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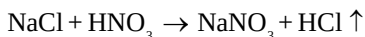
MASS BALANCE EVIDENCE FOR HYDROCHLORIC ACID VAPOR ATTACK ON THE MARBLE OF THE STATUE OF PHOENICIA BY SEA SALT DECHLORINIZATION

R. A. Livingston

Materials Science & Engineering Dept., U. of Maryland, College Park, MD, USA

Abstract

As part of an investigation the role of acid rain in the deterioration of marble outdoor sculpture in the New York City area, a study was carried out on the pink Holston marble of the statue of *Phoenicia* which stands on the cornice of the Alexander Hamilton Custom House in downtown Manhattan. During individual rain storms, samples of rain water falling on the statue and runoff from the statue were collected simultaneously, and the solution chemistry was analyzed by ion chromatography and atomic absorption spectroscopy. Eight complete rainfall and runoff samples were collected during the course of the study. The mass balance is the difference between the rainfall and runoff chemistries and represents the amount of material dissolved from the statue. The mass balances for sodium and chloride showed a significant excess of the chloride/sodium molar ratio over the value of 1.174 that would be expected from sea salt particle deposition. The source of the excess chloride may be the sea salt dechlorinization reaction between sodium chloride and nitric acid vapor:



The hydrochloric acid vapor can then attack carbonate stone. The source of the nitric acid vapor is NO_x air pollutant generated by fossil fuel combustion. The sea salt dechlorinization reaction has been identified in a number of urban areas located on sea coasts by the presence of coarse sea salt particles with surface layers composed of sodium nitrate. It is estimated to be the dominant source of excess chloride deposition in the New York City region. The HCl deposition mechanism accounted for approximately 2% of the dissolution, which is greater than the sum of wet deposition and carbonate dissolution. The remaining calcium imbalance appears to be due to unknown organic acids.

Keywords: New York City, marble, acid deposition, mass balance, organics, sea salt

1. Introduction

Acid rain has been identified as a potential major cause for damage to carbonate stone used for architectural purposes such as marble or limestone. A major complication is that in most urban areas such stone is also exposed to significant amounts of dry acidic deposition due to reaction of the carbonate with sulfur dioxide gas. Discriminating between the effects of sulfur dioxide and acid rain is important not only scientifically, but also for developing air pollution control policies to protect architectural monuments. Since sulfur dioxide comes from local sources, while acid rain is the result of long-range transport and chemical transformation of sulfur dioxide from distant sources, air pollution control policies may be different for local versus remote sources (Livingston, Richard A. 1997).

In order to investigate the relative importance of wet and dry deposition a mass balance study was conducted on a marble statue in New York City (Livingston, R.A.

2008). It was found that wet acid deposition contributed very little to the marble dissolution which was dominated by dry deposition. In the course of the research it was also found that a significant amount of stone dissolution could not be accounted for by either wet or dry deposition. Therefore, the objective of this paper is to extend the geochemical analysis of the data to identify other causes of stone deterioration.

1.1 The mass balance approach

Sabbioni (2003) has reviewed the literature concerning research on the effects of air pollution on stone. There are three different and incommensurate approaches to measuring stone damage: weight change, surface recession and mass balance. The mass balance approach consists of exposing stone specimens to rainfall and then collecting the runoff for chemical analysis (Livingston, Richard A. 1986). Any difference in the concentration of a given ion between the precipitation and the runoff can come only from interactions with the stone. For stones like marble or limestone, which are composed largely of calcium carbonate, the increase in Ca^{2+} in solution is a direct measure of the amount of stone dissolved during a precipitation event. One advantage of the mass balance approach over the other two methods of measuring stone damage is its high sensitivity. The minimum detectable limit for Ca^{2+} can be as low as 20 $\mu\text{g/L}$ (Peden 1983), which implies a surface recession of about 1 unit cell of calcite or 1.7 nm for a single 1 cm rain event. A number of investigators have therefore performed runoff measurements using a variety of experimental designs (Sabbioni 2003).

1.2 The statue of *Phoenicia*

The mass balance experiments were carried out on the statue of *Phoenicia* (Fig.1a) located on the Alexander Hamilton Bowling Green Custom House, formerly the Bowling Green Custom House, in New York City. This was part of a larger program of studies of air pollution and stone deterioration conducted at the site as part of an international program organized by NATO's Committee on the Challenges of Modern Society (Baer *et al.* 1982).

The statue of *Phoenicia* is one of a row of 12 statues representing leading maritime nations that stand on the cornice of the North facade of the Alexander Hamilton Custom House, which is located at the lower end of Manhattan Island (Fig. 1b). Frederick W. Ruckstull received the commission for the statue representing the ancient empire of *Phoenicia*. However, the Custom House's architect, Cass Gilbert, made several major suggestions for the statue's design including the pose, the use of columns and, in particular, the elaborate headdress. The latter was modeled after a sculptural artifact, the *Dama de Elche*, which had recently been excavated in 1897 at Elche, Spain, near ancient Cartagena (Livingston, R.A. 2008).

The marble used for *Phoenicia* is from the Holston marble quarries of East Tennessee. This is a major source of sculptural marble in the United States and has been used in a number of other historic monuments including the National Gallery of Art in Washington, DC. The Holston marbles are fine grained in texture and have characteristic colors ranging from pink to a reddish brown. The marble is essentially pure calcite with minor traces of dolomite and clay stylolites (Dale 1924). The pink color is attributed to traces of hematite.

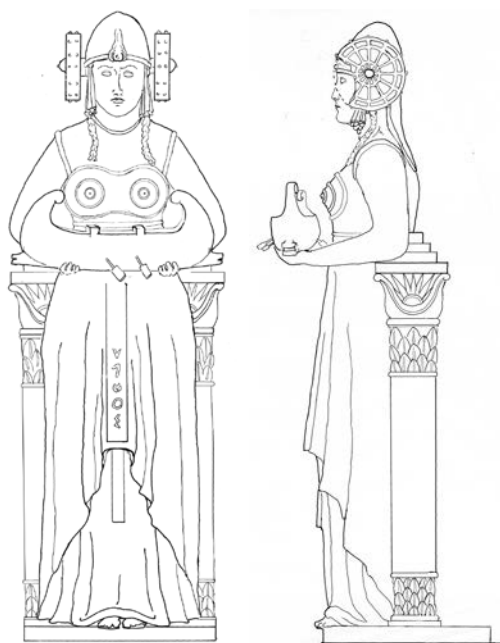


Figure 1a: Statue of Phoenicia

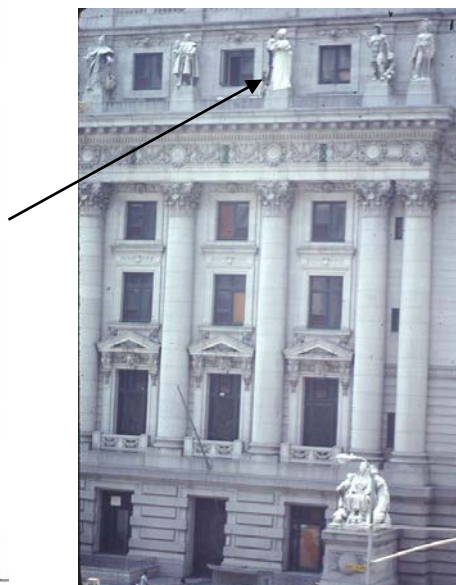


Figure 1b: North Facade, Alexander Hamilton Custom House, Bowling Green, New York City

Phoenicia was chosen over the 11 other statues at the site because of her relatively simple geometry. She is 274 cm tall and stands on a 101 cm by 101 cm base, which is located on the sixth-floor cornice level of the North facade (Fig. 1b). This position, 30.5 meters above the ground, eliminates the complications from groundwater, road salt and other causes of deterioration found at street level. The Statue is mounted in such a way that it is exposed on all sides to the atmosphere and to rainfall. *Phoenicia* was put in place in 1906 and thus had 75 years of exposure to the weather and air pollution at the time the runoff measurements were made. During this period levels of sulfur dioxide in the Manhattan area are estimated to have peaked in the 1950s, but no monitoring data are available. The earliest records, from 1967, show levels as high as $420 \mu\text{g}/\text{m}^3$ (Ferrand and Blade 1969). Subsequent air pollution control measures reduced the level significantly to the point where the concentration of SO_2 averaged $47 \mu\text{g}/\text{m}^3$ at the time of the mass balance measurements (Delaware 1982). Visual inspection showed a characteristic pattern of light-colored stone in the areas washed by rain and darker areas including some biological growth in the rest of the surface.

2. Experimental Methods

The procedure called for collecting simultaneous samples of water of incident rain and of the resulting runoff from the statue. The samples were then analyzed using the U.S Environmental Protection Agency's standard protocol precipitation quality analysis for concentrations of several specified ions, which were: sulfate, nitrate, ammonia,

chlorine, sodium, magnesium, potassium, and phosphate (Rockwell International 1982). Also measured in both types of samples were pH and conductivity.

The runoff collection apparatus consisted of plastic guttering fixed around the perimeter of the base of the statue. Plastic tubing led the runoff by gravity from the gutters to 17 liter containers below the base. Leakage was avoided by the use of inert caulking and Teflon paper barriers.

The incident rainfall was collected in 19 liter glass containers fitted with large plastic funnels. It was found necessary to put out several of these collectors in order to acquire enough sample from a given rain event to provide an adequate volume of water (about 2 liters) to carry out all the specified analyses. These containers remained permanently on the roof as passive samplers, collecting all the rainfall that fell over the duration of the sampling cycle. This approach, in which the collector is always open, also collects particulate matter during dry periods, and is known as bulk collection, as opposed to collectors that collect only during precipitation. After each sample was collected for analysis, the containers and funnels were rinsed with distilled water and put back in position. The analyses were performed by Environmental Protection Agency staff at the Edison Laboratory in Edison, NJ. Atomic absorption spectroscopy was used for the metals and ion chromatography for the anions. The precision of these analyses is typically 1-2%.

3. Results and Discussion

Although it is preferable to collect the samples immediately after each individual rain event, this was usually not possible. In general the samples were taken during the regularly scheduled weekly visits and thus combined several different rain events. A total of 23 runoff samples were collected. However, due to lack of sufficient volume of rainfall samples for the earlier events, only the eight most recent cases could be fully analyzed. These were taken in the months of March through May of 1981. The sampling program had to be discontinued after that time because of the start of restoration work on the Custom House.

Before calculating the mass balances, the solution chemistry was adjusted for carbonate species and ion pairing. The carbonate species present are the result of the absorption of atmospheric carbon dioxide. It is not directly measured in the acid rain protocol, but rather it is estimated from Henry's Law and the association constants of the carbonate species (Livingston, Richard A. 1992). In the pH range usually found in rainfall or runoff, the dominant carbonate species is the bicarbonate ion, HCO_3^- .

Calcium and sulfate ions form a neutral species CaSO_4^0 by ion pairing which accounts for 30% of the total gypsum solubility. The atomic absorption analytical method gives total calcium i.e. the sum of Ca^{2+} and the calcium in. On the other hand, ion chromatography gives only SO_4^{2-} ion, not total sulfate. The algorithm for finding these missing components is given in Nordstrom and Munoz (1985).

After these adjustments to the individual solutions, the runoff-rainfall differences can be calculated. These are presented in Table 1. Also included are columns for total calcium Ca_T , the sum of Ca^{2+} ion and the Ca in the CaSO_4^0 . Similarly SO_{4T} is the sum of SO_4^{2-} and the SO_4 in the CaSO_4^0 . No phosphate ion was detected in any of the solutions. All the ions except H^+ and NH_4^+ showed positive differences. The decrease in H^+ , or increase in pH, is consistent with acid rain neutralization. The NH_4^+ ion showed no consistent trend, which may be due to its instability relative to NH_3 gas. The

increases in Cl^- , Na^+ , Mg^+ and K^+ are possibly the result of sea salt particulate deposition on *Phoenicia*'s surface, given the Custom House's location next to New York Harbor. This is discussed in more detail below.

Table 1. Runoff-Rainfall Differences, mmol/L

ID#	H	$\text{SO}_{4\text{T}}$	SO_4^{2-}	Ca_T	Ca^{2+}	NO_3^-	NH_4^+	Cl^-	Na^+	Mg^{2+}	K^+	HCO_3^-
1	-0.0008	0.77	0.68	0.99	0.90	0.029	0.008	0.169	0.100	0.029	0.014	0.0030
2	-0.0004	1.32	1.08	1.83	1.58	0.035	0.068	0.311	0.165	0.016	0.024	0.0060
3	-0.0048	0.38	0.34	0.60	0.56	0.017	-0.028	0.076	0.061	0.012	0.004	0.0121
4	-0.0049	1.08	0.96	1.25	1.13	0.017	-0.061	0.124	0.061	0.012	0.013	0.0246
5	-0.0250	0.80	0.72	0.98	0.89	0.015	—	0.105	0.048	-0.009	0.007	0.0250
6	-0.0392	0.62	0.50	1.23	1.10	0.007	—	0.096	0.039	-0.008	-0.004	0.0039
7	-0.0075	0.48	0.46	0.38	0.36	0.063	—	0.085	0.052	0.007	0.002	0.0060
8	-0.0023	0.42	0.34	0.92	0.84	0.029	—	0.079	0.043	0.008	0.013	0.0116

3.1 Acidic deposition mass balance

Livingston, Richard A. (1992) pointed out that the total dissolved calcium in the runoff water is the sum of three different reactions, each of which creates a distinctive signature in the runoff chemistry that can be used to estimate its relative importance. The karst reaction, or natural carbonate stone weathering, increases the HCO_3^- concentration. The acid rain neutralization reaction reduces the H^+ concentration. Finally, the dissolution of gypsum, the reaction product of sulfur dioxide gas or ammonium sulfate particulate dry deposition increases, the concentrations of SO_4^{2-} and NO_3^- ions.

In theory, the mass balance for the acid deposition group can be written as:

$$\Delta\text{Ca}_\text{T} = \Delta\text{SO}_{4\text{T}} + \frac{1}{2}\Delta\text{NO}_3^- + \frac{1}{2}\Delta\text{Alk} \quad (1)$$

where Δ is the runoff-rainfall difference operator and Alk is the carbonate alkalinity,

in this case simply as: $\text{HCO}_3^- - \text{H}^+$. defined

The differences for this group are plotted in Figure 2. It can be seen that $\Delta\text{SO}_{4\text{T}}$ is much larger than the contribution of the other anions in every sample. This ion can only increase through the dry deposition process. Thus dry deposition dominates over the acid neutralization and karst processes as the major mechanism of marble mass loss in this situation. Not surprisingly, there is no correlation between the acidity of the incident rainfall and the ΔCa_T ($r = 0.028$). Except for sample pair #7, there is always a significant excess of Ca_T .

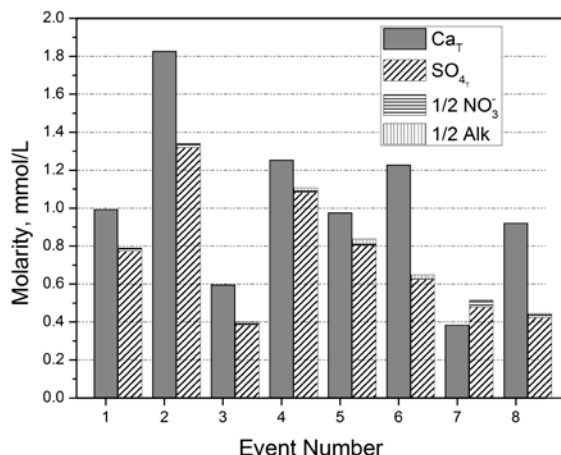
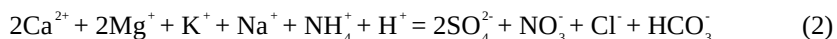


Figure 2. Comparison of Ca_T vs acid deposition components

3.2. Calcium and Chloride Ion Imbalances

The acidic deposition mass balance (Eqn 1) does not take into account all the ions in the solution. As shown in Figure 2, there remains an imbalance after taking into account the acid deposition-related anions. The full electroneutrality condition for the measured ions is:



Inspection of Table 1 shows that the only other significant ions are Na⁺ and Cl⁻, which are presumably the result of sea salt deposition. From the stoichiometry of pure sodium chloride, these two ions should have a 1:1 ratio, but in sea salt the actual Cl:Na ratio is 1.174 due to the presence of other ions in seawater (Zhuang *et al.* 1999). However, as shown in Table 2, in the runoff from *Phoenicia* the ratio ranges from 1.6 to 2.5, indicating a significant excess of Cl⁻ over Na⁺. This excess is thus available to balance the Ca²⁺.

Table 2. Calcium and chloride imbalances

Event #	1	2	3	4	5	6	7	8
Ca-SO ₄ , μmol/L	219 ± 11	506 ± 19	211 ± 7	170 ± 15	171 ± 11	603 ± 12	-95 ± 6	497 ± 9
Cl-Na, μmol/L	69 ± 9	146 ± 16	15 ± 6	63 ± 11	57 ± 9	57 ± 11	33 ± 4	36 ± 8
Cl/Na	1.69	1.88	1.25	2.04	2.19	2.45	1.62	1.82

Apparently a significant amount of the stone is being dissolved as Ca(Cl)₂. However, the simple exchange reaction between sea salt and calcium carbonate expressed as:



is ruled out based on thermodynamic considerations. Sodium chloride and calcium carbonate form a stable equilibrium mineral assemblage under ambient conditions. The reaction of Eqn (3) is in fact the basis for the Solvay process, which is used to produce

sodium carbonate on the industrial scale, but this requires high temperatures and the use of ammonia as an intermediate. As discussed below, another mechanism for chloride attack of the marble is from hydrochloric acid vapor, which is produced by the reaction between nitric acid vapor and sea salt.

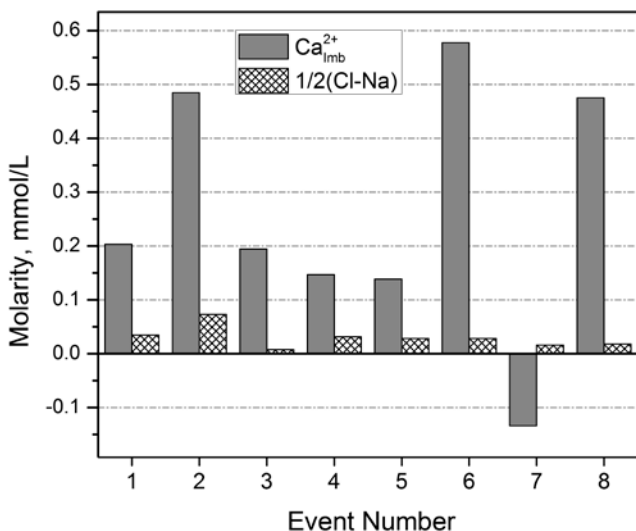


Figure 3: Comparison of Ca^{2+} imbalance vs excess Cl

The Ca^{2+} imbalances are compared against the excess Cl in Figure 3. Event 7 is an anomaly in which the SO_4^{2-} exceeds the Ca^{2+} . This indicates some unmeasured cation. For the other events, even taking into account the chloride effect, there still remains a significant positive Ca^{2+} imbalance in the runoff, associated with some unknown counter ions. The most likely candidates are organic acids, which were not included in the protocol for solution analysis. When the organic content of rain water has been explicitly analyzed, it has been dominated by low-molecular weight carboxylic acids such as acetic, oxalic, formic, pyruvic, *etc.* (Souza *et al.* 1999). These are presumably present in the runoff because of biological attack on the Holston marble. There is visual evidence of biological growth on the surface of *Phoenicia*, but the species have not been identified. Moreover, organic acid aerosols and vapors can be produced by a number of other anthropogenic sources such as chemical plants, incinerators and automobiles (Chebbi and Carlier 1996).

Therefore it is possible to write Ca^{2+} charge balance in terms of five components:

$$\text{Ca}^{2+} = \text{SO}_4^{2-} + \frac{1}{2}\text{NO}_3^- + \frac{1}{2}(\text{Cl}^- - \text{Na}^+) + \frac{1}{2}\text{Alk} + \text{Organics} \quad (4)$$

Dividing the right-hand side of Eqn (4) by Ca^{2+} and multiplying by 100 makes it possible to express the relative importance of each of these components as a percentage of the total amount of dissolved calcium. The mean values of these percentages over all the events, except the anomalous Event # 7, are plotted in Figure 4. Since the percentages all have to sum to 100%, the Additive Log Ratio (ALR) method was employed for calculating the means (Aitchison 1986). As noted previously, the sulfate dry deposition process dominated under the environmental conditions prevailing in the

New York City region in the early 1980s, accounting for over 70% of the dissolved calcium. Next in importance was the inferred organic component, at roughly 24%. The chloride component was third, more than the nitrate and acid neutralization components combined.

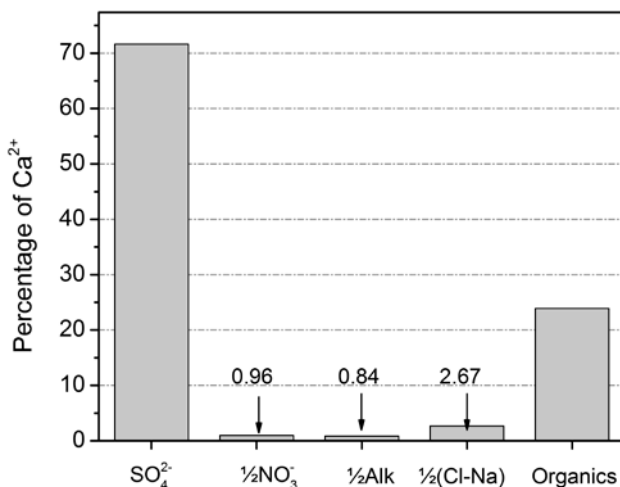
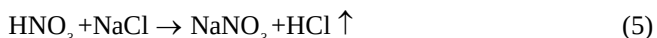


Figure 4. Mean values of components of calcium dissolution. Event 7 omitted

5. Sea Salt Dechlorinization

A possible source for the excess Cl component is the sea salt dechlorinization (SSD) reaction in coastal areas between sea salt particles and nitric acid vapor to produce hydrochloric acid vapor:



The nitric acid vapor is a product of a complicated chain of reactions in the atmosphere beginning with nitrogen oxides (NO_x) emitted from combustion processes (Moussiopoulos *et al.* 1995). Evidence for SSD is found in the bulk chemistry of the coarse fraction of particulate air pollutants, which shows a depleted chloride content relative to sodium (Bardouki H *et al.* 2003). Complementary evidence is the increase in Cl in rainwater samples due to HCl absorption (Shapiro 2007). In addition, TEM examination of individual coarse particles have shown complete Cl depletion (Roth and Okada 1998). A review of the literature on SSD is given by Evans (2003).

Data relevant to SSD in the New York City area are very scarce. A major campaign of particulates monitoring was carried out at the Queens College site in Manhattan in the early 2000s (Drewnick *et al.* 2004). However, the analysis did not include Na or Cl. The coarse particulate fraction (>2.5 μm) did show nitrate concentrations that are indicative of SSD. The nearest available acid rain monitoring station is located at West Point, NY, which is approximately 60 miles inland from New York Harbor (Shapiro 2007). Nevertheless, the rainwater samples contained a significant Cl excess, which the authors concluded is due mainly to SSD.

6. Future Pollution Trends and Potential for Stone Damage

Figure 4 indicates the relative impact of various environmental factors on the dissolution of calcium. However, this ranking is specific to a given geographical location, New York City, and time period, the early 1980s. The relative importance could be different at another location due to climate, topography and distribution of pollution sources. Even for a given location, the impacts can change over time as pollution control measures are put into place or urban and industrial development increases. For example, in New York City the concentration of SO₂ averaged 47 µgm/m³ (17.9 ppb) at the time of the mass balance measurements (Delaware 1982). Since then because of fuel changes and pollution control technology, the levels have decreased. Current levels are roughly 3.7 ppb (NYDEC 2012). Since SO₂ deposition is roughly proportional to concentration (Spiker *et al.* 1995), this implies that the rate of calcium dissolution by this factor has decreased by 80%. Consequently, it would account for only 14% compared to 8% by chlorides, assuming that all other factors stayed the same. On the other hand NO_x related pollution in the region has tended to increase over time. Nitric acid vapor itself is not routinely monitored under EPA regulations. However, monitoring of ozone, which is a precursor to HNO₃, is required. Ozone levels in the New York City region have roughly doubled from 1993 to 2011 (NYDEC 2012), implying that the impact of chlorides on stone deterioration could approach that of sulfate dry deposition.

The sea salt chloride effect could become even more important in other parts of the world where Mediterranean-type climates favor more intense NO_x related pollution such as in the Los Angeles basin (Eldering *et al.* 1991) or Athens, Greece (Moussiopoulos *et al.* 1995). Moreover, in the same coastal areas, increased urbanization in the future would increase both NO_x and organic acid emissions. To monitor these effects, mass-balance studies of stone rainfall-runoff would be highly desirable.

7. Conclusions

The mass balance study of the statue of *Phoenicia* has provided insights into the relative importance of various stone deterioration processes in an urban atmosphere. Concerning the conventional acidic deposition processes, wet deposition i.e. acid rain proved to be insignificant compared to dry deposition. However, in addition to these effects, two other processes were also identified: attack by hydrochloric and organic acid vapors. These may become more significant over time as urbanization continues and sulfur dioxide emissions are controlled. Any future mass balance studies need to include explicit measurement of organic acids.

8. References

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MONITORING FROST SUSCEPTIBILITY OF LIMESTONE FACIES

Tim De Kock^{1,a}, Marijn Boone¹, Jan Dewanckele¹, Wesley De Boever¹, Delphine Vandevoorde^{1,5}, Matthieu Boone², Geert De Schutter³, Eberhard Lehmann⁵, Patric Jacobs¹, Veerle Cnudde¹

¹ UGCT- Research Group Sedimentary Geology and Engineering Geology, Department of Geology and Soil Science, Faculty of Sciences, Ghent University, Belgium.

² UGCT- Radiation Physics Research Group, Department of Physics and Astronomy, Faculty of Sciences, Ghent University, Belgium

³ Magnel Laboratory for Concrete Research, Department of Structural Engineering, Faculty of Engineering, Ghent University, Belgium.

⁴ Department of Conservation and Restoration, Artesis University College of Antwerp, Mutsaardstraat 31, 2000 Antwerp, Belgium

⁵ Neutron Imaging and Activation Group, PSI, CH-5232 Villigen, Switzerland

Abstract

Limestones are among the most frequently used building stones worldwide. Their frost susceptibility has been assessed in many ways, but due to the large amount of existing limestone types and the natural stone heterogeneity, laboratory testing of the freeze-thaw resistance remains a necessary testing method to predict their behavior when used as a building stone. In this research, the frost susceptibility of some frequently used French building stones from the Oolithe Blanche Formation is assessed indirectly and directly in several ways by laboratory testing. The selected stones have similar components (ooids and bioclasts) but differ in dolomite content and thus porosity distribution, resulting in dissimilar water transport properties. The results of experimental freeze-thaw cycles are coupled to the water absorption by capillarity and the saturation coefficient through water imbibition. Mechanical properties as flexural strength provide additional information. Experiments with neutron radiography and X-ray microtomography allow to visualize the water absorption pathways inside the stones. X-ray allows to visualize and quantify the changes in pore structure and the damage propagation.

Keywords: freeze-thaw, Massangis, microstructure, dolomitization, X-ray μ CT

1. Introduction

Limestone from the Oolithe Blanche Formation (Bathonian) are quarried in several places in the Yonne Department (France) to use as building and dimension stones. In this region the Formation is approximately 80 meters thick and well-studied, e.g. for CO₂ storage (Casteleyn *et al.*, 2010). The excavated material is mostly marketed under the name of the location where they are quarried, which is illustrated by names such as Anstrude, Massangis and Vaurion. The Bathonian deposits belong to the Mesozoic sediments of the Paris Basin. Several active and abandoned quarries exist in the neighborhood of the town Massangis, exploited by different owners and with recent activities dating back to 1889 (Dessandier, 2006). Stones from this region play a big role on the Belgian market. They are used in several outdoor applications both in new

buildings as well as for renovation purposes. They are frequently used as replacement material for the local historic building stone called the 'Lede stone' or 'Balegem stone' (Camerman, 1957). Their use became so obvious for restoration purposes of this Lede stone in Belgium, it was called 'massangitis' (Breda, 2005). Nevertheless, Lede stone is a greyish-greenish arenaceous limestone with ochre patina whereas the Massangis is a grey-yellow pure limestone with a pale patina. As such, both esthetical effects after patina formation as well as the microstructure of both stones varies tremendously.

A natural variability exists within the Massangis quarries. Distinctions are mainly based on color, with variants named 'Massangis Claire' and 'Massangis Jaune'. In between, varieties such as 'Massangis Jaune Claire' exist as well. These variants are not regular bedded within the quarry, but rather occur as irregular zones crosscutting the bedding. Studies attributed to this building material report dolomitization/dedolomitization processes as a cause for this variability (Elsen *et al.*, 2005). Since it is stated that they show a difference in freeze-thaw resistance, it is advised to prefer the Massangis Jaune for outdoor applications, as the Massangis Claire is more prone to freeze-thaw deterioration.

Freeze-thaw deterioration is a major cause of damage to natural building stones in moderate and humid climates (Ruedrich and Siegesmund, 2007). The plausible processes causing freeze-thaw deterioration are thoroughly discussed in literature. Two main processes are considered to be volumetric expansion and ice segregation. The first theory is based on the volumetric expansion of approximately 9 % when water freezes to ice at 0° C to 13.5 % at -22° C (Tharp, 1987), exerting pressure on the rock. This damage process requires a high water saturation and rapid freezing and will be limited to the upper few exposed centimeters in diurnal frost cycles (Matsuoka & Murton, 2008). In fact, in 1908, Hirschwald based his saturation coefficient on this volumetric expansion as a first assessment on a rock's frost resistance (Camerman, 1957). In addition, hydrofracture can be related to this process when the volumetric expansion expels pore water and therefore creates a hydraulic pressure.

The ice segregation theory was parallelized from the frost heaving of soils by Walder & Hallet in 1985 and 1986. Based on thermodynamics, they argued the formation of ice lenses due to suction of pore-waters in capillaries and adsorbed on mineral surfaces towards a freezing site to continue the growth of an ice lens, thus exerting a pressure by its growth. They state that repeated low-amplitude cycling at 0 °C may never bring the rock into the favored regime, whereas temperatures in the range of roughly -5 °C to -15° C may favor crack growth. Empirical and physical and numerical modeling (e.g. Murton *et al.*, 2006) has been performed on the ice segregation process in laboratory studies. Matsuoka & Murton (2008) suggest to monitor the process in natural environments, in a context of risk assessment of rock falls and avalanches in permafrost and periglacial environments. Field monitoring of e.g. temperature and dilation on building materials have been done as well in order to understand the mechanism of frost weathering in natural environments (Thomachot *et al.*, 2005).

The prediction of the frost susceptibility of a rock in a certain climate, however, stays a delicate topic. Materials which have proven to be durable in certain regions, might respond differently and less durable when imported into other climatic regions (Cnudde *et al.*, in review). Laboratory freeze-thaw testing always seems advisable for building materials. Nevertheless, the correlation between laboratory tests and natural environments is far from easy (Ingham, 2005). The outcome of laboratory tests should

be interpreted with care. More than an absolute conclusion, the outcome is to be compared with stones whose historical performance is well known in both laboratory and natural environments. In addition, the use of indirect methods and optical petrography is an added value for the assessment of frost susceptibility. Such indirect methods are based on the pore structure or water absorption. Two parameters have been used in Belgium. Firstly, d_{10} (Ingham, 2005) is defined as the pore diameter that corresponds to a 10 cumulative-% intrusion with mercury intrusion porosimetry. Empirically, frost damage should be negligible if $d_{10} > 2.5 \mu\text{m}$. Secondly, the GC-coefficient (NBN B 24-213) is based on the capillary water uptake relative to the total porosity in function of time. The outcome is a number which classifies the rock for certain applications. GC values ≤ -4 indicate a very good frost resistance, whereas stones with number around 0 should not be used in certain frost sensitive applications.

This work characterizes the microstructure of Massangis varieties and compares this information with the material's resistance to freeze-thaw. The Massangis stone type was selected because of its exhaustive use in Belgium and its mutual microstructural variation related to post-depositional processes within similar limestone facies. Freeze-thaw tests are performed in the laboratory to assess their behavior under freeze-thaw conditions to compare this with their microstructure and the use of indirect methods. X-ray microtomography is used for the characterization and visualization of the microstructure and damage patterns such as cracks (Jacobs *et al.*, 1997; Boone *et al.*, 2009; Ketcham *et al.*, 2010; Dewanckele *et al.* 2011).

2. Materials and methods

2.1 Massangis

The 'extreme' Massangis varieties Massangis Roche Claire and Massangis Roche Jaune were selected as they are commercialized in Belgium. The distinction between both is obvious in its color. Alternative commercial names are Vaurion, Val d'Arion, Malpierre, Hervaux, Montaigne & Necker (Dusar *et al.*, 2009) and refer to historic excavations. The rocks are compact, oolitic and bioclastic grainstones with visible shell fragments.

2.2 Characterization methods

A Zeiss Axioscope with camera was used for petrographical description of uncovered 30 μm thin sections stained with Alizarine Red-S.

X-ray computed microtomography (μCT) was performed at the Centre for X-ray Tomography (www.ugct.ugent.be, Masschaele *et al.*, 2007). The experimental setup for the lab-based CT consisted of a FeinFocus FXE160.51 transmission tube operated at 80 kV. Projection images were recorded using a Varian 2520V Paxscan flat-panel detector. The images were processed with the in-house developed software for reconstruction (Octopus) (Dierick *et al.*, 2004; Vlassenbroeck *et al.*, 2007). Image analysis was performed with the in-house developed software Morpho+ (Brabant *et al.*, 2011). 3D visualisation of the CT data was done using the software package VGStudio® MAX.

Neutron radiography, an ideal technique to visualize water uptake inside rocks (Cnudde *et al.*, 2008), was performed at the NEUTRA beamline at the PSI (Villingen, Switzerland). Due to the high difference in neutron scattering for rock and water, water uptake could be visualized in function of time.

Total open porosity and bulk density were determined according to the European standard EN 1936 (1999) using the triple weight method. A total of 50 samples, sized 50 x 50 x 50 mm³, were saturated with water under vacuum of 98.66 kPa

Total porosity and pore throat distribution was assessed using Mercury Intrusion Porosimetry (MIP). This was performed at the Magnel Laboratory for Concrete research (Ghent University, Belgium), using a Thermo Scientific Pascal 140 and Pascal 440 device. The cylindrical samples weighed in between 0.200 – 0.2500 g.

Capillary imbibition was measured on 50 cubic samples of 50 x 50 x 50 mm³ by putting them on supports in demineralized water. The change of mass due to capillary water uptake was measured in function of time. The capillary uptake parameter C [g/m²·√t] is determined by:

$$C = x \frac{m_t - m_i}{A\sqrt{t}}$$

With m_t the weight in g at time t measured on the first slope of the curve, m_i as the initial dry weight and A as the bottom surface of the samples.

Measurements of tensile strength were performed at the Magnel Laboratory for Concrete research using a Digi Con 2000. Samples of 40 x 40 x 160 mm³ were loaded in the center until rupture. Afterwards, the resulting halves were subjected to compressive strength measurements with the same device, using a 40 x 40 mm² loading platform.

2.3 Freeze-thaw testing

Freeze-thaw testing was performed at the Magnel Laboratory for Concrete research. A total of 50 samples of 50 x 50 x 50 mm³ were saturated by progressive immersion and subsequently subjected to 25 freeze-thaw cycles according to NBN B 17-001 (1998). The first 10 cycles had a unidirectional cooling stage to -15 °C in 180 minutes, each followed by a thawing stage in a water bath at 20 °C. This was followed by 15 unidirectional cooling stages to -5 °C, again followed by a similar thawing stage.

3. Results

3.1 Massangis Roche Claire

Massangis Roche Claire is an oolitic grainstone with bioclasts such as echinoderm, shell and coral fragments (Figure 1). The fabric is grain supported with point contacts between the grains. Alizarine Red-S staining reveals a calcite composition for the ooids. A first cementation phase consists of grain-lining microsparite. Secondary, larger sparite crystals filled in the intergranular pore space and formed syntaxial overgrowth on echinoderm fragments.

A moldic mesoporosity with rhombic structure can be attributed to secondary dolomite dissolution. This can be seen on both thin sections and μ CT slices (Figure 1). However, since a considerable amount of dolomite remains in the interparticular space, this dedolomitization process was limited. Interparticular mesoporosity is remnant when the accommodation is not entirely filled with cement. The ooids have microporous outer layers. This can be seen on the μ CT slices, as this microporous material has a lower grey value. An intraparticular meso- to microporosity is sometimes present within the ooids, which is the result of dissolution and possible subsequent dolomite precipitation.

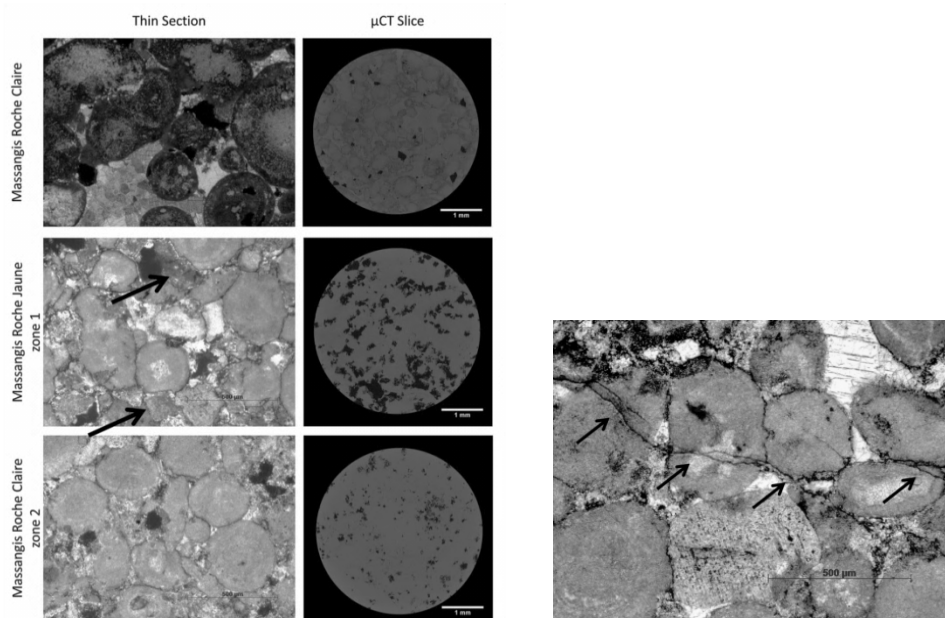


Figure 1. Left: thin sections and μ CT slices of Massangis Roche Claire, Roche Jaune zone 1 and 2. Right: Cemented fissure crosscutting Massangis Roche Jaune.

3.2 Massangis Roche Jaune

Massangis Roche Jaune is also a bioclastic oolitic grainstone, but shows a different texture compared to the Roche Claire (Figure 1). The fabric is condensed grain supported with sutured contacts between the calcite ooid grain boundaries. Rhombic dolomite crystals are present at grain contacts and penetrate into the ooids without inheritance of the ooid texture. Bioclasts consist of echinoderm fragments, shell fragments and corals. The latter two have a calcite edge, but dolomitic internal structure. The cement is a combination of interfering large euhedral dolomite crystals and smaller sub- to anhedral mixed dolomite and calcite crystals. The dominant porosity is a moldic mesoporosity, resulting from the secondary dissolution of dolomite crystals. This is visible in both thin section and μ CT slices (Figure 2). On μ CT slices, a phase that lines the rhombic pores is discernible from the bulk mass, resulting from incomplete dolomite dissolution. Intraparticle porosity is limited to some local ooids.

However, patches with a different microstructure in the magnitude of several cm^3 , occur randomly within the bulk of the Roche Jaune (Figure 1). The latter is referred to as zone 1, while the patches are referred to as zone 2. Zone 2 has similar allochems with sutured contacts, but a lower porosity compared to zone 1. Striking is the absence of euhedral dolomite crystals in comparison to zone 1. Rhombic interparticle porosity suggests the preferential secondary dissolution of dolomite crystals in zone 2, but their size and abundance is rather small in comparison to zone 1. The interparticle cementation in zone 2 consists of a first microsparite cement lining the allochems where no contact dissolution occurred and a second pore filling microsparite mixed dolomite and calcite cement.

Dolomite cemented fissures pierce the fabric and crosscut grains, sutured grain boundaries and microsparite cement (Figure 1). Euhedric dolomite crystals or rhombic moldic porosity occur along this cemented fissures and therefore seem to be related.

3.3 Microstructure

Several techniques were used to characterize the microstructure of Roche Claire and Roche Jaune (Table 1). When possible, the bulk (zone 1) and the patches (zone 2) were treated separately. The different microstructure observed in thin section and μ CT slices is reflected by the results of water absorption and mercury intrusion porosimetry (Table 1 and 2). A significant difference exists in absolute results between the Roche Claire and Roche Jaune, but also within the Roche Jaune a high variability becomes clear.

In general, the Roche Claire has the highest total porosity determined by both water absorption and MIP. From a total porosity of 13.81 vol-%, 87 % is filled with water under atmospheric pressure. MIP reveals a high microporosity for the Roche Claire: over 95 % of the pores have a pore throat smaller than 1 μ m.

In contrast, the general total porosity of the Roche Jaune is lower (10.65 vol-%). Only 70 % of the pore volume fills under atmospheric pressure conditions. The proportion of macro- and mesopores is higher in comparison to the Roche Claire. However, zone 1 and zone 2, show a distinct mutual variance, which makes it ambiguous to generalize the Roche Jaune results. Results from MIP show that the total porosity of zone 1 (13.02 vol-%) is similar to or even exceeds the total porosity of Roche Claire (11.82 vol-%), whereas the total porosity of zone 2 (2.11 vol-%) is much lower. Both have a lower vol-% of microporosity compared to the Roche Claire. The amount of meso- and macroporosity which is present in zone 1, however, lacks in zone 2 which is reflected in the critical and mean pore diameter as determined by MIP.

The tensile strength of both rocks is in the same order of magnitude (Table 1). The compressive strength of the Roche Jaune is higher than the Roche Claire. However, there is a high uncertainty on the results. The measured difference between samples which were separated by only 5 cm in the bedding was up to 67.12 N/mm². This once again reflects the large heterogeneity in the Roche Jaune.

	Porosity [vol-%]	Saturation coefficient	Capillary Uptake Parameter [g/(m ² vt)]	GC-coefficient	Tensile Strength [Nmm ²]	Compressive Strength [N/mm ²]
Massangis Roche Claire	13.81 ± 0.34	0.87 ± 0.02	58.00 ± 4.70	2.06 ± 0.58	4.03	67.69 ± 7.78
Massangis Roche Jaune	10.65 ± 2.48	0.70 ± 0.10	51.41 ± 33.20	-5.37 ± 4.28	4.30	90.43 ± 28.67

Table 1. Results of petrophysical testing.

	Total porosity (vol-%)	Critical diameter [μ m]	Median diameter [μ m]	d10 [μ m]
Massangis Roche Claire	11.82	0.32 – 0.23	0.22	0.32
Massangis Roche Jaune zone 1	13.07	2.14 – 1.62	3.02	19.98
Massangis Roche Jaune zone 2	2.11	0.23	0.09	3.43

Table 2. Results of MIP.

3.4 Indirect methods

Both Roche Claire and Roche Jaune have different capillary uptake parameters. Whilst the capillary uptake is homogeneous in Roche Claire, a huge variability exists within the Roche Jaune. This is visualized by time-lapse neutron images of the capillary uptake (Figure 2). Instead of a steady moving capillary front, the uptake has preferential

pathways and results in locations of higher saturation. These ‘clouds’ of capillary uptake follow preferentially zone 1. Moreover, zone 2 seems to have no capillary uptake at all. When samples are left in place for several weeks, zone 2 areas remain dry whereas neighboring zone 1 areas are saturated. Zone 2 has thus a closed porosity or is separated from zone 1 by a clogged border.

The GC-coefficient is derived from this capillary uptake thus different GC-coefficients can be expected not only for Roche Claire and Roche Jaune, but also for Roche Jaune zone 1 and 2 (Table 1). However, because of the irregular distribution, zone 1 and 2 could not be measured separately. Instead, the high standard deviation is the result of different relative proportions of zone 1 versus zone 2. Despite of the average result (-5.37) which states the Roche Jaune has a very good frost resistance in general, there is a larger spread on a more detailed scale.

μ CT was used to assess the mesoporosity. Pores with an equivalent diameter $\geq 7.47 \mu\text{m}$ (3 voxels) were analyzed with Morpho+. In essence, this is the moldic and interparticular mesoporosity. For each separate pore, the equivalent diameter was calculated together with the amount of neighboring pores it is connected to. The amount of connected neighbors for a given porosity is a fivefold for the Roche Jaune compared to Roche Claire.

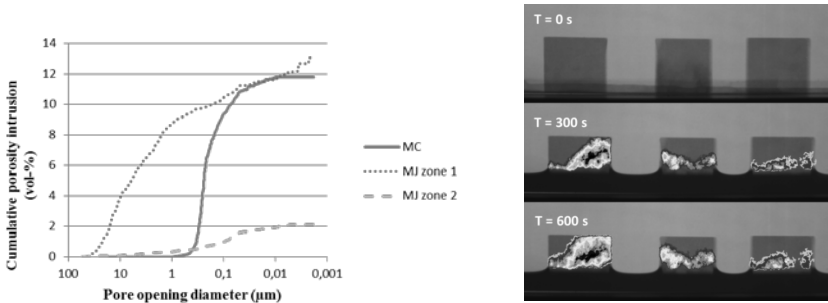


Figure 2. Left: Cumulative pore opening diameter with MIP. Right: time-lapse visualization of capillary water uptake with neutron radiography. Grey values reflect the amount of water inside the stone and the heterogeneity of the water-uptake is visible.

3.5 Direct testing

After 25 freeze-thaw cycles, the hand sized specimen were subjected to visual inspection (Figure 3) and determination of weight loss. In term of weight loss, the damage was low with an average of approximately -0.15 mass-% with a maximum of -1.19 mass-% for the Roche Claire and less than 0.01 mass-% for the Roche Jaune.

The observed damage was different for both varieties. Chipping was the common damage on the Roche Claire at the edges exposed to unidirectional cooling. 1 out of 3 blocks showed significant chipping. Minor chipping occurred at 1 out of 10 samples Roche Jaune. However, fissures and fractures are the more important damage patterns. 1 out of 6 samples shows fissures or fractures. These fissures all occur in zone 1. On μ CT images of a fracture (Figure 3), it can be seen that this fracture is lined with the same phase that is remnant in the rhombic structures. It can be suggested this pore-filling phase is a preferential direction for fissuring, when it forms a continuous body.

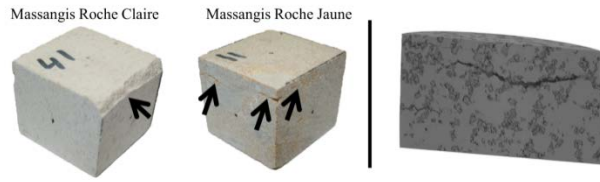


Figure 3. Representative examples of observed damage. Left: chipping (arrows) at the edges of Roche Claire and fracture (arrows) in Roche Jaune. Right: 3D rendering of fracture in Roche Jaune.

4. Discussion

There is a large difference in microstructure between Roche Claire and Roche Jaune. This is the result of different post-depositional processes such as compaction, pressure solution and dolomitization/dedolomitization. Limited compaction caused a grain supported fabric in the Roche Claire with an interparticular accommodation space which was cemented and closed by dolomite cement phases. Limited dedolomitization gave rise to a low percentage of moldic mesoporosity. However, intraparticular porosity in the ooids make up most of the pore space. The Roche Jaune has a more condensed fabric with sutured grain contacts. Intense dolomitization occurred in the bulk of the Roche Jaune (zone 1), however, patches with a lower degree of dolomitization (zone 2) occur randomly throughout the bulk. Both zone 1 and zone 2 have a microporosity of approximately 2 vol-%. In contrast to the Roche Claire, this cannot be observed inside the ooids and this porosity could thus be related to the dolomitization process. Later dedolomitization was more pronounced in zone 1 because of the higher abundance of dolomite. This created a moldic mesoporosity which is unique for the Roche Jaune.

The GC-coefficient and d_{10} point out a possible frost susceptibility for the Roche Claire. This is the expression of the high microporosity remnant in the ooids. Based on d_{10} , the Roche Claire (0.32 μm) could be sensitive to frost action. In contrast, these parameters suggest a good frost resistance for the Roche Jaune. This is the expression of differences in microstructure between both varieties. Whilst the Roche Claire has the highest average porosity, it also has the highest percentage of micropores and in contrast to Roche Jaune, mesopores which can act as accommodation space for ice growth or expelled water are 5 times more isolated according to the μCT analysis. The difference between zone 1 and zone 2 is again reflected in d_{10} . Roche Jaune zone 1 should not be frost sensitive with a d_{10} of 19.98 μm . Zone 2 is also not suggested to be frost sensitive, but its d_{10} (3.43 μm) is positioned much closer to the empirical boundary parameter of 2.5 μm .

Based on thin sections, μCT and capillary water uptake, two zones could be recognized in the Roche Jaune which are responsible for the high heterogeneity within the rock and therefore should be treated separately. However, while zone 2 can be indicated as potentially susceptible to frost by indirect methods, this zone has not the intention of absorbing water, even when the surrounding is saturated. Potential damage however, could occur at the edge between zone 1 and zone 2, where pore waters from a saturated zone 1 are retained from migration.

Freeze-thaw testing illustrate that the Roche Claire and Roche Jaune have a different frost susceptibility, with chipping damage for Roche Claire and fissures and

fractures developing in the Roche Jaune. The difference in deterioration is not related to technical properties such as the tensile strength as these are similar. Both had the same freeze-thaw regime. This suggests the difference in damage arises from their different microstructure.

5. Conclusion

The observations of freeze-thaw testing suggest that the microstructure of Roche Claire is most prone to consequent freeze-thaw deterioration by chipping at the surface. However, the most severe damage occurs in the Roche Jaune. Fissures and fractures seem to be associated with the dolomite phase on places with a higher connectivity. Cemented fissures as observed in thin section might be such a place.

Indirect methods such as the GC-coefficient and d_{10} are reliable methods for the assessment of frost susceptibility (see also: Ingham, 2005) in homogeneous rocks such as Roche Claire. Intuitive interpretations of the relationship between microstructure and frost susceptibility are reflected by these quantitative parameters. However, unconformities in the rock fabric may induce damage, as observed in the Roche Jaune.

Although the varieties between Roche Claire and Roche Jaune, as mentioned in the introduction, are not presented in this work, the Massangis Roche Jaune Claire was incorporated in earlier freeze-thaw testing (De Kock, 2009). These blocks showed little damage. Future work might find out if they lack the zones which cause fracturing.

6. Acknowledgements

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RECORDING OF THE THERMAL EVOLUTION OF LIMESTONES UNDERGOING EXPERIMENTAL ACCELERATED AGEING TESTS.

Ronan L. Hébert¹, Matthieu Angeli², Eric Doehne³, Sandra Dochez⁴ and Andrea Hamilton⁵

¹ G.E.C., Université de Cergy-Pontoise, 95031 Cergy cedex, France

² Department of Geosciences, University of Oslo, 0316 OSLO, Norway

³ Conservation Sciences, Pasadena, CA91103-3263, USA

⁴ INERIS, Parc Technologique Alata, 60550 Verneuil en Halatte, France

⁵ C.M.S.E.I.M.P., The University of Edinburgh, Edinburgh EH9 3JL, UK.

Abstract

Sodium sulfates are widely regarded as the most destructive salts for porous stone, concrete and brick. Thenardite (Na_2SO_4), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and heptahydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$) are the common phases that occur under surface conditions. The heptahydrate phase has been largely neglected in most modern work about salt weathering. However, several recent publications suggest that it could play an important role in geochemical and planetary processes. Therefore its role in the Na_2SO_4 - H_2O system should be clarified.

We present here results of accelerated ageing experiments performed on samples of a micritic limestone under two different ambient temperatures: 20 °C (i.e. below the upper limit of metastability of the heptahydrate), and 30 °C (i.e. above this limit and also below the upper limit of stability of mirabilite). Thermocouples were placed into the samples in order to follow the evolution of the temperature of the stones during the weathering tests. This method allows the recording of exo and endo-thermic reactions that are linked to physicochemical processes, such as crystallization, wetting, evaporative cooling, etc. The experiments show significant differences in the pattern and degree of damage. In the experiment at 20 °C, the loss of material is noticeable, and occurs as crumbling and scaling. In the experiment at 30 °C, we observe just efflorescence with no visible loss of material. The recorded thermal evolution is also different for the two experiments, which provides some clues as to the different physicochemical processes occurring in each situation, depending on the "ambient" temperature.

Keywords: Heptahydrate, Mirabilite, sodium sulfates, accelerated ageing test

1. Introduction

Sodium sulphates are widely regarded as the most destructive salts for porous stones, and other building materials such as concrete or brick (Goudie et al, 1997). ~~Their study is therefore very~~It is important to fully understand their crystallization process in porous networks and, in the future, to find ~~a~~ ways s to prevent or limit their damage to porous materials.

Anhydrous sodium sulphates (i.e. Na_2SO_4) occur in several polymorphic forms labeled I-V (Kracek, 1929; Eysel, 1973; Rasmussen et al., 1996, Rodriguez-Navarro et al., 2000). Phases I, II and IV are high temperature polymorphs (I >270°C and II >225°C).

Phase IV is poorly known (e.g. Rasmussen et al., 1996; Rodriguez-Navarro et al, 2000) but it is considered to be metastable with a small temperature range of existence (210-220°C). Phase V, known as Thenardite (Thn), is the stable phase at low temperature (i.e. close to ordinary temperature), low relative humidity and is the naturally occurring mineral. Phase III is metastable and is frequently observed during evaporation of a sodium sulphate solution (Amirthalingam et al., 1977). Note that there is no indication that phases I, II and IV occur as metastable phases close to ambient temperatures (Steiger & Asmussen, 2008).

Sodium sulphates can also occur as hydrates: the decahydrate (Mirabilite: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; Mir) which is stable below 32.4 °C (Fig.1) and the heptahydrate (unnamed, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$; SS7) which is metastable below 24°C (Fig.1). These limit temperatures of stability (for Mir) and metastability (for SS7) correspond to peritectic temperatures where the hydrates undergo an incongruent melting to Thn. These temperatures are higher when peritectic reactions produce anhydrous form III (34.06°C for mirabilite, 28.525°C for heptahydrate; Steiger and Asmussen, 2008). Although it is known since the middle of the 19th century (Loewel, 1850), the heptahydrate has been largely neglected in almost all modern works about salt weathering. Heptahydrate has been recently the subject of abundant publication (e.g. Genkinger and Putnis, 2007; Hamilton et al., 2008; Hamilton & Hall, 2008; Steiger and Asmussen, 2008, Espinosa Marzal and Scherer, 2008; Derluyn et al. 2011; Saidov et al., 2012) suggesting that it very likely plays an important role into geochemical and planetary processes, and therefore it should be reconsidered in the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system.

Anhydrous Na_2SO_4 (III and V) can form directly upon evaporation of a sodium sulfate solution above 32.4 °C (Amirthalingen et al., 1977) but also by dehydration of mirabilite (Rodriguez-Navarro et al., 2000). Hydrated Na_2SO_4 can form upon evaporation of a sodium sulfate solution below 32.4°C, as well as upon cooling of the same solution. The relationship between the heptahydrate and the decahydrate is not straightforward. There are several studies that show that mirabilite rarely forms directly from supersaturated sodium sulfate solutions (in the absence of seed crystals), and that the first solid to form is the metastable heptahydrate when cooling or evaporating a supersaturated sulfate sodium solution (e.g. Loewel, 1850; Hartley, 1908; Genkinger and Putnis, 2007; Rijniers et al., 2005; Espinosa Marzal and Scherer, 2008; Pel et al., 2010; Derluyn et al., 2011; Saidov et al., 2012).

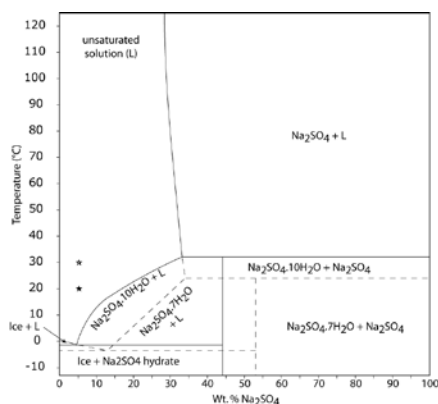


Fig. 1: Phase diagram of the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system. Stars represent the concentration and Temperature for the two experiments.

The destructive effect of sodium sulfates in porous media is attributed to Mir (rather than Thn) especially when forming from highly supersaturated solution originating from the rapid dissolution of Na₂SO₄ (Chatterji and Jensen, 1989; Flatt, 2002; Tsui et al., 2003; Steiger and Asmussen, 2008). SS7, according to Rijniers et al. (2005) is considered to be harmless

Several studies (e.g. Rodriguez-Navarro and Doehne, 1999; Flatt, 2002; Scherer, 2004; Angeli et al., 2010) have shown that temperature plays a major role on salt weathering of sedimentary rocks. For this reason, we present in this study some results of accelerated ageing experiments performed on samples of a detritic limestone under two different ambient temperatures: 20°C, which is below the upper limit of metastability of SS7, and 30°C, which is above this limit and also below the upper limit of stability of Mir. The goal of this experimental study is to evaluate the possible role of SS7 in the damage of porous material by sodium sulfate crystallization. The originality of this study is that we placed thermocouples into the samples in order to follow the evolution of the temperature of the stones during the accelerated ageing tests. We discuss the temperature curves for each phase of the cycle in-with the aim of understanding the processes that occur and that are responsible of-for the damages observed in the two experiments.

2. Material and methods

2.1 Material

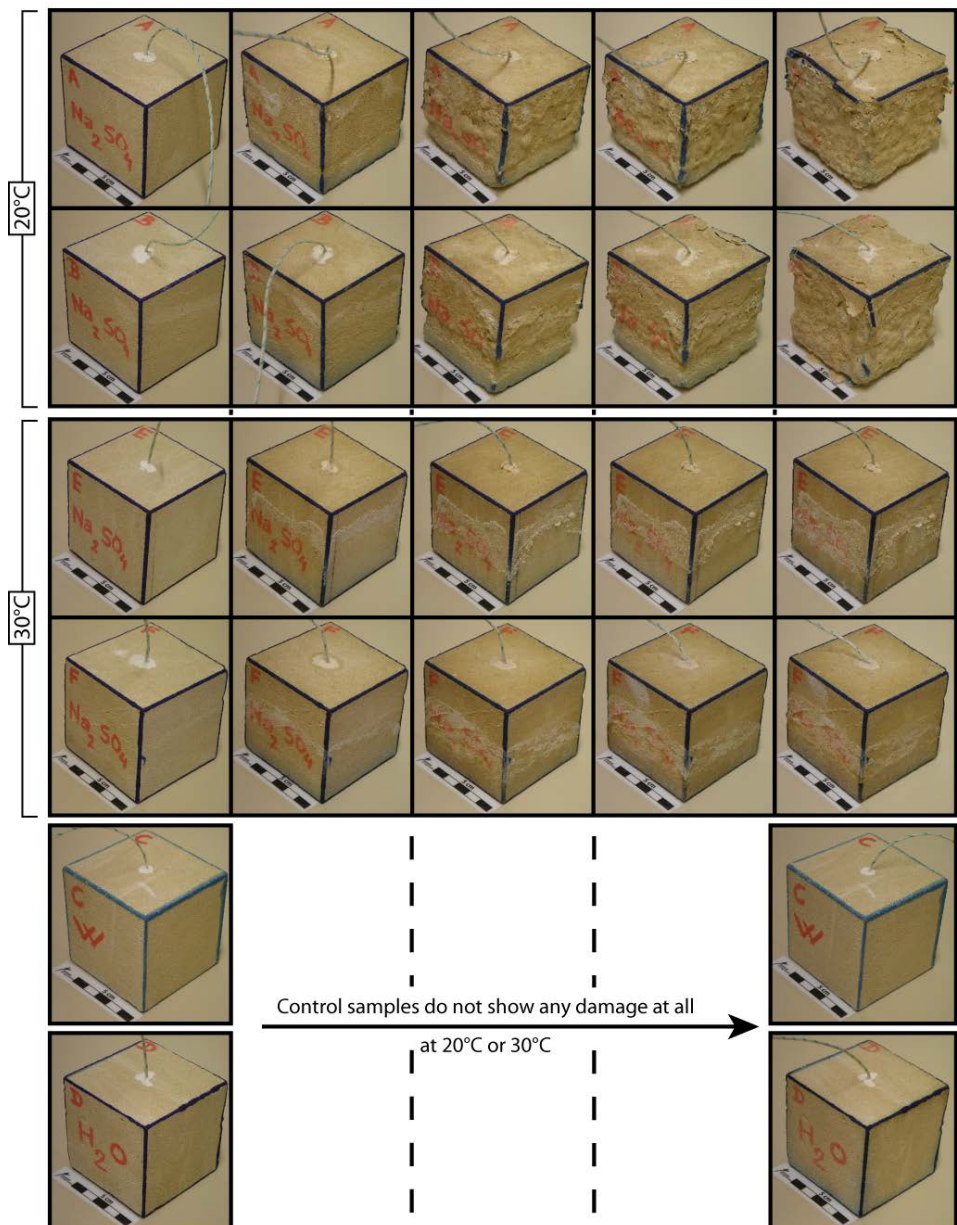
Cubic samples (7 side-cm/side) of a lutetian-aged limestone from the Parisian Basin commercially known as “Roche fine” have been used in this study. This rock has been chosen for several reasons: it is relatively homogenous from onea sample to another, it has been widely used for construction in Paris in-the-past-time (historic buildings and historical monuments), it is one of the rocks-stones imposed-required for use in restoration and construction in the protected areas of the “Ile de France” arearegion, and it is also the rock that has been used in previous experiments from which are-at-the-origin-of-this-the-current study originated (e.g. Angeli et al., 2010). Roche fine It is a fine-grained detritic limestone made of calcite (90%) and quartz (10%) with a very low tensile strength (1.5 MPa), a high porosity (37,2%) with two pore entry sizes (mainly around 20 µm, and another one between 0.03 to 5 µm). Complete hydromechanic properties are available in Angeli et al., 2007).

We used four samples per experiment. All the samples undergo several cycles of washing by immersion withinin demineralized water at room T during-for 6 hours and drying at 105°C until constant weight, in order to remove any possible natural occurrence of soluble salts in the rockstone. A single thermocouple is placed inside-in each cube. It is placed right at the center of the sample. The drill hole realized-to-set upused to insert the thermocouple is filled up with a mixtureing of lime and limestone powder resulting from the drilling of the sample.

The tThermocouples (type K) are connected to a thermal acquisition station (Agilent 34970A) with 22 recording channels. The acquisition station is connected to a personal computer using ® Agilent BenchLink Data Logger software for programming the thermal station and recording data. According to the manufacturer, the accuracy of measurement is ± 0,5°C.

2.2 Methodology

The samples are subjected to 24 hours accelerated ageing cycles modified from the EN 12370 standard test. ~~They are made~~ The cycles consist of three ~~different~~ stages (Fig. 2):



- (i) 2 hours imbibition at “ambient” temperature. The 4 samples are placed in a cooled incubator (® LMS 303NP) where the temperature is fixed at 20°C or 30°C according to the experiment. 2 samples soak in approximately 0.5 mm height of a sodium sulfate solution of 5.5 weight % Na₂SO₄; the two other samples are used for

control and comparison. For one of these samples, the sulfate sodium solution is substituted with demineralized water, and for the other one there is no imbibition solution at all. Each sample is placed into an individual box that is supplied with solution by a system of drop by drop, and with an overflow in order to keep the level of solution constant. The solutions are stored at ambient temperature in the incubator.

- (ii) 16 hours of drying. All the samples are placed in a drying oven (® memmert UE600) at 105°C.

- (iii) 6 hours of cooling. The samples are replaced into the cooling incubator with fixed T so that they return to their initial “ambient” temperature, i.e. respectively 20°C (exp20) and 30°C (exp30).

The samples are weighted and ~~pictured-photographed~~ after each stage. Seven full cycles have been performed during which temperature was regularly recorded (every 3 minutes).

3 Results

3.1. Rock decay vs. cycle

~~Figure-~~ 2 shows the different samples at the different stages of the 7 cycles. The reference samples do not show any damage after 7 cycles. The weight monitoring (Fig. 3) confirms it as their weight remains constant through the full experiment whatever the ambient temperature. It suggests that the limestone is inert with respect to demineralized water.

Fig. 2: macroscopic evolution of the samples during the accelerated ageing cycles

Samples subject to Na₂SO₄ solution at 20°C show intense damage starting with efflorescence (from cycle 1), then contour scaling (from cycle 3), crumbling, and desquamation leading to an important change of shape. The distribution of the damage is heterogeneous. An important loss of material is observed at the bottom of the samples from cycle 4. It seems related to a granular decohesion as suggested by the presence of loose material at the end of the imbibition stage (starting from cycle 3). Vertical faces are more affected by crumbling and the top of the samples by cracking and desquamation. On the opposite, samples in exp30 do not present any major damage but just efflorescence that starts to occur as soon as cycle 1 and increases as the cycles go by. The monitoring of sample weight during cycles (Fig. 3a) shows consistent results with the shape evolution described above. All the samples undergo a similar weight increase during the two first cycles, but the evolution differs from cycle3. Indeed, samples in exp30 show a continuous and progressive weight ~~raise~~gain, while samples in exp20 show a smaller weight increase during the third cycle, before undergoing weight decrease from cycle 4. All these results are consistent with previous ~~works-research~~ (Price, 1978; Angeli et al., 2007, 2010).

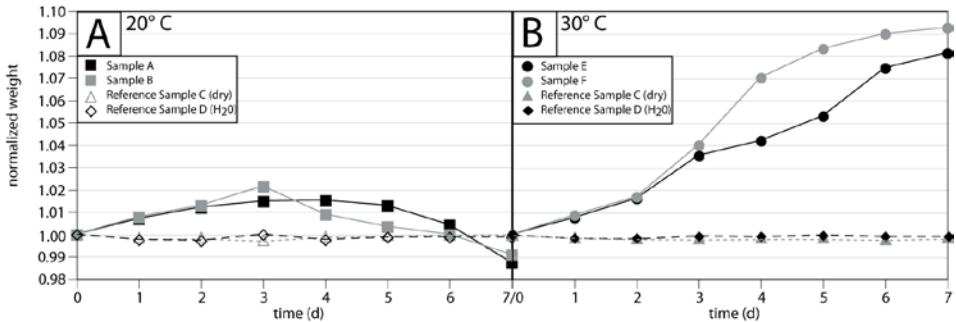


Fig. 3: Weight evolution of the samples in dry state at 20°C (A) and 30°C (B)

3.2. Temperature evolution of the control samples

The temperature curves for the "dry" reference samples are shown on Fig. 4. The curves are very regular. They show in particular a constant and high heating rate of the samples during drying until reaching a plateau at 105°C. Then a progressive and constant decrease of T is observed during cooling until reaching the ambient temperature where a second plateau is observed. This indicates that the studied limestone presents an inert behavior with respect to temperature. T curves are consistent with the model of heat diffusion through the rock.

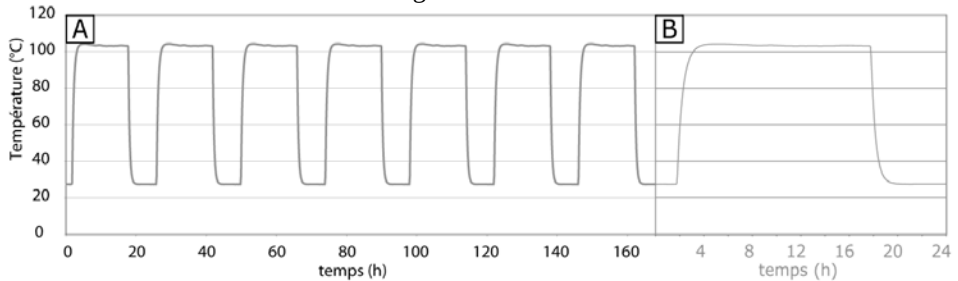


Fig. 4: Temperature evolution of the "dry" reference during the 7 cycles (A), and for a single cycle of 24 hours (B). The Temperature profile is in exp20.

The temperature curves of reference samples undergoing imbibition by demineralized water (Fig. 5) are also very regular and similar whatever the ambient temperature. During wetting, the temperature of the sample decreases (-8 °C in exp20, and -6°C in exp30). This is due to the evaporative cooling. The drying period is characterized by a variation of the heating rate. First we observe a rapid increase of T until a sort of plateau at ~59°C, then a deceleration of the T increase up to an inflection point at ~85°C where it becomes more rapid again (but not as much as the beginning of drying) until reaching the final plateau at 105°C. The variation of the heating rate indicates the occurrence of two endothermic reactions, the first one requiring more energy than the second one. The first one leading to the ~59°C plateau, would correspond to the departure of water on the surface as well as the water trapped in the 20µm size entry pores, the second one (inflection point at 85°C) would correspond to the departure of the water trapped within the small entry size pores. Cooling is characterized by a rapid, progressive and continuous return to ambient T.

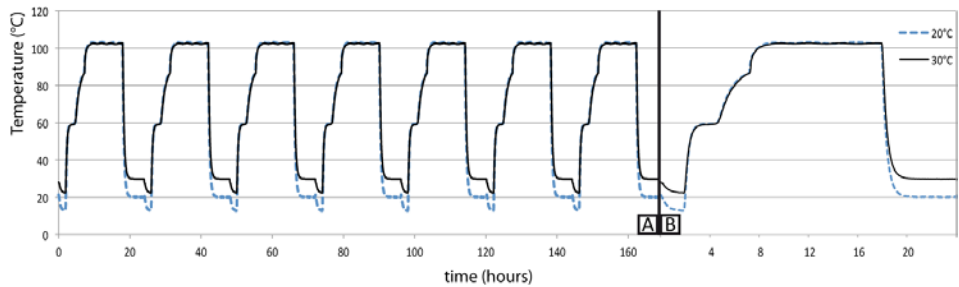


Fig. 5: Temperature evolution of the reference samples undergoing imbibition by demineralized water during the 7 cycles (A), and for a single cycle of 24 hours (B).

3.3. Temperature evolution of the samples subject to salt weathering

Before discussing the different stages of the cycles for each experiment, it is worth noticing that the first cycle is always very different from the following cycles that are more repetitive, as if the first cycle is a transitory phase (Fig. 6). The difference between cycle 1 and following cycles is the absence of salt in the porous network of the stone at the beginning of the imbibition. Therefore cycle one will not be discussed in this study, in particular the drying stage on which we cannot rely.

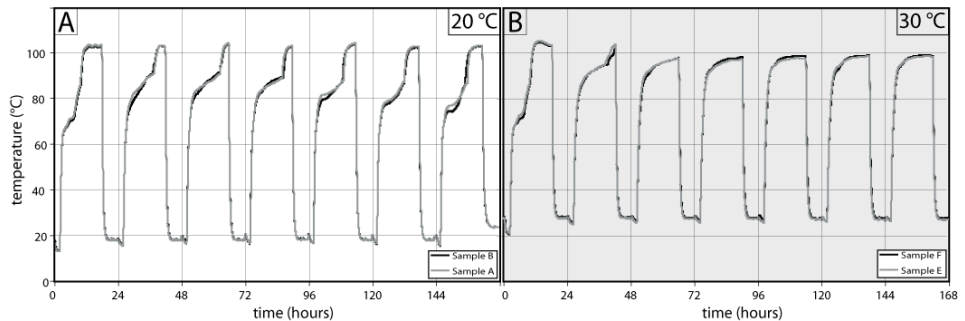


Fig. 6: Temperature evolution of samples undergoing accelerated ageing cycles with sodium sulfates at 20°C (A) and 30°C (B).

3.3.1 Evolution of the temperature during imbibition

First imbibition is characterized by a significant temperature decrease of several degrees ($\sim -5.5^\circ\text{C}$ in exp20, and in exp30) that lasts all along this stage. From cycle 2, the imbibition is characterized first by a temperature rise immediately followed by a fall of temperature. The temperature rise matches with the hydration of the system, which leads to the dissolution of the salts (Thn?) formed during former drying period. Depending on the salinity and T, the rehydration of the system can also correspond with the formation of hydrates. This interpretation is besides consistent with the lack of T increase during the first imbibition as there is no salt in the sample at the beginning of the experiment. Temperature decrease is due to evaporative cooling as in the first imbibition.

It is worth noting that the T rise is more important in exp20 than that in exp30 (more Mir crystallized). In a similar way, the T decrease due to evaporative cooling increases progressively with cycles in exp20 whilst it decreases in exp30. There are then

several chemical phenomena ~~to~~ occur during this part of the cycle, which ~~also~~ corresponds to the major (if not single) phase of damage~~ing~~.

3.3.2. Evolution of the temperature during drying

The drying behavior is very different during the first cycle ~~and~~ than during the ~~other~~ subsequent cycles.

In exp20, the drying period can be decomposed into 4 stages: (i) rapid heating, similar to what happens on the reference samples; (ii) slower heating period; (iii) rapid heating again, same velocity ~~than~~ as in first stage; and (iv) temperature step at 105°C (plateau). The differences in the drying period ~~occur~~ all occur during the lower velocity heating. Comparing this velocity to the dry sample velocity shows that an endothermic reaction occurs at this moment, and that this reaction draws its energy ~~for~~ from the heat ~~produced~~ by the oven. There are several features to be ~~noticed~~ noted in these changes:

- the drying velocity decreases progressively from the 2nd cycle to the 5th cycle
- from the 5th cycle to the end, the temperature remains constant for a period and then starts to increase again
- ~~t~~ The duration of the step at 105°C increases at every cycle.

It ~~looks like~~ appears this endothermic reaction requires more and more energy at every cycle, showing that there ~~is~~ are more and more reactants (salts) at every cycle. Since the salt content in the sample increases at every cycle, we can assume that the hydrate (Mir?) production during the imbibition (damaging) stage increases accordingly. Thus there is a larger amount of hydrate to dehydrate.

From ~~now we will call~~ this point, the "evaporation duration" is defined as the time necessary to reach 105°C. It is a proxy for the amount of time, ~~which is~~ needed to remove all the water in the sample. ~~This~~ The evaporation duration increases until the ~~apparition~~ appearance of decay. ~~It~~ This suggests that the efflorescence partially ~~blocks~~ the pores ~~entries~~ at the surface, thus reducing the evaporative surface. Once the decay starts at cycle 4, the evaporation duration is progressively reduced. This increase in the drying velocity shows that the decay of the surface creates cracks and/or reduces the sealing efficiency of the salt crust.

The drying stage in exp30 is much simpler. The initial drying velocity is similar to the reference sample until water starts to evaporate. Then the evaporation velocity starts to decrease, which corresponds to the evaporation of water in the sample and the precipitation of Thn. The remaining bulk (stone + Thn) is then heated to 105°C. ~~This can be correlated with the fact that no crystallization or very~~ Apparently very little of the damaging hydrated phase occurred during imbibition, ~~and that~~ no damage has been observed in the sample after 7 cycles. Mir is a mineral, ~~which~~ that grows easily but nucleates very seldomly. A possible explanation for the lack of Mir crystallization in exp30 could be that since Mir is difficult to nucleate (Hartley et al., 1908), it could need an intermediate heptahydrate phase nucleation to be initiated and later ~~precipitate~~ grow from ~~this~~ the heptahydrate nucleus ~~in case of~~ as saturation increases by evaporation or cooling (but T is over the limit of metastability of SS7 in this precise case). Another explanation ~~(~~ — according to the phase diagram) is that until supersaturation ~~has not been~~ is reached, no Mir can precipitate, and ~~when once~~ it has, there will be just little only a small amount of Mir ~~to~~ crystallizes.

3.3.3. Evolution of the temperature during cooling

The temperature evolution during cooling is more straightforward. It requires about 2 hours for each sample to return to its ambient temperature from the peak of T achieved at the end of the drying stage (Fig. 6). This cooling is fast (~50°C/hour) at the beginning, and slows down when approaching ambient T. We can consider that all the samples have returned to their ambient T after 2 hours and therefore, they do not undergo further temperature variation until the beginning of next cycle.

4 Conclusion

After 7 complete cycles of 24 hours, the samples at 20°C and 30°C show completely different damage patterns as well as different temperature curves. It shows illustrates the difficulty to-of completely removinge totally the water from the rock under certain conditions--as illustrated by the impossibility to-of reaching 105°C at the end of the drying period for the experiment at 30°C. It-This suggests that the crystallization of salts can fill in the pore entries, trapping sodium sulfate solutions or more likely hydrated phases. It requires either more energy or a longer period of drying to release water from the samples. This result raises questions about the accuracy and the relevance of the standard stone durability tests for stones.

The evaporative cooling phenomenon shows that imbibition is a favorable stage for the precipitation of sodium sulfate hydrates, especially if the concentration of the solution is close to supersaturation. EThe evaporation during this stage can trigger nucleation, and the cooling favors crystal growth.

The temperature profiles of this experiment do not allow-enable distinguishing-the positive identification of two different hydrates. Supersaturation is achieved sooner at 20 than 30°C which drives more hydrates to precipitate during imbibition. In addition, as complete dehydration of the sample is not reached in exp30, there is less (or even no) Thn to transform during imbibition. Therefore this-study-does-the current results do not allow estimating-the-possible-an estimage of the role of SS7 in the weathering of rocks by sodium sulfates.

Finally, this study shows that the-following-of-recording temperature cycles can be provide a simple and cheap-inexpensive method that allows-enables the-observation-of-monitoring exo/endothemic physico-chemical processes such as phase crystallization. It can be useful to identify mineral precipitation, sequences of crystallization and the important -or-even- stages (wetting, evaporation, cooling) that are involved in rock damages.

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FABRIC INFLUENCES ON MICROCRACK DEGRADATION OF MARBLES

Victoria Shushakova¹, Edwin R. Fuller¹, Jr., Florian Heidelberg² and Siegfried Siegesmund¹

¹ *Geowissenschaftliches Zentrum der Universität Göttingen Goldschmidtstrasse 3,
37077 Göttingen, Germany*

² *Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth, Germany*

Abstract

Microstructure-based finite element simulations were used to study an actual degradation phenomenon of marble structures, microcracking. Microcrack nucleation and growth were characterized, as were their dependence on grain shape preferred orientation (SPO), lattice preferred orientation (LPO), grain size, marble composition and grain-boundary fracture toughness. Three extremes of shape fabric or SPOs were analyzed: equiaxed grains; elongated grains; and a mixture of equiaxed and elongated grains. Six LPOs were considered: a random orientation distribution function (ODF); an ODF with strong directional crystal texture generated via March Dollase fiber-texture; and four actual marble textures, as measured by electron-backscattered diffraction (EBSD). Three grain sizes were considered: fine grains of order 200 μm ; medium size grains of order 1 mm; and large grains of order 2 mm. The fracture surface energy for the grain boundaries was chosen to be 20 % and 40 % of the fracture surface energy of a grain, so that both intergranular and transgranular fracture were possible. Simulations were performed for both heating and cooling by 50 °C in steps of 1 °C. Microcracking results were correlated with the thermoelastic responses (indicators) related to degradation. Certain combinations of SPO, LPO, grain size, grain-boundary fracture toughness and marble composition were shown to have a significant influence on the thermal-elastic response of marble. For instance, thermal stresses and elastic strain energy were a strong function of LPO. With increasing LPO the strain energy density and the maximum principal stress decreased. Given the same morphological properties and crystallographic texture, calcite showed larger thermal stresses than dolomite, as well as calcite has an earlier onset of microcracking upon heating and cooling, and a greater area of microcracking at a given temperature differential.

Keywords: marble, finite element simulations, EBSD, microcracking, elastic strain energy density, maximum principal stress, thermal expansion anisotropy

1. Introduction

Marble has been used as decorative and constructive material for centuries. Many historical monuments, sculptures, and façade claddings are made from marble due to its workability, pureness and bright colour. However, marbles can be particularly sensitive to weathering and to degradation, and hence can have limited durability. Such deterioration phenomena depend mainly on ambient climate. Many experimental studies have shown that thermal heating and cooling is responsible for the degradation of marble, e.g., Kessler (1919), Battaglia et al. (1993), Winkler (1994), Siegesmund et al. (2000), Zeisig et al. (2002). Studies of the mechanisms of deterioration are important for protecting historical heritage.

The main rock forming minerals in marble, calcite and dolomite, have large anisotropy in their coefficients of thermal expansion. Due to the thermal expansion anisotropy between the adjacent crystalline grains residual stresses are generated predominately at triple junctions and along the grain boundaries, which governs a granular decohesion of stone with time (Siegesmund et al. 2000).

Microstructure-based finite element analysis was used to elucidate these stresses and to simulate an actual degradation phenomenon, microcracking. Such modelling is in good agreement with actual experiments. It has been showed in experimental studies by Ruedrich et al. (2002), Zeisig et al. (2002) and Siegesmund et al. (2008) that the shape preferred orientation (SPO), lattice preferred orientation (LPO), and grain size can cause different amounts of residual strain. Shushakova et al. (2010) pointed out that certain combinations of SPO, LPO, and their directional relationship have significant influence on the thermomechanical response of marbles.

The goal of the present study is to investigate crack initiation and propagation, as well their dependence on different fabric parameters. Simulations were performed for both heating and cooling by 50 °C in steps of 1 °C. Microcracking results were correlated with the thermoelastic responses related to degradation, such as elastic strain energy density and maximum principal stress.

2. Methods

2.1 Shape fabric and textures

Microstructure is the geometric input for simulations via finite element analysis. To investigate the influence of shape fabric on thermoelastic response, several extremes of SPOs were analyzed: equiaxed grains; elongated grains; and a mixture of equiaxed and elongated grains (Fig. 1). Microstructures were generated by a grain growth algorithm, details could be found in Ito and Fuller (1993); Saylor et al. (2004); Saylor et al. (2007), Shushakova et al. (2010). The microstructural images have a resolution of 1,000 x 1,000 pixels.

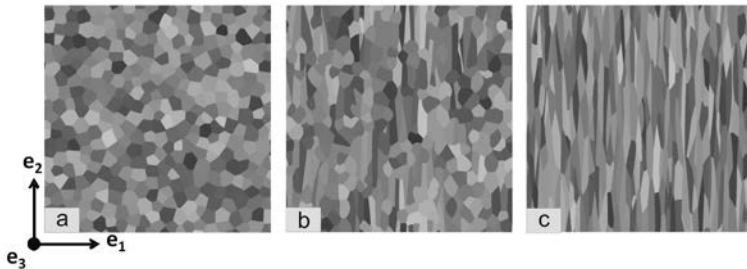


Figure 1. Microstructures used for the finite element analysis: **a.** an equiaxed microstructure of 382 grains; **b.** a mixed microstructure of 347 grains; **c.** an elongated microstructure of 312 grains. The coordinate system, e_i , is also indicated, where the e_2 direction is parallel to the SPO; the e_1 direction is perpendicular to the SPO and in the plane of the microstructure; and the e_3 direction is perpendicular to the SPO and out of the plane of the microstructure.

Orientations assigned to each grain were either generated from a March-Dollase fiber texture orientation distribution functions (ODF), Dollase (1986) and Blendell et al. (2004), (see Fig. 2), or measured with electron back-scattered diffraction (EBSD) on actual marble samples (see Fig. 3).

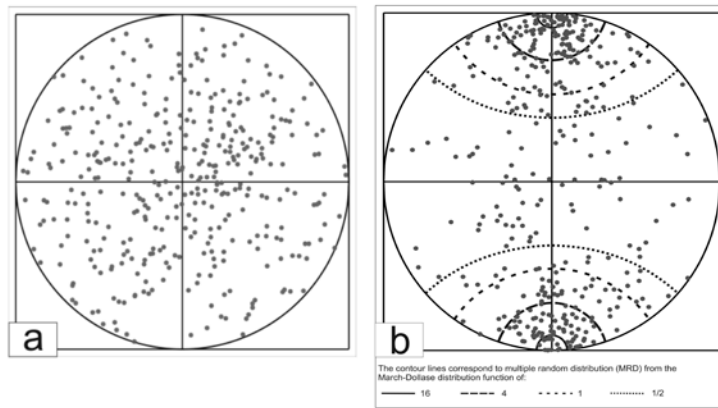


Figure 2. Representative pole figures showing individual poles of the crystallographic c-axis for each grain in the microstructure. **a.** The orientations chosen from a random ODF (denoted $M=1$). **b.** The orientations chosen from a March-Dollase ODF with fiber texture that is 20 times random along the North and South pole (denoted $M=20$). The contour lines correspond to multiple random distribution (MRD) from the March-Dollase distribution function of 16 (nearest to NS pole), 4, 1, and $1/2$ (nearest to the equator).

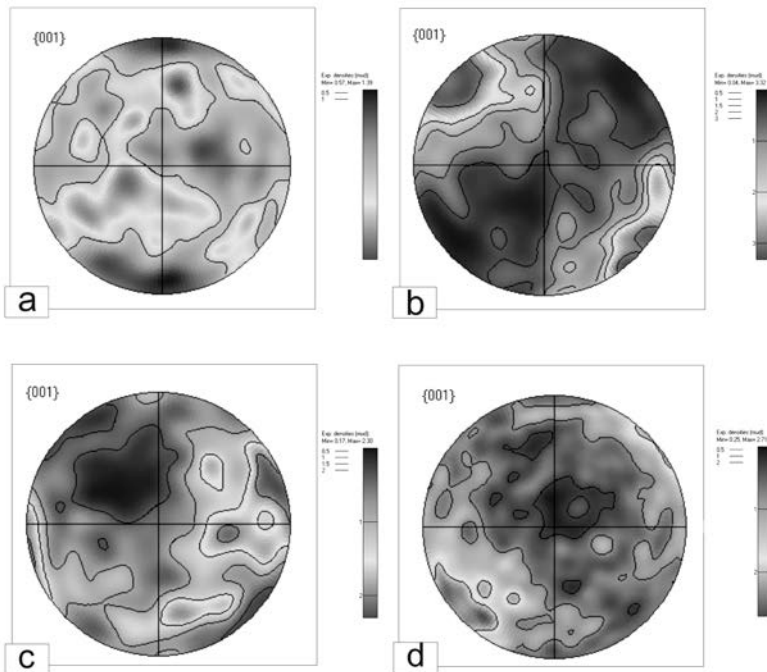


Figure 3. Pole figures from the EBSD HKL Channel 5 software for marble samples in xz planes: **a.** Arabescato Altissimo (a Carrara marble from Italy); **b.** Sölk (a calcitic marble from Austria); **c.** Lasa (a calcitic marble from Italy); **d.** HT-Carrara (a Carrara marble from Italy).

Six different LPOs were considered: a random ODF; an ODF with strong directional crystal texture generated via March-Dollase fiber-texture with a maximum multiple random distribution (MRD) of 20; and four actual marble textures, as measured with EBSD with maximum MRDs from 1 (Arabescaro Altissimo) to 3 (Sölk). The algorithm implemented to generate the March-Dollase ODFs is described elsewhere (Saylor et al. 2007; Shushakova et al. 2010). The c-axis crystal texture was parallel to the $\mathbf{e}_3$ direction (see Fig. 1).

ODFs were measured with EBSD for four marble types: a Carrara marble with weak LPO; a Sölk marble with more pronounced LPO; a Lasa marble with a c-axis girdle distribution; and a HT-Carrara with high temperature texture. The orientations of the individual grains in the microstructure were determined by EBSD. Only a small fraction of the orientations were randomly assigned to the idealized microstructures, i.e., 382 grain orientations for the equiaxed microstructure, 347 orientations for the mixed microstructure and 312 for the elongated microstructure.

2.2 Finite-element simulations

The microstructure-based finite-element approach used here is based on the Object-Oriented Finite Element program OOF developed at the National Institute of Standards and Technology (Langer et al. 2001). The OOF software is in the public domain. Executables, source code, and manuals are available at: <http://www.nist.gov/mml/ctcms/oof/>. The OOF1 software was used here.

An adaptive meshing algorithm was implemented to create a mesh with a grain-boundary phase that has the same thermo-elastic properties as the grains, but with a different fracture toughness. The final mesh consisted of 140,358 elements for the equiaxed microstructure, 207,208 elements for the mixed microstructure and 163,668 elements for the elongated microstructure. After the mesh was generated, thermal and elastic properties of calcite and dolomite (Table 1) were assigned to the constituent grains.

Table 1. The single-crystal elastic constants, C_{ij} , in GPa (Bass 1995) and the crystalline coefficients of thermal expansion, α_{ij} , in $10^{-6} \text{ }^\circ\text{C}^{-1}$ for calcite (Kleber 1959) and dolomite (Reeder and Markgraf 1986).

Material	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{33}	C_{44}	α_{11}	α_{33}
Calcite	144.0	53.9	51.1	-20.5	0	84.0	33.5	-6.0	26.0
Dolomite	205	70	57.4	-19.5	13.7	113.0	39.8	6.0	26.0

In the microcracking simulations three grain sizes were considered: fine grains of order 200 μm (calcitic marble); medium size grains of order 1 mm (calcitic and dolomitic marbles); and large grains of order 2 mm (dolomitic marble). The grain-boundary fracture surface energy, γ_{ig} , was chosen to be 20 % and 40 % of the crystalline fracture surface energy, γ_{xtal} , so that both intergranular and transgranular fracture were possible. The crystalline, or grain fracture toughness, γ_{xtal} , was assumed to be 0.5 Jm^{-2} and isotropic. For these configurations the following fabric parameters were used: equiaxed; mixed; and elongated microstructures with random texture and strong texture generated via a March-Dollase distribution. Three replications of orientations were generated for calcite microstructures with a grain size of 1 mm and a grain boundary toughness of $0.40 \gamma_{\text{xtal}}$. For the other combinations of fabric parameters only one set of

orientations was generated to elucidate fabric effects. Textures from four actual calcitic marble types were used in simulations with both equiaxed and elongated microstructures with a grain size of 1 mm and a grain boundary toughness of $0.40 \gamma_{\text{xtal}}$. Hereby, 50 unique configurations were used as the basis for the finite-element simulations.

The finite-element calculations are based on two-dimensional plane-stress elasticity, and thereby simulated the results for a free surface. The typical thermoelastic responses that are computed are the maximum principal stress and the elastic strain energy density. A microcracking algorithm, as described in Zimmermann et al. (2001) and S. Gala Yousef et al. (2005), was used to initiate and propagate microcracks.

3. Results

3.1 LPOs generated via March Dollase distribution

The elastic strain energy density can be considered as a key precursor of potential microcracking in a microstructure. It provides the surface energy necessary to create the fracture surfaces of the microstructural cracks. To elucidate factors related to marble degradation due to microcracking phenomena, the influence of SPO, LPO, grain size, grain boundary toughness and marble composition on the elastic strain energy density were studied by microstructural simulations.

The elastic strain energy density was monitored during heating and cooling for temperature step changes of 1°C for both cracked and uncracked samples. The uncracked simulations are those for which the no microcracking was allowed. The thermoelastic response values are plotted for the temperature interval from 10°C to 50°C during heating and from -10°C to -50°C during cooling (see Fig. 4). Since elastic strain energy is converted to fracture surface energy on microcracking, one suspects that in the equiaxed microstructure one would have more microcracking with random crystallographic texture than with strong fiber texture ($M=20$). To verify this conjecture, the percentage of microcracked elements versus the heating or cooling temperature change is displayed in Fig. 5, where this is demonstrated.

More microcracking is observed in the equiaxed microstructure with random texture upon heating (7.6 % of the total area at $\Delta T = 50^\circ\text{C}$) and cooling (9.5 % at $\Delta T = -50^\circ\text{C}$) than in the mixed grain-size microstructure with random texture, where only 5.6 % of whole area is cracked upon heating and 7.6 % upon cooling. Even fewer elements are cracked in the elongated microstructure with random texture: 4.4 % and 8.3 % upon heating and cooling, respectively. In all microstructures more microcracking is observed upon cooling, than upon heating. An apparent reason for this asymmetry is not obvious. A basic observation is that the strain energy density and the percentage of microcracked elements due to heating and cooling depend significantly on both SPO and LPO. When texture is twenty times random less microcracking is observed in the elongated microstructure upon heating (0.2 % of the total area at $\Delta T = 50^\circ\text{C}$) and cooling (2.7% at $\Delta T = -50^\circ\text{C}$) in comparison with the equiaxed microstructure where 3.9 % of whole area is cracked upon heating and upon cooling, and with the mixed microstructure where 2.1% and 3.3% is observed, respectively.

To investigate the relation between maximum principal stress and microcracking initiation, high-stress regions in an uncracked material were compared to the microcracks in the cracked material. Microstructural maps show the spatial dependence of maximum principal stress for the equiaxed microstructure with the random texture (see Fig. 6), when $\Delta T = 50^\circ\text{C}$ and $\Delta T = -50^\circ\text{C}$ in uncracked and cracked materials.

The regions with high maximum principal stress in the uncracked state correspond to microcracks in the cracked material.

It is evident that microcracks that occurred upon heating do not form upon cooling and vice versa (Weiss et al. 2002).

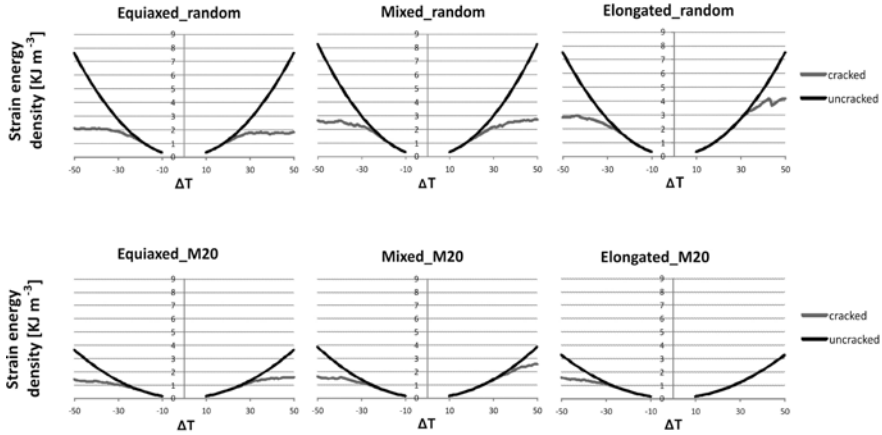


Figure 4. Elastic strain energy density for microcracked and uncracked idealized marble microstructures versus the temperature change from the unstressed state. Results are shown for three idealized calcitic microstructures (equiaxed grains; mixture of equiaxed and elongated grains; and elongated grains) and for two LPOs: random texture and 20 times random texture (denoted as M20) with a grain size of 1 mm and a grain boundary toughness $0.40 \gamma_{\text{xtal}}$.

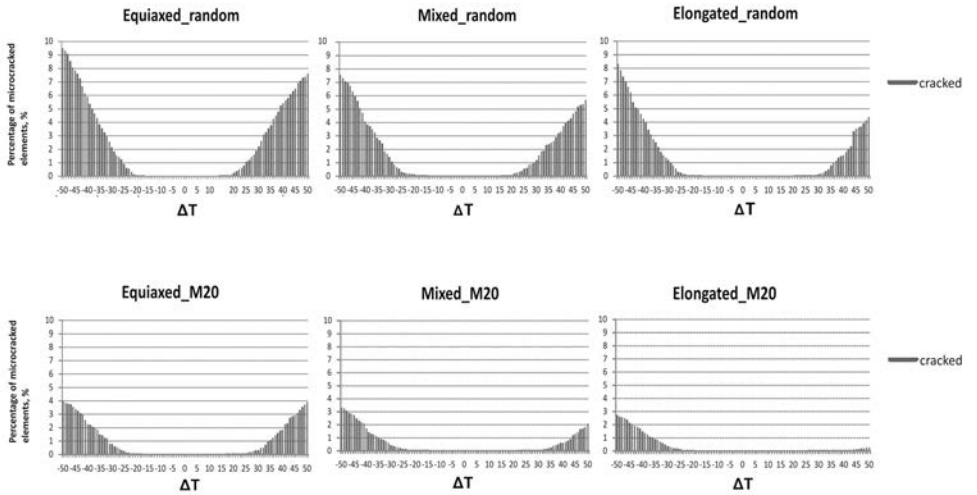


Figure 5. Percentage of microcracked elements for the three idealized marble microstructures with two textures: random texture and 20 times random texture (denoted as M20).

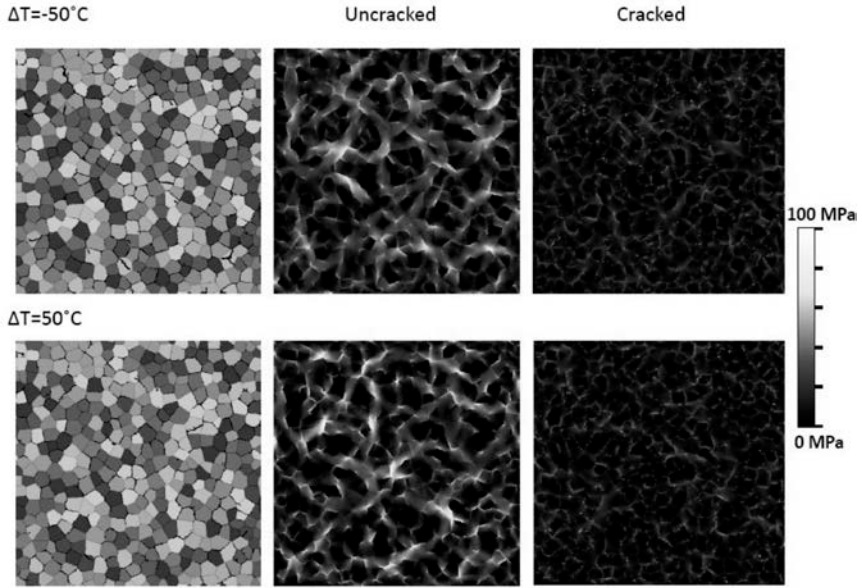


Figure 6. Representative microstructural maps showing the spatial dependence of the maximum principal stress for an equiaxed calcitic marble microstructure with a random ODF, grain size of 1 mm, and grain boundary toughness of $0.40 \gamma_{\text{xtal}}$, when $\Delta T = -50^\circ\text{C}$ and $\Delta T = 50^\circ\text{C}$ in uncracked and cracked materials. Black regions in the micrographs show the microcracks. Stresses in the maps are shown with a greyscale that ranges from black (0 MPa) to white (≥ 100 MPa).

To investigate effect of grain boundary toughness on the resultant microcracking, simulations were performed for a dolomitic marble with a grain size of 1 mm. More microcracking was observed for the case of a grain boundary toughness of $0.20 \gamma_{\text{xtal}}$ than for $0.40 \gamma_{\text{xtal}}$. Moreover, simulations with a grain boundary toughness of $0.20 \gamma_{\text{xtal}}$ commences to microcrack at a lower temperature differential. Results are shown in Fig. 7. When grain boundary toughness is 20 % of γ_{xtal} , intragranular cracking is reduced or vanishes completely.

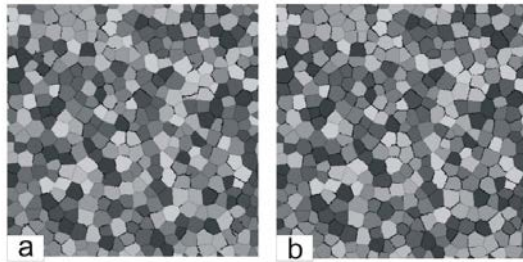


Figure 7. Simulations of microcracking in a dolomite marble with a grain size of 1 mm upon heating by a temperature differential of 50°C : **a.** equiaxed microstructure with random texture and grain boundary toughness of $0.40 \gamma_{\text{xtal}}$; **b.** equiaxed microstructure with random texture and grain boundary toughness of $0.20 \gamma_{\text{xtal}}$.

To elucidate the influence of grain size and marble composition, calcitic microstructures with grain sizes of 200 μm and 1 mm, and dolomitic microstructures with grain sizes of 1 mm and 2 mm were analyzed. With increasing grain size for both calcitic and dolomitic marbles, the percentage of microcracked elements is greater and microcracks occur at a lower temperature differential. For instance, an equiaxed microstructure with a grain size of 200 μm and calcitic thermo-elastic properties has only 0.5 % of microcracked area at $\Delta T = 50\text{ }^{\circ}\text{C}$ and microcracking commences at 31 $^{\circ}\text{C}$, while the same calcitic microstructure with a grain size of 1 mm has 7.6 % of microcracked area at $\Delta T = 50\text{ }^{\circ}\text{C}$ and starts to crack at 14 $^{\circ}\text{C}$. For dolomitic microstructures the increase of microcracked area is not extremely large: it is approximately two times larger for the case of the grain size of 2 mm compared to 1 mm (i.e., 4.9 % of microcracked area at $\Delta T = 50\text{ }^{\circ}\text{C}$ in the equiaxed microstructure with the grain size 1 mm in comparison with 8.4 % at $\Delta T = 50\text{ }^{\circ}\text{C}$ of microcracked area in the microstructure with the grain size 2 mm).

The comparison of the results for microstructures with a grain size of 1 mm but different marble composition revealed that the dolomitic marble has less of a tendency for microcracking, i.e., microcracking begins at a higher temperature differential, and the percentage of cracked area is reduced by 1.5 times in comparison with a calcitic marble. While dolomite is stiffer than calcite, calcite has a greater thermal expansion anisotropy, resulting in a higher maximum principal stress. The percentage of microcracked area in the dolomitic marble with a grain size of 2 mm is comparable with results for the calcitic marble with a grain size of 1 mm.

3.2 LPO measured on four actual marbles with EBSD:

The simulations were performed for equiaxed and elongated calcitic microstructures with a grain size of 1 mm and a grain boundary toughness of $0.40\gamma_{\text{xtal}}$. The percentage of microcracked area (Table 2) for an equiaxed microstructure with the random texture (Arabescaro Altissimo marble), girdle texture (Lasa marble) and high-temperature texture (Carrara marble) upon heating and cooling is comparable with the results of simulations for microstructure with equiaxed grains with random texture generated via March Dollase distribution. For stronger texture (Sölk marble) this value is smaller, but not significantly. Elongated microstructures with the girdle texture exhibited by Lasa marbles show the smallest percentage of microcracked elements. This type of texture has *not* been simulated for idealized ODFs. Elongated microstructures with random texture (i.e., Arabescaro Altissimo) and with more pronounced LPO (i.e., Sölk) have similar amounts of microcracking.

Table 2. The percentage of the microcracked area for equiaxed and elongated microstructures at $\Delta T = 50\text{ }^{\circ}\text{C}$ upon heating and at $\Delta T = -50\text{ }^{\circ}\text{C}$ upon cooling.

Marble sample	Strain energy density and percentage of microcracked elements			
	Heating		Cooling	
	Equiaxed	Elongated	Equiaxed	Elongated
Arabescaro Altissimo	7.6%	4.2%	8.4%	5.3%
Sölk	7.1%	4.4%	7.6%	5.4%
Lasa	7.6%	1.5%	8.7%	2.6%
HT-Carrara	8.0%	5.2%	9.1%	5.8%

The influence of SPO is significant. For microstructures with elongated grains the percentage of microcracked elements is reduced by 1.5 times. Similar to the results for the idealized LPOs, there is less microcracking upon heating than upon cooling.

4. Discussion and conclusions

Many fabric parameters influence thermal degradation of marbles. Most of them have been investigated in the present study. It was shown that lattice preferred orientation (LPO), shape preferred orientation (SPO), grain size, grain boundary toughness and marble composition control the thermoelastic response of marble microstructures. The present investigation revealed that with decreasing grain size and increasing LPO and SPO microcracking is less and it commences at greater temperature differentials. It was observed that microcracking upon heating is generally less than upon cooling. Dolomitic marbles have less of a tendency to microcrack. While dolomite is stiffer than calcite, calcite has a greater thermal expansion anisotropy, thus resulting in higher maximum principal stresses. In agreement Zeisig et al. 2002 experimentally showed that dolomitic marbles do not have residual strains after thermal treatment.

Microstructural maps were generated that show the spatial dependence of the maximum principal stress. To investigate the relation between maximum principal stress and microcracking initiation, high-stress regions in an uncracked material were compared to the microcracks in the cracked material. The regions with high maximum principal stress in uncracked state correspond to microcracks in the cracked material.

Simulations that used textures from actual marble samples showed results that are comparable with results from simulations with the March-Dollase generated ODFs.

In summary, microstructure-based finite-element simulations are an excellent tool for elucidating influences of the rock fabric and crystal texture on the thermoelastic behavior and microcracking response of marbles.

5. Acknowledgments

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QUANTITATIVE ASSESSMENT OF POST-RESTORATION ACCELERATED STONE DECAY DUE TO COMPATIBILITY PROBLEMS (ST. SEBASTIAN'S ABBEY CHURCH, MANGLIEU, FRENCH MASSIF CENTRAL)

Marie-Françoise André^{1,4}, Bruno Phalip², Olivier Voldoire¹, Erwan Roussel³, Franck Vautier^{1,3}, David Morel²

Contact author: m-francoise.andre@univ-bpclermont.fr

¹ *Laboratory of Physical and Environmental Geography – GEOLAB, CNRS/Blaise Pascal University, Clermont-Ferrand, France* - ² *Centre of History 'Spaces and Cultures', Blaise Pascal University, Clermont-Ferrand, France* - ³ *Maison des Sciences de l'Homme, CNRS/University of Clermont-Ferrand, France* - ⁴ *Institut Universitaire de France*

Abstract: Most Romanesque churches of the French Massif Central have been built during the 11-12th centuries and restored between the mid-19th and the mid-20th centuries. Restoration campaigns including stone replacement and cement repointing are assumed to have caused accelerated stone deterioration. A quantitative assessment of this post-restoration accelerated decay is provided by the St. Sebastian's Church at Manglieu (Puy-de-Dôme, France), which displays conspicuous decay forms affecting the medieval stone facings. An interdisciplinary approach involving geoscientists and archaeologists specialized in the medieval period is developed, which combines: (1) the deciphering of the complex history of the facade, (2) the 3D-modeling of stone decay by laser scanning and (3) the analysis of the composition and properties of the building and restoration materials. Laser scanning data reveal that the most severely decayed part of the facade is located between 2 and 3 m a.g.l., i.e. just above the modern granite stones, incorporated at the base of the facade during the underpinning operation conducted in the 1860s. Contact sponge data indicates that these replacement stones, which were chosen because of their esthetical compatibility with the original ones, are four less permeable, and therefore create a major discontinuity zone above which capillary rise is enhanced; this induces an accelerated granular disintegration of the overlying medieval gneiss ashlar. On the whole, the post-restoration stone recession has been 20 mm on average since the 1870s (max. 130 mm). By contrast, on the rest of the facade non affected by restoration, the stone recession has been less than 2 mm since the 12th century as shown by the preservation of the medieval 'fish-bone' finish and mason's marks. It means that the post-restoration stone recession has proceeded up to 100 times faster than the pre-restoration recession. At a local scale, the replacement of lime mortar by Portland cement during the late 19th century repointing operations is an additional factor of accelerated decay.

Keywords: accelerated stone decay, restoration practices, compatibility problems, medieval architecture, France

1. Introduction

Selecting the most suitable replacement stone when undertaking monument restoration or repair is a growing concern for many quarries have been mined out or are abandoned and no longer accessible. Atlases and databases are being developed to help restorers to select appropriate replacement stones.

Although the term ‘compatibility’ mainly refers to the mechanical, physical and chemical compatibility of new stones with the historic stone materials (Teutonico et al. 1997), the selection of substitution stones has for long mainly been based on their esthetical compatibility (i.e. their colour and texture) with the original stones. An additional factor considered for selecting replacement stones has often been the stone ‘hardness’, which mainly refers to their compressive strength. In its *Dictionnaire raisonné de l’architecture française du XIe au XVIe siècle* published in 1854, the French architect Viollet-le-Duc already recommended to select ‘better’ materials than the original ones, and high hardness and high density were consequently taken by many restorers as positive properties (cf. for instance the replacement of limestone by trachyte during the restoration of Our Lady in Breda, Netherlands, as reported by Quist 2009). No clear attention was paid to the relations between material properties of replacement stones and those of historic stones.

Since the 1990s, several studies have pointed out the deleterious effects on stone conservation of inadequate stone replacement: the selection of harder stones than the original ones has been reported to create new problems by Blanc (1992), Přikryl and Smith (2007) and Quist (2009), due to differences of water transfert properties between new and old stones. The replacement of soft and permeable lime mortar by hard and stiff cement mortar has also been pointed out as a frequent cause of accelerated stone deterioration. Portland cement, patented in England by Joseph Aspdin in 1824, has rapidly supplanted the lime-based mortars which had been in use since the Antiquity (Dotter et al. 2009). In Europe, large use of cement in various styles such as ‘ribbon’ and ‘bastard tuck’ was made during the 19th-20th century restoration campaigns. This caused drastic changes in the water balance and the chemistry of masonry stones. The responsibility of cement repointing in the acceleration of stone decay has been incriminated in rural areas of Ireland, based on a national assessment commissioned by the Heritage Council. Of the 112 investigated monuments, 32.5% had been repointed with modern Portland cement which had reacted chemically with the original masonry, inducing damage in 46% of these cases (Pavia and Bolton 2001).

Although geomorphologists have developed new methods to quantify stone deterioration (Pope et al. 2002; André et al. 2008; Vautier & Voldoire 2011), scarce quantitative data is currently available concerning the man-induced acceleration of stone deterioration. Measurements on nine granite churches of Brittany suggest that post-repointing weathering rates are three times faster than pre-repointing rates (Paris 1998), but to date, the accelerated deterioration induced by incorporation of incompatible stone materials has never been quantified. This gap in knowledge motivated the multidisciplinary study of the medieval church of St. Sebastian in Manglieu (French Massif Central) which has been restored in the late 19th century. The aim of the present study is to quantify the impact of restoration (stone replacement and cement repointing) on the activation of stone decay at this monument which had been exposed for seven centuries to atmospheric attack before restoration. Such a quantitative assessment requires to reach three objectives: (i) to reconstruct the history of the monument and to distinguish the historic from the replaced stones, based on archival research and stone-by-stone surveys ; (ii) to characterize the old and new stone materials, regarding their

geochemical and mineralogical composition, and their water transfert properties, based on ICP-AES, polarizing microscopy and the contact sponge method; (iii) to provide a 3D-model of the stone decay at the study site based on long range laser scanning in order to provide estimates of stone recession rates before and after restoration.

2. Study site

The Auvergne region, which is located in the French Massif Central, is characterized by the diversity of its architectural heritage, with a particular mention for hundreds of Romanesque churches mainly dating back to the 11-12th centuries (Figure 1). Since their building, most of these monuments have been subject to modifications, additions and repairs, including a major restoration phase which started in the mid-19th century.

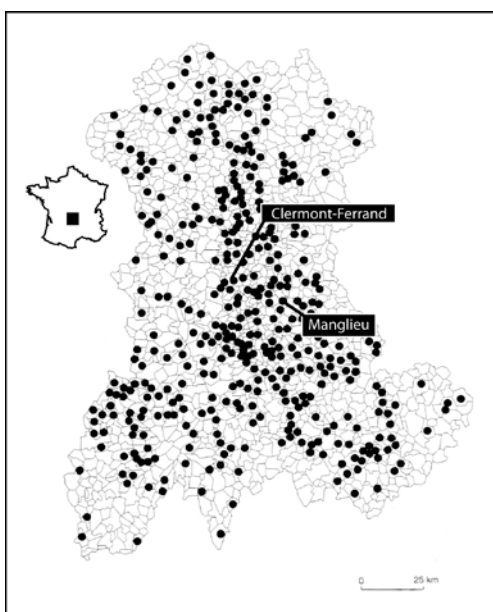


Figure 1. Location of Romanesque churches in the Auvergne region, French Massif Central (after Phalip 2001)

St. Sebastian's abbey church is one of these medieval restored monuments. It is located 44 km south of Clermont-Ferrand, the main city of the Auvergne region (Figure 1). This church is a protected monument, which has been inscribed in 1840 on the national list of historical monuments. It is renowned for the antiquity of its apse which dates back to the 8th century. Whereas other parts of the church such as the narthex and most of the façade date back to the 12th century, the nave and the quadrangular tower were rebuilt in the 15-16th centuries, and the upper part of the façade was completed in the late 19th century (Cabréro-Ravel 1997; Phalip 2001). The geological setting of St. Sebastian's abbey church is characterized by the abundance of local building materials associating Paleozoic basement rocks (migmatitic gneisses and granites), and Cenozoic sedimentary rocks mainly represented by arkosic sandstones. This geological diversity is expressed

by the multicoloured appearance of St. Sebastian's western façade, which includes grey gneiss and granite, and yellow and red arkosic sandstone. This façade, which is the focus of the present study, illustrates the complex history of St. Sebastian, with four building phases ranging from the 12th to the 19th century (Figure 2). The lower part of this façade, which faces the prevailing winds blowing from the west, is decorated with three semicircular blind arches, four meters wide by five meters high, which mainly display grey ashlar blocks. The inner part of these arches displays conspicuous decay features. Surprisingly, these have not developed within the capillary fringe, but 2.5 meters a.g.l. The severity of decay and the anomalous distribution of decay forms has motivated the present study.

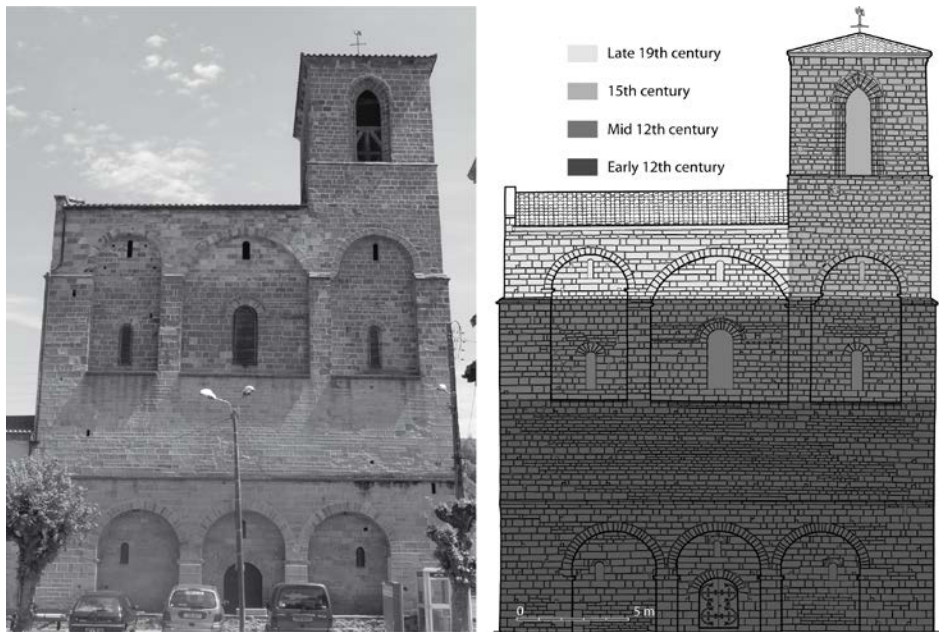


Figure. 2. Multi-phased façade of St. Sebastian's abbey church. © M.F. André (left) and David Morel (right)

3. Methods

Methods combine approaches from various disciplinary fields including art history, archeology, geomorphology, geology and geomatics.

Archival research in various documentary sources (including the Mérimée architecture database of the French Ministry of Culture) and on-site stone-by-stone surveys were carried out to precise the chronology of building and restoration periods, and to discriminate the original from the restored parts of the blind arches, mainly based on the presence or absence of medieval mason's marks and 'fishbone' tooling marks. These marks were also used to reconstruct a secure reference surface (i.e. dated 'zero-datum level') to be able to quantitatively assess stone decay (André and Phalip 2010). Stone-by-stone surveys aimed also to determine the petrography of every ashlar block.

Visual categorization of stone decay forms (such as flaking, scaling and alveolar weathering) was then carried out based on the existing nomenclatures (Fitzner and Heinrichs, 2002; Vergès-Belmin, 2008). Quantitative assessment of stone decay was based on 3D-modeling of stone decay by laser scanning. Scans were obtained with the Optech Ilris 3D laser scanner, which is long range, accurate and fast, and provides a comprehensive view of the stonework conditions. Polyworks and Geomagic softwares were used to obtain 3D models of the decayed surfaces to be compared with the reconstructed 'zero-datum level' in order to calculate stone recession rates.

Petrographical characterization was carried out based on laboratory analyses of small pieces of stone materials fallen from the monument. Geochemical composition was determined by using ICP spectrometry (Murray et al. 2000). Each sample aliquot (100mg) was mixed with LiBO₂ flux and fused for 5 min at about 1050° in 2000 W induction furnace. The melt was poured into a disposable polystyrene beaker containing 50 ml of 2 M HNO₃ stirred by a magnetic bar, and after complete dissolution, the solution was passed through a filter paper to remove graphite particles. Major element compositions of rock samples were measured on ULTIMA C Horiba-Jobin-Yvon ICP-AES, based on the ICP-AES analytical techniques described in Cantagrel & Pin (1994). Mineralogical identification was performed based on polarizing microscopy. Stone samples were cut to fit a 45×30 mm glass slide and due to their friability, impregnated with an epoxy resin under vacuum. Thin sections were examined using an optical polarizing microscope (LEICA DMLP) equipped with a camera (LEICA DFC295).

Due to sampling restrictions, porosity analyses could not be carried out, but the comparative assessment of water transfert properties between the replacement and original stones was performed based on on-site contact sponge tests. This recently developed method (Pardini and Tiano 2004) complements the Karsten pipe and capillary rise methods (Vandervoort et al. 2009). It is a non-destructive and portable method which can be employed *in situ* as well as in laboratory to measure the water uptake by stone materials. This method consists of a 1034 Rodac contact-plate, 5.6 cm in diameter, containing a Calypso sponge. After filling the sponge with approximately 7 g of water, the contact-plate is pressed manually against the stone surface during a given time (30 or 60 seconds), and the sponge is weighed on a precision balance before and after contact with the stone surface. The difference between weights corresponds with the amount of water absorbed by the stone surface under test. Water absorption is expressed in g/cm². min. Overall, 90 contact sponge tests were carried out at the investigated site in order to compare the water absorption by historical and replacement ashlar.

4. Results

4.1. Monument history

The historical documentation provided by the Mérimée national database and the Conservation of Historical Monuments in Clermont-Ferrand indicates a major restoration operation undertaken between 1868 and 1888 at the base of St. Sebastian's façade which has affected the three investigated blind arches. Probably due to a severe

deterioration caused by capillary rise, the façade was underpinned up to 2.5 m above the ground level. The decayed medieval gneisses were replaced by new granitic ashlar blocks, and both the new granites and old gneisses were (re)pointed by cement mortar instead of the original lime mortar. This operation is documented by architectural surveys conducted by the architect Louis-Clémentin Bruyère in 1870, and by the photographs taken by the architect Gabriel Ruprich-Robert in 1909, i.e. after restoration.

Stone-by-stone surveys allowed to provide maps of the original and restored parts (Figure 3), and of the lithological nature of stone materials (Figure 4). The esthetical compatibility of the granitic replacement stones with the historic gneissic ashlars was considered by the restorers: the grey colour of the granite matches perfectly with the colour of the medieval gneiss to such an extent that at first sight, they are hardly distinguishable. However, closer examination reveals substantial textural differences between them. The gneiss, which is a migmatitic gneiss ('nebulite') displays a foliated organization, with alternating layers of leucocratic minerals (mainly quartz and potassic feldspars) and melanocratic minerals (mainly biotite). The granite, which is medium-grained, displays the same minerals but its texture is homogeneous and equant. The arkosic sandstones, which are mainly represented in the upper part of the arches, include various lithotypes, due to their variable quartz and mica content.

4.2. Qualitative and quantitative assessment of stone decay

The stone-by-stone survey of the three blind arches reveals that the state of deterioration of the ashlar blocks highly varies according to their lithology and their height above the ground level. The granite ashlars, which were inserted at the base of the wall during the 19th c. restoration, are invariably sound and fresh. The 12th c. arkosic sandstones, which are located in the highest part of the arches, are moderately affected by a very superficial (<3 mm) granular disintegration; some are fresh and completely free of weathering; a single arkosic ashlar, which is located above the window of the left arc is more severely affected and has receded by 1.5 cm due to granular disintegration. As to the 12th c. gneiss ashlars, their behaviour differs drastically according to their position on the wall. In the highest parts, they are perfectly preserved and still display the medieval 'fishbone' finish and mason's marks of the original surface; by contrast, in the middle part of the wall, they display a very irregular topography due to granular disintegration and alveolar weathering; 'caves' in gneiss reach up to 10 cm deep, especially when being surrounded by sound granite ashlars.

Post-processing of laser scanner data and overlapping of the 3D-models of the decayed surface and the reference surface allowed to provide a spatialized view of stone recession rates since the 12th century (in the unrestored parts) and since the 19th century (near the restored parts). Both the upper part of the arches, which still displays the 12th c. mason's marks, and the lower part, which consists of new granite, appear almost free of deterioration. By contrast, the middle part, which lies just above the restored part, is severely decayed (Figure 5), with stone recession values ranging from 10 to 60 mm, with extreme values at almost 130 mm obtained on single medieval gneissic stones completely surrounded by new granitic stones. This implies that in areas impacted by the 19th c. underpinning operation, stone decay of historical gneissic stones has

proceeded very fast (0.2 mm per year on average and up to almost 1 mm per year). By contrast, most of the same historic gneissic stones located higher on the wall, which have been exposed for almost nine centuries to the atmospheric attacks but have not been impacted by the 19th c. restoration, still display their medieval ‘fishbone finish’: the overall decay has affected less than 2 mm, with resulting stone recession rates lower than 0.002 mm per year.

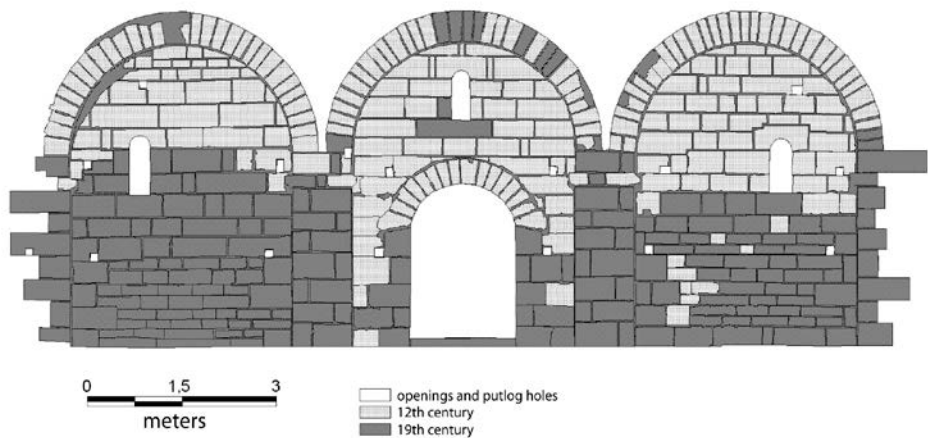


Figure 3. Differentiation between historic and replaced stones based on stone-by-stone surveys.
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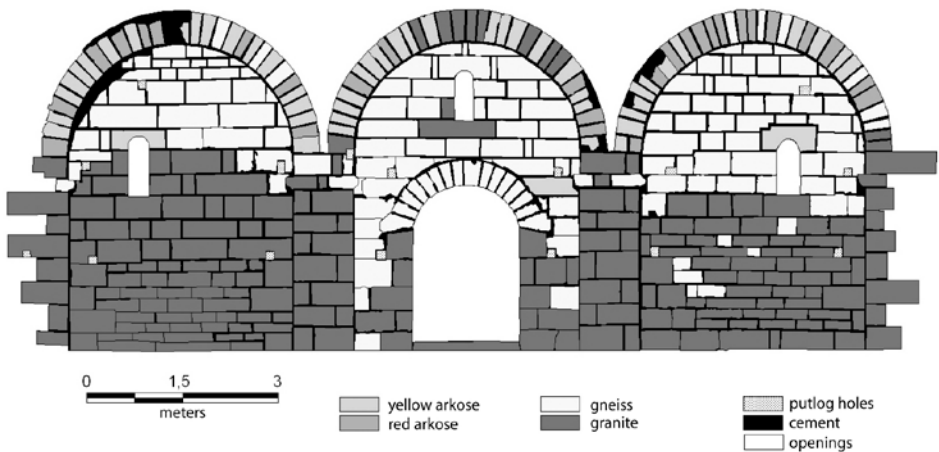


Figure 4. Lithological nature of stones based on stone-by-stone surveys. © Marie-Françoise André / Olivier Voldoire



Figure 5. Accelerated stone recession just above the underpinned part of the arches based on 3D-modeling of stone decay by laser scanning. © Olivier Voldoire / Franck Vautier

4.3. Geochemical and mineralogical composition of stone materials

ICP-analyses reveal the similarity of geochemical composition of the medieval gneiss and new granite incorporated at the base of the monument in the 1870s: gneiss and granite respectively comprise 67 and 65% SiO_2 , 17 and 16% Al_2O_3 , and 3 and 4% Fe_2O_3 . The arkosic sandstones appear more silica-rich (mean 74%, maximum 87.6%).

Unlike geochemical analyses, microscopical observations reveal a sharp contrast between the original gneiss and the new granite ashlar. The 12th c. gneiss displays completely pulverized biotites, microcracked quartz grains and argilized feldspars; muscovite is the only intact mineral. By contrast, although the least quartz-rich (65% SiO_2) and the richest in Fe-Mg (> 6%) and Ca-Na (> 7%) minerals, the 19th c. granite appears very fresh and display sealed grain contacts. Quartz grains and biotite flakes are intact. Feldspars, though slightly misty, are perfectly recognisable, based on their Carlsbad twins (orthoclase) and polysynthetic twins (plagioclase). Thin sections also indicate a high variability of the arkosic lithotypes which are a minor constitutive material of the blind arches. Whereas the high quartz content and the low feldspar and mica content of the siliceous arkose subtype makes it close to a quartzitic sandstone, the yellow micaceous arkose is characterized by its mineralogical heterogeneity (quartz, orthoclase, plagioclase, biotite, muscovite, epidote, etc.), its weathered feldspars, and its cracked or pulverized quartz grains and biotite flakes. The red arkose is rather similar to this yellow micaceous arkose but is richer in iron oxides and slightly laminated.

4.4. Water absorption of original and new stone materials

The results of contact sponge tests reveal a high contrast in water absorption between the historical and the replacement stones. Water absorption is 0.056 and 0.052 $\text{g/cm}^2\cdot\text{min}$ for the medieval gneissic and arkosic ashlar, and only 0.016 $\text{g/cm}^2\cdot\text{min}$ for the granitic replacement stones. These granites inserted in the lower part of the façade in the 1870s are therefore three to four times less permeable than the original gneissic stone materials.

5. Discussion and conclusions

The St. Sebastian case study illustrates the severity of damages caused to ashlar masonry by inappropriate stone replacement, based on a quantitative assessment of the man-induced acceleration of stone deterioration. In the middle part of the arches impacted by the underpinning operations, the stone recession has proceeded 100 times faster during the 140 year post-restoration period than during the 700 preceding years of atmospheric attacks. The main cause of this accelerated decay is obviously the incorporation of granite at the base of the façade. Although esthetically compatible with the original stone, this replacement stone is four times less permeable and creates a floor above which capillary rise conducive to granular disintegration is enhanced. The present study emphasizes the absolute necessity to take into account before selecting substitution stones not only their petrochemical compatibility with the original stones but most importantly their petrophysical compatibility, water transfer properties being the key driver of stone deterioration (Rozenbaum et al. 2008). It also confirms that cement repointing represents an additional cause of accelerated decay due to its low permeability, which prevents the joints to act as a drainage network for the historical monuments, and drives moisture to the stonework (Grunau 1971; Collombet 1989; Dotter et al. 2009). From a methodological point of view, this case study demonstrates both the interest of long-term natural exposure trials as reliable durability tests (Doehne & Price 2010) and of the contact sponge as a non-destructive and portable method for *in situ* assessments of water absorption by stone materials (Pardini and Tiano 2004; Vandervoorde et al. 2009).

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