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Abstract

This work aims at identifying the reactive zones inside limestone used in monuments exposed to fog. The location of these zones and the depth of the water penetration front is of primary relevance to evaluate the transport of aggressive species and the influence of environmental conditions on alteration mechanisms and kinetics of limestone exposed to the atmosphere. We report here the results of weathering experiments conducted in a deuterium-enriched environment and the characterization of reactive zones analyzed by NanoSIMS. It was determined that water penetrated several hundred micrometers inside the limestone and that only the first micrometers were significantly altered.

1. Introduction

In France, 52\% of the patrimonial historical monuments are built out of limestone and the preservation of this material is a challenge from a scientific, economic and cultural point of view. The alteration mechanisms need to be

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well understood in order to supply proper treatments for their conservation. These processes and associated kinetics depend on the mineralogy of the sample and on the environmental conditions.

We have decided to select one type of limestone, the so called “Saint-Maximin roche fine” widely used for the restoration of historical monuments in France, especially in the Paris Basin. This limestone of Lutetian age (45 My) is relatively homogeneous as far as chemical composition (on a pristine sample, ca 95% of CaCO\(_3\) and 5% of SiO\(_2\)) and physical properties (water transfer properties). The physical and chemical properties of pristine and weathered materials from monuments have been presented in other studies [1]. The main alteration phase in weathered samples is gypsum (CaSO\(_4\), 2H\(_2\)O) resulting from the reaction between calcite in the stone, water from the environment and sulfate from atmospheric SO\(_2\) [2]. Moreover, dissolution patterns caused by meteoric water can be observed on samples from monuments. In both cases, water action is the main parameter that needs to be investigated.

To this purpose, we have developed a methodology based on the use of deuterated water. To investigate the alteration mechanisms on pristine limestone, a stone block was exposed to controlled environmental conditions, aiming at reproducing a succession of dry and wet episodes. During the wet episodes, the use of the deuterium-enriched synthetic water allowed to locate the water penetration front inside the material and the preferred zone where alteration takes place. Locating the reactive zones inside the materials is an important first step to the understanding of the alteration mechanisms.

2. Methods

2.1. Weathering experiments

Limestone block was a cube of 5×5×5 cm\(^3\). To simulate an exposition close to natural weathering in the field, only one face of the sample was exposed to the environmental conditions, the other being protected by aluminum foil. The sample was exposed during 15 weeks to cycles as such: 1 day of fog followed by 6 days of dry atmosphere. The frequency of the cycles and the composition of the alteration solution (presented in Table 1) were set based on environmental data measured in a Parisian atmosphere.

Table 1. Composition of the synthetic water used in weathering experiments

<table>
<thead>
<tr>
<th>Species</th>
<th>Deuterium</th>
<th>pH</th>
<th>Na(^+)</th>
<th>NH(_4^+)</th>
<th>Ca(^{2+})</th>
<th>HCO(_3^-)</th>
<th>Cl(^-)</th>
<th>NO(_3^-)</th>
<th>SO(_4^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mol.L(^{-1}))</td>
<td>33%</td>
<td>5.4</td>
<td>1,20×10(^{-4})</td>
<td>6,75×10(^{-3})</td>
<td>5,90×10(^{-3})</td>
<td>3,98×10(^{-6})</td>
<td>1,29×10(^{-4})</td>
<td>4,80×10(^{-5})</td>
<td>3,55×10(^{-5})</td>
</tr>
</tbody>
</table>

2.2. Sample characterization and isotopic analyses

To evaluate the influence of the alteration conditions on the water transfer inside the limestone, cores of 1 cm diameter and 5 cm high have been extracted from the stone blocks. Imbibition measurements enabled calculating the capillarity absorption coefficient A according to EN 1925 [3]. During the test, the surface in contact with water was the one that had been exposed to the environmental conditions. As the capillary properties of the stone are important due to the connection between the pores, automatic tests have been performed with a weight measurement every 5 seconds.

H isotope, elemental \(^{32}\)S and \(^{16}\)O distributions were imaged on a Cameca NanoSIMS 50 at the MNHN in Paris. We acquired quantitative images covering surface areas of 20×20 \(\mu\)m\(^2\), divided into 256 by 256 pixels, at a raster speed of 1ms/pixel, on transverse sections of the limestone embedded in epoxy. Prior to each analysis, the sample area was pre-sputtered with a current of 40 pA for the D analyses and of 650 pA for the \(^{18}\)O and \(^{32}\)S analyses for about 5 minutes in order to remove surface contamination and reach sputtering steady state. Due to instrumental limitations, H-isotopes were recorded in a first set of images with a current of 3 pA. Then \(^{16}\)O and \(^{32}\)S were acquired at the exact same location during a second set of image acquisitions with a current of 50 pA.
3. Results and discussion

3.1. Imbibition kinetics

Fig. 1a. presents the water absorption kinetics expressed as a weight evolution measurement as a function of the square root of the time for weathered and pristine limestone cores. During the first seconds of absorption, the kinetics remained the same between the pristine sample and the weathered sample (15 weeks in laboratory). This is the result of the initial very high capillary pressure applied at the beginning of the experiment. After this first stage, the imbibition kinetics is different between pristine and weathered samples. The decrease of the absorption coefficient after several successive cycles simulating dry and wet atmosphere is a well-established phenomenon [4]. The evolution could be related to a change of the interfacial tension between the mineral and the water, and/or a localized obstruction of the porosity at the surface of the sample linked to a phase precipitation in this zone.

![Imbibition kinetics measured on pristine and weathered limestone samples](image)

Fig. 1. (a) Imbibition kinetics measured on pristine and weathered limestone samples, (b) $^{32}$S and (c) $^{16}$O repartition mapping on the surface of the weathered limestone sample. Calcareous zone is on the right side and resin is on the left side of the map. The left side of the calcareous zone has been exposed to the fog.

3.2. Location of the reactive zones

Fig. 1b. and c. presents the $^{16}$O and $^{32}$S mapping obtained using NanoSIMS for a transverse section of the stone on a zone located at the surface of the sample in contact with the fog. $^{16}$O map allows differentiating the calcareous (right side on the map) from the resin zones (left side). At the extreme surface of the sample, a 1 $\mu$m thick sulfur-enriched layer is observable. The presence of this layer is probably due to a sulfate-formation process and then corresponds to the first alteration stages of the stone. The formation of a sulfate-rich phase at the surface is in good agreement with the previous hypothesis of an obstruction of pores located at the surface of the sample that would reduce water transfer kinetics. Regarding the composition of the alteration water and the nature of the phases formed on samples from monuments, the nature of this phase is probably a calcium sulfate.

3.3. Water front penetration

The deuterium concentration in the water present in the pores of the limestone is expressed as $\delta D$, which is calculated following Eq (1).

$$\delta D (\%) = \left(\frac{((D/H)_{sample})}{(D/H)_{standard}} - 1\right) \times 1000$$  \hspace{1cm} (1)

On a reference limestone sample that has not been exposed to a deuterated environment, $\delta D$ is of -390±70‰. Fig. 2 presents the evolution of $\delta D$ measured at the surface of grains of the weathered sample as a function of the distance to the surface exposed to the deuterated fog. The general trend is a $\delta D$ decrease from the surface to the
inner part of the stone. At 200 μm below the surface, δD is still higher than in a non-deuterated sample, but at 300 μm below the surface, δD is in the reference range for non-deuterated sample. Consequently, such alteration conditions with exposition to cycles of fog and dry episodes only result in limited penetration of the water inside the stone. As presented before, it has been possible to identify the presence of a sulfur-rich zone only in the first micrometers below the surface. However, modifications are possible to around 300 μm below the surface because the water can penetrate to this distance inside the stone. At a macroscopic scale, it influences the water transfer inside the stone, as it has been seen with the imbibition tests.

Fig. 2. Evolution of δD of water in pores as a function of the distance to the surface exposed to the deuterated fog.

4. Conclusion

It has been possible to simulate in laboratory conditions the cyclic change of fog and dry episodes on limestone samples with D-rich water. After 15 weeks of alteration, only the first few micrometers below the surface seem to be modified by a visible sulfation process. Moreover, the use of a deuterated solution enabled determining that the alterable zone where the water penetrates is of few hundred micrometers below the surface of the sample (under the weathering conditions used in laboratory experiments). Besides, the absorption of a thin water layer could facilitate the water penetration inside the stone in the case of a heavy-rainy episode. Such events need to be further investigated.

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