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Lucile Gentaz, Mandana Saheb, Aurélie Verney-Carron, Loryelle Sessegolo, Anne Chabas, et al.. Elsevier Editorial System(tm) for Science of the Total Environment Manuscript Draft Manuscript Number: STOTEN-D-20-08334 Title: Reactivity of secondary phases in weathered limestone using isotopic tracers (D and 18O): the case study of the 'Tribunal Administratif' of Paris Article Type: Research Paper. Environmental Science and Pollution Research, 2021, 28 (3), pp.2810-2821. 10.1007/s11356-020-10644-z . hal-03402473

HAL Id: hal-03402473

<https://hal.science/hal-03402473>

Submitted on 25 Oct 2021

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Article Type: Research Paper

Keywords: limestone, weathering, air pollution, syngenite, secondary phase

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Abstract: For a long time, limestone has been massively used in stone building and monuments because of its easy extraction and common presence in the landscape. On ancient monuments, mostly built in urban areas, it is exposed to urban-borne pollutants responsible for specific alteration mechanisms and weathering kinetics. Especially, the dissolution of calcite and the precipitation of new phases will affect the limestone pore network, modify the stones capillary properties and influence the further alteration. In order to better understand these processes, an altered limestone sample from 'Tribunal Administratif' (TA) in Paris was studied. The main secondary phase was found to be syngenite, which can be explained by the location of the sample close to the soil, a potential source of K (fertilizers). This phase is more soluble than gypsum that is commonly found on altered limestone. In order to assess the reactivity of the system (limestone and new phases), oxygen and hydrogen isotopes were used to trace the transfer of water (D_2^{18}O) and identify the location of the reactive areas (susceptible to alteration). For that, TA samples were exposed in a climatic chamber to relative humidity (RH) cycles (25% RH for 2.5 days and 85% RH for 4.5 days) for 2 months with a D_2^{18}O vapor to simulate alteration occurring in conditions sheltered from the rain. Results have shown that the water vapor easily circulates deep in the sample and reacts preferentially with syngenite the most reactive phase (compared to calcite and quartz). This phase could evolve in gypsum when exposed to an environment different from the one resulting in its formation.

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Saint Victor sur Loire, April 20th 2020

Dear Editor,

We would like you to consider the manuscript "**Reactivity of secondary phases in weathered limestone using isotopic tracers (D and ¹⁸O): the case study of the 'Tribunal Administratif' of Paris**" for publication in Science of the Total Environment. This manuscript is an original work and has not been submitted for publication in another journal.

The alteration of limestone is a key topic as this sedimentary stone is largely used in historic buildings in Europe and especially in France, whereas it is sensitive to weathering by climate and air pollution. The main alteration features are black crusts in the sheltered areas of the monument and erosion in the unsheltered from rain parts. Whatever the facies, the limestone is porous and undergoes processes of dissolution and precipitation of secondary phases that change the pore network, the petrophysical properties and influence the further alteration.

In this context, this study deals with the characterization of limestone samples from a famous monument in Paris (Tribunal Administratif) weathered for 60 years and the assessment of the reactivity of the system (limestone + secondary phases) when reexposed to a simulated atmosphere by using a D₂¹⁸O vapor. The results show that for studied samples the main secondary phase is syngenite, and not the most common phase usually observed, i.e. gypsum, which can be explained by the capillary rise and the supply of K from soil and fertilizers. The use of an original approach based on isotopes (D and ¹⁸O) and SIMS analyses has also allowed to trace the circulation of water vapor within the sample and locate the reactive zones. D maps have highlighted that water vapor easily circulates in the pore network, whereas ¹⁸O only reacts with syngenite. The change of weathering conditions in the lab experiment compared to the in situ exposure shows that syngenite is not stable and could evolve in gypsum.

We think that this paper fits the aims and scopes of your journal as limestone alteration results here from climatic factors, air pollution and capillary rise from the ground and from dissolution and secondary phase precipitation processes that are controlled by the circulation of liquid water and vapor through the pore network. To investigate these processes are key to better preserve monuments and to assess the impact of the environment, especially in urban areas. Moreover, your journal has previously published very interesting papers dealing with built cultural heritage in calcareous stones (e.g. Kloppmann et al., 2014; Ruffolo et al., 2015; Pozo-Antonio et al., 2017; La Russa et al., 2017). Therefore, we hope that our paper could provide new results to address these questions.

All authors are aware of and accept responsibility for the manuscript.

Yours sincerely,

Aurlie Verney-Carron and coauthors.

Reactivity of secondary phases in weathered limestone using isotopic tracers (D and ¹⁸O): the case study of the 'Tribunal Administratif' of Paris

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Abstract

For a long time, limestone has been massively used in stone building and monuments because of its easy extraction and common presence in the landscape. On ancient monuments, mostly built in urban areas, it is exposed to urban-borne pollutants responsible for specific alteration mechanisms and weathering kinetics. Especially, the dissolution of calcite and the precipitation of new phases will affect the limestone pore network, modify the stones capillary properties and influence the further alteration. In order to better understand these processes, an altered limestone sample from 'Tribunal Administratif' (TA) in Paris was studied. The main secondary phase was found to be syngenite, which can be explained by the location of the sample close to the soil, a potential source of K (fertilizers). This phase is more soluble than gypsum that is commonly found on altered limestone. In order to assess the reactivity of the system (limestone and new phases), oxygen and hydrogen isotopes were used to trace the transfer of water (D218O) and identify the location of the reactive areas (susceptible to alteration). For that, TA samples were exposed in a climatic chamber to relative humidity (RH) cycles (25% RH for 2.5 days and 85% RH for 4.5 days) for 2 months with a D218O vapor to simulate alteration occurring in conditions sheltered from the rain. Results have shown that the water vapor easily circulates deep in the sample and reacts preferentially with syngenite the most reactive phase (compared to calcite and quartz). This phase could evolve in gypsum when exposed to an environment different from the one resulting in its formation.

**Weathered limestone from the
'Tribunal administratif' of Paris**

1.5 mm

SEM-EDS + ToF-SIMS

150 μ m

S (syngenite)
**D (circulation of
vapor in pores)**
 **^{18}O (reactivity
of syngenite)**

HIGHLIGHTS

- Limestone samples from ‘Tribunal Administratif’ of Paris have been characterized.
- In these samples, calcite has been partly transformed in syngenite (K-Ca sulfates).
- Syngenite was formed by reaction with SO₂ and K from capillary rises (fertilizers).
- Water vapor easily circulates within the pore network (D tracing).
- Syngenite is reactive (¹⁸O tracing) and could evolve into gypsum.

Reactivity of secondary phases in weathered limestone using isotopic tracers (D and ¹⁸O): the case study of the ‘Tribunal Administratif’ of Paris

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Abstract

For a long time, limestone has been massively used in stone building and monuments because of its easy extraction and common presence in the landscape. On ancient monuments, mostly built in urban areas, it is exposed to urban-borne pollutants responsible for specific alteration mechanisms and weathering kinetics. Especially, the dissolution of calcite and the precipitation of new phases will affect the limestone pore network, modify the stones capillary properties and influence the further alteration. In order to better understand these processes, an altered limestone sample from ‘Tribunal Administratif’ (TA) in Paris was studied. The main secondary phase was found to be syngenite, which can be explained by the location of the sample close to the soil, a potential source of K (fertilizers). This phase is more soluble than gypsum that is commonly found on altered limestone. In order to assess the reactivity of the system (limestone and new phases), oxygen and hydrogen isotopes were used to trace the transfer of water (D218O) and identify the location of the reactive areas (susceptible to alteration). For that, TA samples were exposed in a climatic chamber to relative humidity (RH) cycles (25% RH for 2.5 days and 85% RH for 4.5 days) for 2 months with a D218O vapor to simulate alteration occurring in conditions sheltered from the rain. Results have shown that the water vapor easily circulates deep in the sample and reacts preferentially with syngenite the most reactive phase (compared to calcite and quartz). This phase could evolve in gypsum when exposed to an environment different from the one resulting in its formation.

1. Introduction

Owing to its ubiquitous presence in the sedimentary landscape and easy extraction, limestone has been largely used in buildings, which raises the question of its preservation and conservation, as limestone is naturally eroded by water. Preserved monuments are often located in urban and polluted areas. Thus, the presence of gas and particulate pollutants in the atmosphere can modify the natural weathering of limestone and the associated kinetics.

Limestone is mainly composed of calcite CaCO_3 . It is weathered in the atmospheric environment by meteoritic water through rainfall (runoff) or small water particulate (aerosols) and vapor (relative humidity). Great changes in exposure conditions can take place in the atmospheric environment, with cyclic recurrence of high and low temperature or relative humidity (RH), wet and dry episodes, pollution peaks. Calcite chemical alteration encompasses two processes: calcite dissolution and new phase precipitation. Calcite dissolution is driven by local conditions such as the available water volume, saturation, chemistry (pH, anions and cations concentrations) and temperature (kinetic rates). The pH of the altering solution can be modified by dissolved gas species. Under current CO_2 atmospheric concentration, the pH of meteoritic water (rain droplets) is comprised between 5 and 7 and can induce a karst effect responsible for calcite dissolution (Buhmann and Dreybrodt, 1985; Plummer and Wigley, 1976). Other gaseous pollutants such as SO_2 , NO_2 and NH_3 , can induce an even greater drop in the rain pH (below pH 5) and are responsible for the phenomenon of acid rain (Bonazza et al., 2009; Smith and Viles, 2006). The dissolution of calcite affects the limestone pore network and can modify the stone capillary properties (Reddy et al., 1986). Moreover, new phase formation can also take place inside or at the surface of the stone and lead to a partial obstruction of the pores, as elements can be dissolved and precipitated again in other parts of the material. The location of these new phases can trace the circulation of water in the pore network. The presence of anions from calcite dissolution or dissolved atmospheric gases in solution leads to the precipitation of carbonates and sulfates (from dissolved SO_2), such as gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Sabbioni, 2003; Saheb et al., 2016) and syngenite $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (Janssens and Van Grieken, 2004). The precipitation of new phases is especially active on zones sheltered from rain (by roof, cornice or other various relief or sculpted elements) and can be favored by the variability of the hygroscopic conditions in the atmosphere. In sheltered zones, this favors the formation of black crusts (Camuffo et al., 1983; Sabbioni and Zappia, 1992), whereas in unsheltered zones the dissolution leads to erosion and loss of material.

As alteration processes influence the evolution of the pore network and the petrophysical properties of limestone, the kinetics of limestone alteration can evolve. Moreover, the secondary phases have a different reactivity. The cyclic nature of the atmospheric medium implies that

alternating dissolution and precipitation episodes will repeat on a material constantly changing and further and further altered. Therefore, to understand alteration mechanisms of weathered limestone, it is essential to identify the secondary phases and determine their reactivity.

In this context, the purpose of this work is to understand the fine scale processes taking place during the atmospheric weathering of monumental limestone. This study focuses on the alteration occurring in conditions sheltered from the rain and resulting solely from the action of water as vapor. Indeed, in those conditions, since run-off should not occur, calcite, ions and most of the dissolved elements will remain on the original sample.

In order to follow the transfer of water vapor inside the limestone and its reactions with the substrate, whilst providing information on the location of the reactive areas, experimental weathering of ancient building stones was conducted using $D_2^{18}O$. The use of these isotopic tracers provides information on both the depth of the water penetration front and specific reactive zones in the substrate. Indeed, deuterium can be linked to adsorption processes, as it is likely to form weak hydrogen-bonds with the substrate. Deuterium location can be therefore seen as the tracer of the water penetration front. For ^{18}O to remain in a dry sample after the experiment, stronger bounds are required. This oxygen isotope is itself a tracer of alteration and precipitation reactions occurring in the limestone. This identification calls for an isotope analytical technique with sensitivity ranging from the micrometer to the nanometer. In order to obtain in depth information, up to several millimeters, cross sections of the samples were made and subsequently analyzed. Two isotopic investigation methods were used: NanoSIMS and ToF-SIMS, both based on Secondary Ion Mass Spectrometry and sharing capabilities of high spatial resolution imaging.

2. Materials and methods

2.1. Samples

Many historical Paris monuments in Paris are characterized by limestone from the Paris Basin. One specific type of limestone was chosen for this study, the “*Saint-Maximin roche fine*” formed during Lutetian age (45 My). This stone is often used for the restoration of historical monuments for its easy shaping and its physical and mechanical properties. “*Saint-Maximin roche fine*” is a chemically homogeneous rock composed originally of *ca.* 95% of $CaCO_3$ and 5% of SiO_2 . Porosity, sorption and hygroscopic properties and evaporation, have been explored in previous work (Chabas et al., 2018; Saheb et al., 2016).

The chosen sample is an altered sample from ‘Tribunal Administratif’ in Paris, a pre-haussmannian monument originally built in the 17th c. This sample, referred to as “TA”, was part of a

restoration stone block dating to the 20th century (ca. 1950) and has been therefore altered for more than 60 years. The retrieved sample was collected at 1m above ground, thus subjected to capillary rising (Saheb et al., 2014).

2.2. Isotopic labelling experiment

To investigate the alteration mechanisms induced on limestone by water vapor, a methodology based on the use of D₂¹⁸O water was applied (Saheb et al., 2015). The sample was submitted to a series of humidity cycles with water vapor doped in D and ¹⁸O, in controlled conditions, in order to reproduce variations of RH found in atmospheric outdoor sheltered conditions.

The original limestone sample was divided into 5 cm-long rods with a 1x1cm² section. To reproduce the exposure conditions of a stone block on a building façade, only one face (perpendicular to the length) was exposed to the environment. The other sides were shielded by an aluminum foil. For 61 days (2 months), the limestone was exposed in the CIA (Chamber for Isotherm Adsorption) regulated at 20 ± 1°C and iteratively and alternatively placed inside desiccators whose RH was controlled by supersaturated saline solution at 25% RH (for 2.5 days) and at 85% RH (for 4.5 days). Solutions of CH₃COOK and K₂SO₄ were used to set relative humidity at 25% and 85%, respectively. In both cases, the water vapor present in the desiccators was enriched in deuterium, 90% of all hydrogen nuclei, and oxygen 18, 10% of all oxygen nuclei; with regards to water molecules, 18 D nuclei for every ¹⁸O nucleus. Residual traces of these isotopes present in the samples should indicate the location of the reactive alteration zones inside the materials. After the experiment, samples were kept in a desiccator (14% RH) to prevent further alteration. The samples were then cut, imbedded in resin and their surface polished using SiC discs and for finer grind velour discs and diamond suspensions down to 0.25 µm.

2.3. Analytical techniques

2.3.1. Chemical characterization. Preliminary observations of the samples were conducted on polished sample cross sections imbedded in resin, up to 2 mm in depth. Morphological and chemical surveys of the samples were led in order to locate the areas of interest, using a Zeiss ULTRA55 SEM using a FEG-Schottky electron gun. The images were acquired at 15 kV. The SEM is equipped with energy dispersive spectrometer Quantax (Bruker). Elements of interest were mapped using the EDS: K, Si, C, Ca, O and S. Preliminary mineralogical surveys of the alteration phases were carried out through Raman spectrometry, using a Renishaw InVia spectrometer equipped with a 532 nm NdYAG

laser source and a Leica microscope. Reference spectra were obtained through RRUFF database (Buzgar et al., 2009; Gunasekaran et al., 2006).

2.3.2. Isotopic analyses. In order to understand the general make-up of isotopic composition of the first millimeters of the sample, ToF-SIMS analyses were conducted. ToF-SIMS spectra measurements were carried out using an IONTOF TOF.SIMS⁵ (GmbH, Germany) instrument. This machine is equipped with a Bismuth (25keV) source for analysis and a cesium source for sputtering. Before each 500X500 μm^2 analysis, surface was sputtered with Cs^+ at 2 keV over a $750 \times 750 \mu\text{m}^2$ areas for ca. 20 min, to remove surface contamination.

Acquisition were performed in negative polarity using burst mode 6 pulses to avoid 1H^- and 16O^- detector saturation and to obtain both good lateral resolution ($\approx 200 \text{ nm}$) and mass resolution ($m/\Delta m > 5000$ at $m=16$ for oxygen). $500 \times 500 \mu\text{m}^2$ areas were analyzed (256×256 pixels) in a row from the surface to 1.85 mm inside the sample. Smaller regions of interest ($150 \times 150 \mu\text{m}^2$) inside these larger areas were subsequently mapped in order to identify more specifically the location of isotopic enrichments.

Data post-treatment allowed us to finely calculate deuterium and ^{18}O concentration over large area from sample surface to 1.85mm inside. For D/H ratio, calculation can be done directly from peaks corrected intensity at $m/z=1$ and $m/z=2$. $^{18}\text{O}/^{16}\text{O}$ ratio calculations were more challenging since mass resolution was not sufficient to avoid overlapping of $^{18}\text{O}^-$ ($m/z=17.9992$) with $^{16}\text{OD}^-$ ($m/z=18.009$) and $^{16}\text{OH}_2^-$ ($m/z=18.0106$). These overlapping are represented in Fig. 1a. The first peak corresponds to ^{18}O and the second peak corresponds to the signal of both D^{16}O and H_2^{16}O . These two hydrogen-containing species are closer in mass ($1.5 \cdot 10^{-3} \text{ u}$ distance) and could not be discriminated efficiently given the mass resolution.

The treatment of the pulsed burst, in order to enhance the intensity of the collected signal, was implemented based on the work of (De Souza and Martin, 2008). In this previous study, the authors added the first individual pulse to itself 6 times in order to enhance the signal from the 18u region. Only the first burst was selected in order to neutralize the phase shift observed in the subsequent bursts. This enhanced the signal but the background noise as well. In the present study, the pulsed burst provided 6 individual pulses (Fig. 1a) of very similar periods: $0.0620 \pm 0.0006 \text{ u}$ around 18 u. The choice was made to sum up the intensity count from each pulse, due to the limited shift in the period observed for each pulse. This provided a meta-signal presenting a smaller noise to signal ratio (Fig. 1b). A subsequent deconvolution of the signal was undertaken using the software Origin 8. The meta-signal was fitted, using Gaussian functions (high symmetry for the peaks) to fit each individual species (D^{16}O , H_2^{16}O and ^{18}O) to the signal (Fig. 1c). Using the calculated area of each

peaks, A_{18O} / A_{tot} ratio were calculated in order to assess the individual contribution of ^{18}O to the signal. The isotopic intensity count was then corrected by this ratio.

The identification of the reactive areas at the grain-interface (on the surface or inside the bulk) requires a finer mapping grid. Similar studies on the water vapor circulation have been successful at identifying these reactive areas on glass using NanoSIMS (Sessegolo et al., 2018). These regions of interest were studied at the submicron-scale using a Cameca NanoSIMS (Secondary Ion Mass Spectrometry) NS50 operated at the National Museum of Natural History in Paris (MNHN Paris) using a 16 keV primary Cs^+ beam. Secondary ions were collected in multicollection mode. Quantitative images covering surface areas of $20 \times 20 \mu m^2$, divided into 256 by 256 pixels were acquired at a raster speed of 1ms/pixel. In order to map D/H and $^{18}O/^{16}O$, we recorded the distribution of H^- and D^- on the one hand, and then $^{16}O^-$, $^{18}O^-$, $^{28}Si^-$ and $^{32}S^-$ on the second hand. Contrary to ToF-SIMS, no treatment was needed to discriminate $^{18}O^-$ from $D^{16}O$ and $H_2^{16}O$ with NanoSIMS, due to its sufficient mass resolution. An electron flooding gun was used to offset charge effects. Before, each analysis, the sample surface was presputtered over $25 \times 25 \mu m^2$ surface area with a current of 650 pA for about 20 minutes in order to remove surface contamination and to reach a steady-state sputtering (Thomen et al., 2014). $^{16}O^-$, $^{18}O^-$, $^{28}Si^-$ and $^{32}S^-$ were analyzed in a first session with a primary beam current of 1.5 pA. Then D^- and H^- images were acquired at the exact same location during a second session of image acquisitions with a 50 pA beam current for analysis. Ratio maps were calculated for hydrogen and oxygen isotopes using the L'IMAGE software developed by Larry Nittler (Carnegie Institution in Washington DC, USA). This image processing included a stage of co-registration of multiple frames to account for drift in the location of the ion beam from frame to frame.

3. Results

3.1. Identification of the altered phases

Before the experiment, the sample of the Tribunal Administratif – weathered for more than 60 years – displayed the presence of alteration phases up to a depth of 6 mm below the surface. Most of these phases were concentrated within the first 2 mm underneath the surface. *Saint-Maximin roche Fine* limestone can be classified as a grainstone and a biosparite (Dunham, 1962; Folk, 1959). In the case of TA sample, the alteration has somewhat modified the original limestone. These altered samples are characterized by the presence of large angular bioclastic fragments (up to 500 μm in length) and rounded quartz grains (50 to 200 μm in diameter) typical of the limestone. A finer section, more akin to micritic fragments, is present. These fine grains are located around the grains

and pores and correspond to the alteration phases. TA samples porosity was relatively high, 43.0 ± 0.2 % (Saheb et al., 2014), but still in the range observed for this type of limestone.

After a two-month exposure to the RH cycles, SEM-EDS mapping of an in-depth section of the sample shows the presence of elements characterizing limestone. The presence of Ca was somewhat ubiquitous in the sample (Fig. 2a orange), inherent to the calcite rich substrate (limestone), with two exceptions: areas presenting high relative concentration of Si (Fig. 2a blue) and O most likely associated most likely to quartz grains, and areas characterized by the presence of C and O mostly associated with the resin filling pores (Fig. 2a black). In some of these Ca-containing areas, the concentration of said element was relatively lower and accompanied with the presence of S (Fig. 2a,b). Sulfur is not inherent to the original limestone; it is the evidence of the presence of exogenous deposition inside the material, showing the influence of gaseous pollutant SO_2 . EDS mapping also shows the quasi ubiquitous presence of K (Fig. 2c) in the sulfur enriched areas (Fig. 2b). Therefore, S-enriched areas could correspond to the presence of syngenite (for K, Ca and S) and/or gypsum (for Ca and S).

Raman spectra were collected in order to identify the alteration phases present in depth underneath the sample surface in areas enriched in sulfur (Fig. 3). On TA sample exposed 2 months, well-defined peaks were observed at 984, 1008 and 1085 cm^{-1} on some spectra. The peak at 1085 cm^{-1} is very characteristic of calcite (Gunasekaran et al., 2006), the other peaks can both be associated to syngenite (Buzgar et al., 2009). The presence of gypsum cannot be ruled out since its main peak around 1007 cm^{-1} coincides with the second peak of syngenite. Therefore, TA samples presented a mixture of several minerals including calcite, syngenite and possible gypsum (Fig. 3a). The presence of ^{18}O isotopes can be associated with shifts in the Raman peaks (Perdikouri et al., 2013). In TA samples, no significant shifts were observed in the Raman peaks compared to the reference. This would suggest that tracer isotopes were not present in high concentrations in the identified minerals. Another Raman spectrum, obtained on a TA sample exposed 1 year presents peaks corresponding to calcite (1085 cm^{-1}) and to salts containing K and S respectively: niter – KNO_3 (1053 cm^{-1}) and thenardite – NaSO_4 (994 cm^{-1}) displaying a slight shift from the references of 1048 cm^{-1} and 989 cm^{-1} respectively observed in (Morillas et al., 2015). These minerals can be added to the list of sulfates and carbonates identified at 2-month exposure (Fig. 3).

3.2. Penetration of heavy isotope enriched vapor

The penetration of D_2^{18}O enriched water cannot be monitored directly during the experiment but the presence of D and ^{18}O can be observed in the sample afterwards using SIMS instruments. Traces of these isotopes in the sample were found after the experiment in concentration superior to

their natural abundance. The D/H and $^{18}\text{O}/^{16}\text{O}$ ratios were calculated for the first 2 mm in depth inside the TA sample using ToF-SIMS maps. These isotopic maps (Fig. 4) correspond to the area presented in Fig. 2 and corresponding to previously acquired EDS maps.

Average isotope count over the analytical areas of $500 \times 500 \mu\text{m}^2$ was used to calculate ratios. In addition, for the first millimeters below the surface, regions of interest (ROI) were created in the maps, allowing for the calculation of average isotopic count over smaller sections of $250 \mu\text{m}$ in depth by $500 \mu\text{m}$ in width. These average values were compared to natural abundance of deuterium (Fig. 5).

A very high concentration of D was found directly on the surface, and registered between 1.19×10^{-3} and 3.74×10^{-3} further inside the sample (10 to 30 times above the natural ratio of 1.5×10^{-4}) (Table 1). This observation confirms that D remained in the sample after the experiment and interacted with substrate. This infers that water vapor has diffused throughout the entire sample. This was corroborated by punctual NanoSIMS measurements in depth in the sample.

Higher concentrations of ^{18}O were found near the surface (Fig. 5) (1.29 times above the natural ratio of 0.0020), with a progressive decrease in depth in the sample. The concentration gradient observed for the oxygen isotope between the surface and the samples depth suggests a progressive effect of the isotopic exchange (Table 1).

NanoSIMS mapping of D/H and $^{18}\text{O}/^{16}\text{O}$ ratios in TA samples was conducted as well on smaller areas of interest in the sample. NanoSIMS was chosen to investigate specific areas more prone to exhibit heavy isotope enrichments. Similar to ToF-SIMS, the enrichment ratio was calculated using the average isotopic count over each NanoSIMS map. The maps correspond to $20 \mu\text{m}$ by $20 \mu\text{m}$ areas.

The comparison of the deuterium ratio to the natural abundance provides information on the local enrichments in the reactive areas of the sample (Table 1). The studied areas of interest showed the deuterium concentration in these specific areas could reach 900 times the natural ratio, with a median value over the 7 studied areas of 0.0264 (230 times the natural ratio) (Table 1). In the case of ^{18}O , the local enrichments could reach 1.76 times the natural ratio, with a median value over the 7 studied areas of 3.52×10^{-3} (1.89 times the natural ratio) (Table 1).

Comparing the two SIMS techniques, the enrichments calculated on the smaller areas of interest with NanoSIMS results register an order of magnitude above ToF-SIMS ratio for D. Ratios were very similar for the two techniques for ^{18}O , although slightly superior for NanoSIMS. One should note that the values obtained for each technique are averaged over different surface, with a higher dilution of the signal for the larger areas analyzed with ToF-SIMS. NanoSIMS, on the contrary, provides information on smaller areas of interest displaying higher isotopic concentrations and where more reactions are expected to have occurred.

3.3. Identification of the reactive zones

The identification of the phases throughout the sample showed the presence of calcite, quartz and syngenite (Fig. 3). ToF-SIMS maps of an area of interest are presented in Fig. 6. These maps show that the locations of ^{18}O and D high enrichment zones are identical. These two elements are most likely correlated here in the structure. When comparing the regions enriched in ^{18}O and D on Fig. 6, these zones correspond to phases enriched in S, most likely corresponding to syngenite evidenced in Raman spectrometry. On a larger scale, a more systematic comparison can be made between the areas on Fig. 4 and the EDS maps on Fig. 3, where enriched region corresponds to K and S containing areas.

NanoSIMS maps were used to identify the specific reactive areas at a finer scale. Results show punctual enrichment in (Fig. 7) both D and ^{18}O located in S-rich alteration phases, but none located in the resin (characterized by ^{12}C) or quartz grains (characterized by ^{28}Si), as already observed in ToF-SIMS (Fig. 6). The reactive area is up to 4 μm in thickness. It is located on the edge of the alteration phase (right side of the maps), in contact the quartz grain and the pore (left side of the maps). The information provided by nano-scale observation shows that reactive areas are located either at the grain boundary or on the surface of the pores where water vapor can come directly in contact with the alteration phase.

4. Discussion

4.1. Specificity of the TA sample

The alteration phases present in TA sample before the study are somewhat different from the usual phases observed in similar objects (Saheb et al 2013, Saheb et al 2016). Whereas gypsum is the main secondary phase usually found on limestone exposed to an urban area (Saheb et al, 2016; Camuffo et al, 1983), the TA sample is enriched in K (Fig. 2 c). The presence of this element has been associated with the precipitation of syngenite ($\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$) in the sample (Fig. 3). In literature, potassium-rich phases observed on the surface of limestone have been associated to the presence of an organic source in the atmosphere or in the soil (Matović et al., 2012). In an urban area, potassium rich salts on cultural heritage buildings have been associated to the presence of pigeon droppings (Gomez-Heras et al., 2004) or linked to the deposition of biomass burning particles (Frenay et al., 2009). The high K concentration observed in TA samples is most likely to come from a complementary source as well. TA sample was collected in an area of the building close to the

ground (c.a. 1m above ground). At this elevation, the stone is subjected to capillary rise. In this case, a non-atmospheric source of potassium is very likely to be the soil. Since the building is located in an urban area, the source of organic material is most likely be associated to punctual use of chemical fertilizer (KNO_3) on the few grass-beds present around the building but can also be associated to the presence of pigeon droppings. Indeed, Raman analyses (Fig. 3) of a separated TA sample (exposed 1 year to the vapor) presented traces of niter (KNO_3) as well as thenardite, a fairly common salt in altered porous limestone (Doehne et al., 2002; Rodriguez-Navarro et al., 2000; Shahidzadeh-Bonn et al., 2010).

4.2. Isotope interactions with the sample

When the D_2^{18}O enriched water penetrates into the sample, it interacts with the surface of the accessible grains, either at the grain boundary or in the open porosity (Fig. 7). Measurements obtained with the two different SIMS techniques showed general increase in the isotopic ratio (fD and $f^{18}O$) throughout the sample. These isotopic fractions are relatively similar according the SIMS technique and small differences can be explained by the difference of data treatment (see 2.3.2). The overall penetration of the water vapor in the porous system confirms that interaction between water and limestone can occur during the dry period and that the alteration, although at different intensities, could be occurring not only during the rainfall events but almost continuously. The depth of the vapor penetration could also infer that the risk areas are not limited to the sub-surface alone but could take place further inside the stone. Nevertheless, these enrichments differ between ^{18}O and D, with ratio always greater fD for than $f^{18}O$, due to different original enrichment in solution for the two species (Table 1).

In the TA samples, the enrichment factors of the tracer isotopes vary as well. This can be in part explained by the enrichment in the water vapor, as the deuterium enrichment is 90% of the total hydrogen but the oxygen 18 correspond to only 10 % of the oxygen. The enrichments observed in the TA samples are both very inferior to the ones measured in the alteration solution. Therefore, these results in sample were compared to the natural abundance ratios of the isotopes and not the alteration solution. ToF-SIMS shows a 10- to 30-fold enrichment in D compared to the natural abundance, whereas the ^{18}O enrichment was only 1.07 to 1.27 the natural abundance (Table 1). For NanoSIMS as well, D enrichment is greater than ^{18}O enrichment. Looking at $\text{D}/^{18}\text{O}$ ratios (Table 1), sample enrichments are very different from the ones measured for the alteration solution. The discrepancy in the enrichment could therefore indicate that the two elements present in solution might not interact in the exact same way with the sample.

Water vapor can firstly form a hydrated layer adsorbed onto the surface of the pores. Deuterium forms Van der Waals forces with the surface site hydrogen. These surface sites can be enriched in deuterium up to the point where they are all saturated forming an enriched hydrated layer at the pores and minerals surface. Therefore, the presence of deuterium in the newly altered samples is an effective tracer of the depth of the water vapor penetration. Since the samples were kept in a dry environment (desiccator) after alteration and analyses were performed in vacuum chamber, most adsorbed residual water has been removed from the sample. However, despite the desorption induced by the experiments, a significant D enrichment remains. Indeed, during the experiment and to a lesser extent afterwards, isotopic exchange can occur between the hydrogen present on the surface of the minerals and the deuterium in the hydrated enriched layer (Sessegolo et al., 2018). The presence of ^{18}O in the sample can be also related either to the presence of residual water or to the presence of newly precipitated phases resulting in interactions between the substrate and the vapor. ^{18}O found in the samples can be considered as a tracer of interactions between the substrate and the vapor.

In most cases, ^{18}O and D can be found in the same location (Fig. 4, 6, 7). The conjoined presence of these two species in ratios comparable to their original vapor concentration could indicate that the isotopes are present under the D_2^{18}O form in the reactive species. Syngenite ($\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$), the reactive phase, is a hydrated mineral and the substitution of ^{16}O for ^{18}O can occur in the molecular H_2O or in the sulfate. In the present case, the simultaneous presence of ^{18}O and D shows that the integration of the isotopes to the sample has occurred in the syngenite molecular water, with a newly formed enriched syngenite: $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{D}_2^{18}\text{O}$. A similar result should be expected, on gypsum precipitates that could be present in the sample ($\text{CaSO}_4 \cdot 2\text{D}_2^{18}\text{O}$).

In parallel to this general case, small differences can occur here and there. On Fig. 4 a large D enriched area can be observed at 100 μm below the surface (vertically centered) but is far less reactive for ^{18}O . These variations could account for the discrepancy with the original vapor found in some cases with ToF-SIMS, with greater deuterium enrichment and could correspond mainly to sorption of water without significant reaction. On Fig. 7 conversely, on the lower left of the reactive area, ^{18}O is present where D enrichment is tenuous. This specific area could be the location of a different molecular substitution. Indeed, a substitution in carbonate or sulfate molecules can be traced by the presence of ^{18}O alone. In this area, the relative absence of deuterium could infer the integration of ^{18}O in SO_4^{2-} . The presence of marked sulfate could be indicating of the precipitation of new alteration phase during the experiment, but the nature of this new sulfate-rich phase was not specifically identified: syngenite, gypsum or thenardite (Fig. 3).

4.3. Reactivity of the different phases

Comparing the information provided by Fig. 2 and Fig. 4, isotope tracers have not been observed in areas corresponding to quartz grains or purely calcite grains. Syngenite was identified as the main reactive phase in TA sample and is more likely to be altered again in the future. The dissolution of syngenite occurs preferentially to the dissolution gypsum or calcite. Syngenite solubility is $8.3 \text{ mmol} \cdot \text{L}^{-1}$ (Darvell, 2018) and higher than gypsum which is $4.9 \text{ mmol} \cdot \text{L}^{-1}$ (Colombani, 2008); $K_s = 5 \cdot 10^{-5}$) or calcite, $0.06 \text{ mmol} \cdot \text{L}^{-1}$ (Visconti et al., 2010); $K_s = 3 \cdot 10^{-9}$). Furthermore, the lack of Raman signal in highly altered areas suggests that the altered phases are not as well crystallized as calcite or quartz grains and their grain size is generally smaller. For a similar volume of mineral, smaller syngenite grains possess a greater specific surface and therefore a greater reactive surface area. This morphological difference can influence the preferential alteration of syngenite.

The ubiquitous presence of syngenite in the TA sample is associated with a large source of potassium in the system, stemming from an organic source and influenced by the capillary rise from the soil. If we consider the future evolution of similarly altered limestone, one fundamental question is: are these specific alteration phases stable once the local potassium source is removed? For the experiment in isotopically labelled water vapor, the samples have been removed from the local source of potassium present at the base of the TA building. In new environmental conditions, the syngenite is not at equilibrium with its surroundings. The main interaction between the vapor and the sample after two-month exposure is a substitution in the hydrated molecule of syngenite, but evidence was found that new sulfate phase might have precipitated as well (Fig. 7). Since NanoSIMS analyses monitored sulfur but not potassium or calcium, and Raman analyses did not provide sufficient lateral resolution for these small phases, it is unclear if the new precipitate is syngenite.

Using CHESS thermochemical code (van der Lee and De Windt, 2002) in association with “Thermo-chimie” database, calculations were carried out to trace the evolution of syngenite in a solution with a composition similar to rainwater. When increasing the potassium concentration in the solution in comparison to typical rain composition, the syngenite remained. In typical rain conditions (no additional potassium), the syngenite was partially replaced by gypsum. This replacement of syngenite by gypsum in an environment only influenced by rain water composition shows that the presence and conservation of syngenite in the sample is inherent to the local condition to which it is exposed in the building.

If the local environmental conditions change in the building, the syngenite is likely to react to form new alteration phases, most likely gypsum. Since the dissolution of syngenite will occur preferentially it can be inferred that this phase will be progressively replaced.

4.4. Estimation of the reaction rate

Mercury intrusion porosity (MIP) measurements have already been performed on ancient samples from the study frame (Saheb et al., 2016). The value of the specific surface area for TA before vapor alteration is of $0.22 \text{ m}^2 \cdot \text{g}^{-1}$ (Saheb et al., 2015). Surface analyses were conducted using Histolab® software on large SEM images (Fig. 2) obtained at a resolution of $0.74 \text{ }\mu\text{m}$ per pixel. This resolution did not allow for an accurate evaluation of the specific surface, but the values calculated via Histolab® were in the same order of magnitude as mercury porosity measurements (2.3 times lower than MIP). This surface estimation allowed for an approximation of relative contribution of each phase to the specific surface of the sample. Quartz grains contributed to 0.5 % of the surface area, calcite contributed to 82.5% of the surface area and sulfur-containing alteration phases (syngenite) contributed to 17% of the surface area. Relatively to the specific surface area measured via MIP, the specific surface area of the reactive phases, *e.g.* the sulfur-containing alteration phases, is about $0.04 \text{ m}^2 \cdot \text{g}^{-1}$.

On the NanoSIMS analyses, the thickness of the reactive mineral reached up to $4 \text{ }\mu\text{m}$ in thickness (Fig. 7) but was only present in limited sections of the surface of the alteration phase. Using the same surface analyses technique on large ToF-SIMS images (Fig. 4), the zones enriched in ^{18}O and D were estimated to represent 31% of the potential reactive phase volume. Taking into account the maximum thickness of $4 \text{ }\mu\text{m}$ for these reactive areas, an average surface of 0.01 mm^2 can be estimated for the reactive areas, as well as the specific surface area for enriched phase of $0.004 \text{ m}^2 \cdot \text{g}^{-1}$. Given that the substitution of H_2O by D_2^{18}O has been shown to occur at the mineral surface (in the pores or at grain boundary), the specific surface area provides information on the rate of substitution. Comparing this specific surface area for enriched phase with syngenite phase specific surface area, substitution occurred on 10% of syngenite phase after two-month exposure to water vapor. This rate corresponds to the isotopic exchange rate of H and O atoms in the syngenite. However, it highlights that even if the exposure is short, the syngenite is highly reactive with the water vapor and that the system (limestone and new phases) can rapidly evolve.

5. Conclusion

The study of an altered limestone sample from ‘Tribunal Administratif’ in Paris has shown the alteration phases already present are the result of a very specific environment, enriched in potassium. Contrary to many similar samples where gypsum is the main alteration phase, TA sample main alteration phase is syngenite. This phase reflects the presence of a very specific pollution source in the sample immediate surrounding and the influence of capillary rising on building limestone close

to the ground. Modifications in the limestone environment are responsible for the evolution of the alteration phases.

The use of isotopic labels has allowed for the identification of reactive areas in the sample more likely to be altered again. The use of high concentration of ^{18}O studied via ToF-SIMS was key in the implementation of a new methodology of signal treatment that allowed for the specific quantification of species presenting very similar atomic mass. This new methodology allowed for the accurate calculation of the oxygen isotopic ratio even in highly hydrated areas.

When studying this system using isotopically labelled vapor, syngenite was found to be the main reactive phase. The larger part of the isotopes is integrated into the sample under the D_2^{18}O form by substitution in the syngenite molecular water. There is nevertheless some evidence that ^{18}O was present without D in some alteration phases, suggesting its integration to sulphates, most likely through the precipitation of new alteration phase in the system.

This new phase precipitation happened in an environment presenting a very specific unforeseen difference in composition to the original location of the sample. Thermodynamic calculations have shown that the syngenite could be replaced by newly formed gypsum in such a case. This example is key to understand the evolution of altered material faced with evolution in its environment.

Considering the field of heritage material conservation, key pieces of material can be transferred from one environment to another. Here, we see that a modification of the concentration of one specific element can impact the reactivity of the alteration phases present in the object. Therefore, to ensure the durability of the material, any drastic change in the object direct environment should be limited as much as possible or heavily monitored.

Acknowledgements

The authors would like to thank the French National Research Agency (ANR) for their financial support (ANR GLAM). The NanoSIMS Facility at MNHN was funded by CNRS, Région Île de France, Ministère délégué à l'Enseignement supérieur et à la Recherche and MNHN.

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632 Figure 5: Oxygen and hydrogen isotopic ratio obtained via ToF-SIMS at varying depth inside TA

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653 Table 1: Isotopic fraction and enrichment factor compared to the natural abundance for D and ¹⁸O.

	Isotopic fraction (f)				Enrichment factor		
	Natural abundance	Experiment Solution	ToF-SIMS	NanoSIMS	Solution	ToF-SIMS	NanoSIMS
D	$1.15 \cdot 10^{-4}$	0.9	$1.19-3.74 \cdot 10^{-3}$	$2.64 \cdot 10^{-2}$	x 7800	x 10-30	x 230
¹⁸ O	$2.005 \cdot 10^{-3}$	0.1	$2.14-2.56 \cdot 10^{-3}$	$3.52 \cdot 10^{-3}$	x 50	x 1.07-1.27	x 1.75
D/ ¹⁸ O		9			156	9-24	7

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: