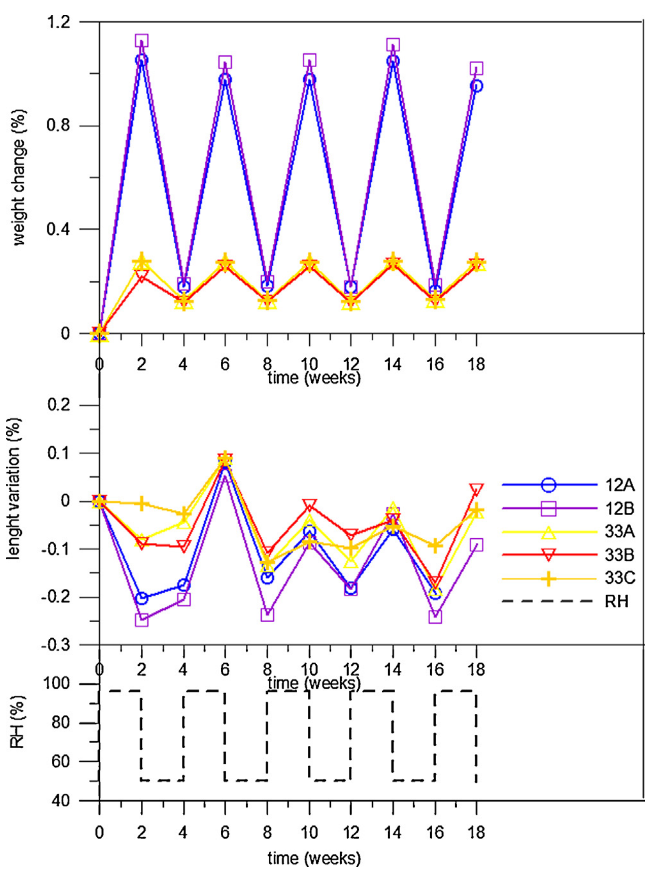

Fig. 3. Hygroscopic moisture uptake and hygric dilation of decayed Tournai limestone from the monument (12A and 12B) and of fresh stone from the quarry (33A, 33B and 33 C) in response to RH changes.

The length variation of the decayed stone from the monument is only slightly larger (max ± 0.15%) than that of the fresh stone (max ± 0.10%). These values are very high for natural stone (see for example [12,13]) and can therefore be considered sufficient to cause damage.

The high hygric dilation and the only slight difference in dilation between the decayed gypsum-rich stone from the monument and fresh stone from the quarry, suggest that the combination of the high hygric dilation, possibly caused by the clay minerals present, and the naturally thin laminated structure of the stone is the main cause of the damage.

2.3.6. *Optical microscopy and SEM-EDS observations*

The stone samples to be submitted to the RH cycles were investigated by optical microscopy before and after the test, in order to study the eventual increase of damage due to the RH cycles. The stone from the monument shows, already before the test, the presence of cracks in between the layers; these cracks are filled with a white deposit. After five RH cycles, no sign of increase of damage, as for example a widening of the cracks, was detected at the used magnification (66x).

SEM-EDS observations on stone samples from the monument show the presence of cracks filled with crystals in between the natural layers of the limestone (Fig. 4). The EDS spectra measured on the crystals show the presence of Ca, S and O; these results allow to conclude that this deposit is constituted by gypsum. No gypsum has been observed in the fresh stone from the quarry. The presence of Al and Si in the matrix of the stone, combined with morphology, indicate the presence of clay minerals.

The SEM-EDS results confirm the finding of the chemical analysis and optical microscopy observations: the gypsum crystals present in the cracks are probably the result of a reaction of the calcite constituting the stone, with water and sulfur present at the surface.

3. Discussion and conclusions

The main aim of this research was to assess the damage mechanism affecting the Tournai limestone of the monument of Tromp in order to come to a sound based plan for its conservation. In particular it was necessary to determine the role of soluble salts in the damage and decide about the convenience of a desalination intervention.

On the basis of the results the following conclusions can be drawn:

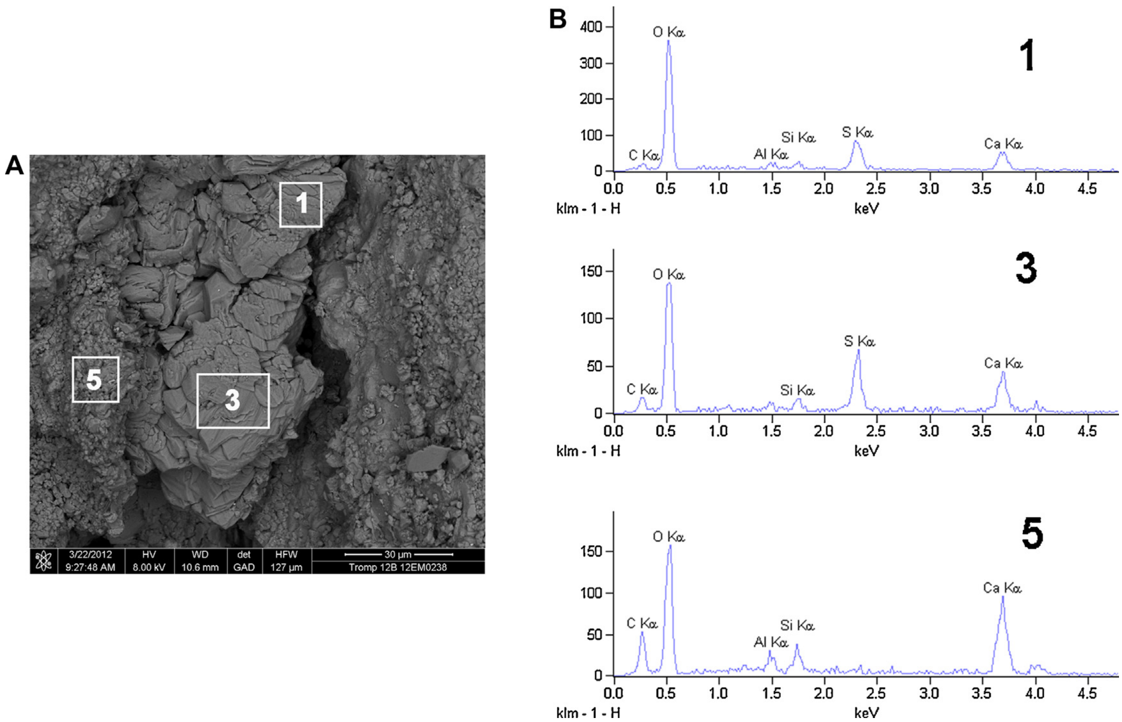

Fig. 4. SEM microphotograph (GAD mode) of gypsum crystals in a crack between layers of Tournai stone from the monument (A) and EDS spectra (B) measured on areas in the stone matrix (location 5) and in the deposit in the crack (locations 1 and 3).

- gypsum is present in the Tournai limestone in a considerable amount, accumulating near the outer surface of the stone blocks. Only small amounts of other salts have been measured. These finding have been confirmed by XRD, IC and SEM-EDS analyses;
- gypsum is not originally present in the stone but has formed or deposited in a later stadium, probably by transformation of calcite into gypsum;
- both the fresh stone from the quarry and the stone from the monument show a very large hygric dilation in response to RH changes, dilation that can be considered sufficient to cause damage. The difference in hygric dilation between fresh and decayed, gypsum-enriched, stone is small. This suggests that gypsum does not play a significant role in the damage. The damage is caused by the combination of the high hygric dilation, probably caused by the clay minerals present, and the naturally thin laminated structure of the Tournai limestone;
- the climate in the church, with repeated occurrence of RH changes and, in some period of the year, even of surface condensation, has enhanced this process.

The results of this research point out once again [12,13] the importance of hygric dilation in clay bearing stones. The presence of high RH and/or large RH variations can significantly enhance the natural ageing of these stones. The phenomenon can be even more relevant in stones, like the Tournai limestone, having a laminated structure. Further research is necessary to better define the relative importance of clay type and content, stone microstructure and climate conditions.

Regarding the question of the opportunity of an eventual desalination intervention, it can be concluded that, being the amount of soluble salts other than gypsum limited and gypsum not the main cause of the damage, desalination does not seem necessary. Moreover, considering the low solubility of gypsum, the low porosity of the stone and, above all, the high sensibility of the stone to moisture (water is necessary for salt extraction), desalination would be very risky.

In order to limit damage development in the future, it is advised to improve the climate in the church by limiting RH changes and avoiding the occurrence of surface condensation.

Acknowledgments

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