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## Reactivity of secondary phases in weathered limestone using isotopic tracers (D and $^{18}\text{O}$ ): the case study of the 'Tribunal Administratif' of Paris

Lucile Gentaz, Mandana Saheb, Aurélie Verney-Carron, Loryelle Sessegolo, Anne Chabas, Nicolas Nuns, Laurent Remusat, Adriana Gonzalez-Cano, Chloé Fourdrin, Jean-Didier Mertz, et al.

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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.

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Saint Victor sur Loire, April 20<sup>th</sup> 2020

Dear Editor,

We would like you to consider the manuscript "**Reactivity of secondary phases in weathered limestone using isotopic tracers (D and <sup>18</sup>O): 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 D<sub>2</sub><sup>18</sup>O 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 <sup>18</sup>O) 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 <sup>18</sup>O 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,

Aurélie Verney-Carron and coauthors.

1 **Reactivity of secondary phases in weathered limestone using isotopic tracers (D and <sup>18</sup>O): the case**  
2 **study of the 'Tribunal Administratif' of Paris**

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28  
29

30 **Abstract**

31 For a long time, limestone has been massively used in stone building and monuments because of  
32 its easy extraction and common presence in the landscape. On ancient monuments, mostly built in  
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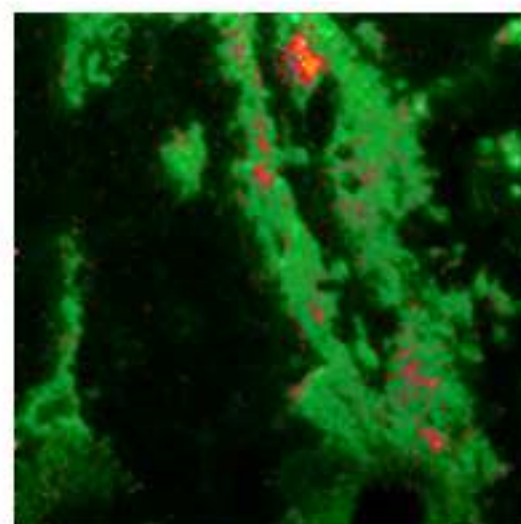
**Weathered limestone from the  
'Tribunal administratif' of Paris**



**1.5 mm**



**SEM-EDS + ToF-SIMS**



**150  $\mu$ 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 SO<sub>2</sub> and K from capillary rises (fertilizers).
- Water vapor easily circulates within the pore network (D tracing).
- Syngenite is reactive (<sup>18</sup>O tracing) and could evolve into gypsum.



1 **Reactivity of secondary phases in weathered limestone using isotopic tracers (D and <sup>18</sup>O): the case**  
2 **study of the 'Tribunal Administratif' of Paris**

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34 reactive phase (compared to calcite and quartz). This phase could evolve in gypsum when exposed to  
35 an environment different from the one resulting in its formation.

36

## 37 **1. Introduction**

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

43 Limestone is mainly composed of calcite  $\text{CaCO}_3$ . It is weathered in the atmospheric  
44 environment by meteoritic water through rainfall (runoff) or small water particulate (aerosols) and  
45 vapor (relative humidity). Great changes in exposure conditions can take place in the atmospheric  
46 environment, with cyclic recurrence of high and low temperature or relative humidity (RH), wet and  
47 dry episodes, pollution peaks. Calcite chemical alteration encompasses two processes: calcite  
48 dissolution and new phase precipitation. Calcite dissolution is driven by local conditions such as the  
49 available water volume, saturation, chemistry (pH, anions and cations concentrations) and  
50 temperature (kinetic rates). The pH of the altering solution can be modified by dissolved gas species.  
51 Under current  $\text{CO}_2$  atmospheric concentration, the pH of meteoritic water (rain droplets) is  
52 comprised between 5 and 7 and can induce a karst effect responsible for calcite dissolution  
53 (Buhmann and Dreybrodt, 1985; Plummer and Wigley, 1976). Other gaseous pollutants such as  $\text{SO}_2$ ,  
54  $\text{NO}_2$  and  $\text{NH}_3$ , can induce an even greater drop in the rain pH (below pH 5) and are responsible for  
55 the phenomenon of acid rain (Bonazza et al., 2009; Smith and Viles, 2006). The dissolution of calcite  
56 affects the limestone pore network and can modify the stone capillary properties (Reddy et al.,  
57 1986). Moreover, new phase formation can also take place inside or at the surface of the stone and  
58 lead to a partial obstruction of the pores, as elements can be dissolved and precipitated again in  
59 other parts of the material. The location of these new phases can trace the circulation of water in the  
60 pore network. The presence of anions from calcite dissolution or dissolved atmospheric gases in  
61 solution leads to the precipitation of carbonates and sulfates (from dissolved  $\text{SO}_2$ ), such as gypsum  
62  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (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  
63 Grieken, 2004). The precipitation of new phases is especially active on zones sheltered from rain (by  
64 roof, cornice or other various relief or sculpted elements) and can be favored by the variability of the  
65 hygroscopic conditions in the atmosphere. In sheltered zones, this favors the formation of black  
66 crusts (Camuffo et al., 1983; Sabbioni and Zappia, 1992), whereas in unsheltered zones the  
67 dissolution leads to erosion and loss of material.

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

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

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

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

92

## 93 **2. Materials and methods**

94

### 95 *2.1. Samples*

96

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

104 The chosen sample is an altered sample from 'Tribunal Administratif' in Paris, a pre-  
105 haussmannian monument originally built in the 17<sup>th</sup> c. This sample, referred to as "TA", was part of a

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

109

## 110 *2.2. Isotopic labelling experiment*

111

112 To investigate the alteration mechanisms induced on limestone by water vapor, a  
113 methodology based on the use of D<sub>2</sub><sup>18</sup>O water was applied (Saheb et al., 2015). The sample was  
114 submitted to a series of humidity cycles with water vapor doped in D and <sup>18</sup>O, in controlled  
115 conditions, in order to reproduce variations of RH found in atmospheric outdoor sheltered  
116 conditions.

117 The original limestone sample was divided into 5 cm-long rods with a 1x1cm<sup>2</sup> section. To  
118 reproduce the exposure conditions of a stone block on a building façade, only one face  
119 (perpendicular to the length) was exposed to the environment. The other sides were shielded by an  
120 aluminum foil. For 61 days (2 months), the limestone was exposed in the CIA (Chamber for Isotherm  
121 Adsorption) regulated at 20 ± 1°C and iteratively and alternatively placed inside desiccators whose  
122 RH was controlled by supersaturated saline solution at 25% RH (for 2.5 days) and at 85% RH (for 4.5  
123 days). Solutions of CH<sub>3</sub>COOK and K<sub>2</sub>SO<sub>4</sub> were used to set relative humidity at 25% and 85%,  
124 respectively. In both cases, the water vapor present in the desiccators was enriched in deuterium,  
125 90% of all hydrogen nuclei, and oxygen 18, 10% of all oxygen nuclei; with regards to water molecules,  
126 18 D nuclei for every <sup>18</sup>O nucleus. Residual traces of these isotopes present in the samples should  
127 indicate the location of the reactive alteration zones inside the materials. After the experiment,  
128 samples were kept in a desiccator (14% RH) to prevent further alteration. The samples were then cut,  
129 imbedded in resin and their surface polished using SiC discs and for finer grind velour discs and  
130 diamond suspensions down to 0.25 µm.

131

## 132 *2.3. Analytical techniques*

133

134 *2.3.1. Chemical characterization.* Preliminary observations of the samples were conducted on  
135 polished sample cross sections imbedded in resin, up to 2 mm in depth. Morphological and chemical  
136 surveys of the samples were led in order to locate the areas of interest, using a Zeiss ULTRA55 SEM  
137 using a FEG-Schottky electron gun. The images were acquired at 15 kV. The SEM is equipped with  
138 energy dispersive spectrometer Quantax (Bruker). Elements of interest were mapped using the EDS:  
139 K, Si, C, Ca, O and S. Preliminary mineralogical surveys of the alteration phases were carried out  
140 through Raman spectrometry, using a Renishaw InVia spectrometer equipped with a 532 nm NdYAG

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

143

144 *2.3.2. Isotopic analyses.* In order to understand the general make-up of isotopic composition of the  
145 first millimeters of the sample, ToF-SIMS analyses were conducted. ToF-SIMS spectra measurements  
146 were carried out using an IONTOF TOF.SIMS<sup>5</sup> (GmbH, Germany) instrument. This machine is  
147 equipped with a Bismuth (25keV) source for analysis and a cesium source for sputtering. Before each  
148 500X500  $\mu\text{m}^2$  analysis, surface was sputtered with  $\text{Cs}^+$  at 2 keV over a  $750 \times 750 \mu\text{m}^2$  areas for ca.  
149 20 min, to remove surface contamination.

150 Acquisition were performed in negative polarity using burst mode 6 pulses to avoid  $1\text{H}^-$  and  
151  $16\text{O}^-$  detector saturation and to obtain both good lateral resolution ( $\approx 200 \text{ nm}$ ) and mass resolution  
152 ( $m/\Delta m > 5000$  at  $m=16$  for oxygen).  $500 \times 500 \mu\text{m}^2$  areas were analyzed ( $256 \times 256$  pixels) in a row  
153 from the surface to 1.85 mm inside the sample. Smaller regions of interest ( $150 \times 150 \mu\text{m}^2$ ) inside  
154 these larger areas were subsequently mapped in order to identify more specifically the location of  
155 isotopic enrichments.

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

164 The treatment of the pulsed burst, in order to enhance the intensity of the collected signal,  
165 was implemented based on the work of (De Souza and Martin, 2008). In this previous study, the  
166 authors added the first individual pulse to itself 6 times in order to enhance the signal from the 18u  
167 region. Only the first burst was selected in order to neutralize the phase shift observed in the  
168 subsequent bursts. This enhanced the signal but the background noise as well. In the present study,  
169 the pulsed burst provided 6 individual pulses (Fig. 1a) of very similar periods:  $0.0620 \pm 0.0006 \text{ u}$   
170 around 18 u. The choice was made to sum up the intensity count from each pulse, due to the limited  
171 shift in the period observed for each pulse. This provided a meta-signal presenting a smaller noise to  
172 signal ratio (Fig. 1b). A subsequent deconvolution of the signal was undertaken using the software  
173 Origin 8. The meta-signal was fitted, using Gaussian functions (high symmetry for the peaks) to fit  
174 each individual species ( $\text{D}^{16}\text{O}$ ,  $\text{H}_2^{16}\text{O}$  and  $^{18}\text{O}$ ) to the signal (Fig. 1c). Using the calculated area of each

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

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

197

### 198 **3. Results**

199

#### 200 *3.1. Identification of the altered phases*

201

202 Before the experiment, the sample of the Tribunal Administratif – weathered for more than  
203 60 years – displayed the presence of alteration phases up to a depth of 6 mm below the surface.  
204 Most of these phases were concentrated within the first 2 mm underneath the surface. *Saint-*  
205 *Maximin roche Fine* limestone can be classified as a grainstone and a biosparite (Dunham, 1962; Folk,  
206 1959). In the case of TA sample, the alteration has somewhat modified the original limestone. These  
207 altered samples are characterized by the presence of large angular bioclastic fragments (up to 500  
208  $\mu m$  in length) and rounded quartz grains (50 to 200  $\mu m$  in diameter) typical of the limestone. A finer  
209 section, more akin to micritic fragments, is present. These fine grains are located around the grains

210 and pores and correspond to the alteration phases. TA samples porosity was relatively high,  $43.0 \pm 0.2$   
211 % (Saheb et al., 2014), but still in the range observed for this type of limestone.

212 After a two-month exposure to the RH cycles, SEM-EDS mapping of an in-depth section of the  
213 sample shows the presence of elements characterizing limestone. The presence of Ca was somewhat  
214 ubiquitous in the sample (Fig. 2a orange), inherent to the calcite rich substrate (limestone), with two  
215 exceptions: areas presenting high relative concentration of Si (Fig. 2a blue) and O most likely  
216 associated most likely to quartz grains, and areas characterized by the presence of C and O mostly  
217 associated with the resin filling pores (Fig. 2a black). In some of these Ca-containing areas, the  
218 concentration of said element was relatively lower and accompanied with the presence of S (Fig.  
219 2a,b). Sulfur is not inherent to the original limestone; it is the evidence of the presence of exogenous  
220 deposition inside the material, showing the influence of gaseous pollutant  $\text{SO}_2$ . EDS mapping also  
221 shows the quasi ubiquitous presence of K (Fig. 2c) in the sulfur enriched areas (Fig. 2b). Therefore, S-  
222 enriched areas could correspond to the presence of syngenite (for K, Ca and S) and/or gypsum (for Ca  
223 and S).

224 Raman spectra were collected in order to identify the alteration phases present in depth  
225 underneath the sample surface in areas enriched in sulfur (Fig. 3). On TA sample exposed 2 months,  
226 well-defined peaks were observed at 984, 1008 and  $1085 \text{ cm}^{-1}$  on some spectra. The peak at  $1085$   
227  $\text{cm}^{-1}$  is very characteristic of calcite (Gunasekaran et al., 2006), the other peaks can both be  
228 associated to syngenite (Buzgar et al., 2009). The presence of gypsum cannot be ruled out since its  
229 main peak around  $1007 \text{ cm}^{-1}$  coincides with the second peak of syngenite. Therefore, TA samples  
230 presented a mixture of several minerals including calcite, syngenite and possible gypsum (Fig. 3a).  
231 The presence of  $^{18}\text{O}$  isotopes can be associated with shifts in the Raman peaks (Perdikouri et al.,  
232 2013). In TA samples, no significant shifts were observed in the Raman peaks compared to the  
233 reference. This would suggest that tracer isotopes were not present in high concentrations in the  
234 identified minerals. Another Raman spectrum, obtained on a TA sample exposed 1 year presents  
235 peaks corresponding to calcite ( $1085 \text{ cm}^{-1}$ ) and to salts containing K and S respectively: niter –  $\text{KNO}_3$   
236 ( $1053 \text{ cm}^{-1}$ ) and thenardite –  $\text{NaSO}_4$  ( $994 \text{ cm}^{-1}$ ) displaying a slight shift from the references of  $1048$   
237  $\text{cm}^{-1}$  and  $989 \text{ cm}^{-1}$  respectively observed in (Morillas et al., 2015). These minerals can be added to the  
238 list of sulfates and carbonates identified at 2-month exposure (Fig. 3).

239

### 240 3.2. Penetration of heavy isotope enriched vapor

241

242 The penetration of  $\text{D}_2^{18}\text{O}$  enriched water cannot be monitored directly during the experiment  
243 but the presence of D and  $^{18}\text{O}$  can be observed in the sample afterwards using SIMS instruments.  
244 Traces of these isotopes in the sample were found after the experiment in concentration superior to

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

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

253 A very high concentration of D was found directly on the surface, and registered between  
254  $1.19 \times 10^{-3}$  and  $3.74 \times 10^{-3}$  further inside the sample (10 to 30 times above the natural ratio of  $1.5 \times 10^{-4}$ )  
255 (Table 1). This observation confirms that D remained in the sample after the experiment and  
256 interacted with substrate. This infers that water vapor has diffused throughout the entire sample.  
257 This was corroborated by punctual NanoSIMS measurements in depth in the sample.

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

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

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

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



280

### 281 3.3. Identification of the reactive zones

282

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

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

299

## 300 4. Discussion

301

### 302 4.1. Specificity of the TA sample

303

304 The alteration phases present in TA sample before the study are somewhat different from  
305 the usual phases observed in similar objects (Saheb et al 2013, Saheb et al 2016). Whereas gypsum is  
306 the main secondary phase usually found on limestone exposed to an urban area (Saheb et al, 2016;  
307 Camuffo et al, 1983), the TA sample is enriched in K (Fig. 2 c). The presence of this element has been  
308 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,  
309 potassium-rich phases observed on the surface of limestone have been associated to the presence of  
310 an organic source in the atmosphere or in the soil (Matović et al., 2012). In an urban area, potassium  
311 rich salts on cultural heritage buildings have been associated to the presence of pigeon droppings  
312 (Gomez-Heras et al., 2004) or linked to the deposition of biomass burning particles (Frenay et al.,  
313 2009). The high K concentration observed in TA samples is most likely to come from a  
314 complementary source as well. TA sample was collected in an area of the building close to the

315 ground (c.a. 1m above ground). At this elevation, the stone is subjected to capillary rise. In this case,  
316 a non-atmospheric source of potassium is very likely to be the soil. Since the building is located in an  
317 urban area, the source of organic material is most likely be associated to punctual use of chemical  
318 fertilizer ( $\text{KNO}_3$ ) on the few grass-beds present around the building but can also be associated to the  
319 presence of pigeon droppings. Indeed, Raman analyses (Fig. 3) of a separated TA sample (exposed 1  
320 year to the vapor) presented traces of niter ( $\text{KNO}_3$ ) as well as thenardite, a fairly common salt in  
321 altered porous limestone (Doehne et al., 2002; Rodriguez-Navarro et al., 2000; Shahidzadeh-Bonn et  
322 al., 2010).

323

#### 324 4.2. Isotope interactions with the sample

325

326 When the  $\text{D}_2^{18}\text{O}$  enriched water penetrates into the sample, it interacts with the surface of  
327 the accessible grains, either at the grain boundary or in the open porosity (Fig. 7). Measurements  
328 obtained with the two different SIMS techniques showed general increase in the isotopic ratio ( $fD$   
329 and  $f^{18}\text{O}$ ) throughout the sample. These isotopic fractions are relatively similar according the SIMS  
330 technique and small differences can be explained by the difference of data treatment (see 2.3.2). The  
331 overall penetration of the water vapor in the porous system confirms that interaction between water  
332 and limestone can occur during the dry period and that the alteration, although at different  
333 intensities, could be occurring not only during the rainfall events but almost continuously. The depth  
334 of the vapor penetration could also infer that the risk areas are not limited to the sub-surface alone  
335 but could take place further inside the stone. Nevertheless, these enrichments differ between  $^{18}\text{O}$   
336 and D, with ratio always greater  $fD$  for than  $f^{18}\text{O}$ , due to different original enrichment in solution for  
337 the two species (Table 1).

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

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

363 In most cases,  $^{18}\text{O}$  and D can be found in the same location (Fig. 4, 6, 7). The conjoined  
364 presence of these two species in ratios comparable to their original vapor concentration could  
365 indicate that the isotopes are present under the  $\text{D}_2^{18}\text{O}$  form in the reactive species. Syngenite ( $\text{K}_2$   
366  $\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ), the reactive phase, is a hydrated mineral and the substitution of  $^{16}\text{O}$  for  $^{18}\text{O}$  can occur  
367 in the molecular  $\text{H}_2\text{O}$  or in the sulfate. In the present case, the simultaneous presence of  $^{18}\text{O}$  and D  
368 shows that the integration of the isotopes to the sample has occurred in the syngenite molecular  
369 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  
370 expected, on gypsum precipitates that could be present in the sample ( $\text{CaSO}_4 \cdot 2\text{D}_2^{18}\text{O}$ ).

371 In parallel to this general case, small differences can occur here and there. On Fig. 4 a large D  
372 enriched area can be observed at 100  $\mu\text{m}$  below the surface (vertically centered) but is far less  
373 reactive for  $^{18}\text{O}$ . These variations could account for the discrepancy with the original vapor found in  
374 some cases with ToF-SIMS, with greater deuterium enrichment and could correspond mainly to  
375 sorption of water without significant reaction. On Fig. 7 conversely, on the lower left of the reactive  
376 area,  $^{18}\text{O}$  is present where D enrichment is tenuous. This specific area could be the location of a  
377 different molecular substitution. Indeed, a substitution in carbonate or sulfate molecules can be  
378 traced by the presence of  $^{18}\text{O}$  alone. In this area, the relative absence of deuterium could infer the  
379 integration of  $^{18}\text{O}$  in  $\text{SO}_4^{2-}$ . The presence of marked sulfate could be indicating of the precipitation of  
380 new alteration phase during the experiment, but the nature of this new sulfate-rich phase was not  
381 specifically identified: syngenite, gypsum or thenardite (Fig. 3).

382

383 *4.3. Reactivity of the different phases*

384

385 Comparing the information provided by Fig. 2 and Fig. 4, isotope tracers have not been  
386 observed in areas corresponding to quartz grains or purely calcite grains. Syngenite was identified as  
387 the main reactive phase in TA sample and is more likely to be altered again in the future. The  
388 dissolution of syngenite occurs preferentially to the dissolution gypsum or calcite. Syngenite  
389 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,  
390 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  
391 lack of Raman signal in highly altered areas suggests that the altered phases are not as well  
392 crystallized as calcite or quartz grains and their grain size is generally smaller. For a similar volume of  
393 mineral, smaller syngenite grains possess a greater specific surface and therefore a greater reactive  
394 surface area. This morphological difference can influence the preferential alteration of syngenite.

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

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

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

417

418 *4.4. Estimation of the reaction rate*

419

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

432 On the NanoSIMS analyses, the thickness of the reactive mineral reached up to  $4 \text{ }\mu\text{m}$  in  
433 thickness (Fig. 7) but was only present in limited sections of the surface of the alteration phase. Using  
434 the same surface analyses technique on large ToF-SIMS images (Fig. 4), the zones enriched in  $^{18}\text{O}$  and  
435 D were estimated to represent 31% of the potential reactive phase volume. Taking into account the  
436 maximum thickness of  $4 \text{ }\mu\text{m}$  for these reactive areas, an average surface of  $0.01 \text{ mm}^2$  can be  
437 estimated for the reactive areas, as well as the specific surface area for enriched phase of  $0.004$   
438  $\text{m}^2 \cdot \text{g}^{-1}$ . Given that the substitution of  $\text{H}_2\text{O}$  by  $\text{D}_2^{18}\text{O}$  has been shown to occur at the mineral surface  
439 (in the pores or at grain boundary), the specific surface area provides information on the rate of  
440 substitution. Comparing this specific surface area for enriched phase with syngenite phase specific  
441 surface area, substitution occurred on 10% of syngenite phase after two-month exposure to water  
442 vapor. This rate corresponds to the isotopic exchange rate of H and O atoms in the syngenite.  
443 However, it highlights that even if the exposure is short, the syngenite is highly reactive with the  
444 water vapor and that the system (limestone and new phases) can rapidly evolve.

445

## 446 5. Conclusion

447

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

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

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

460 When studying this system using isotopically labelled vapor, syngenite was found to be the  
461 main reactive phase. The larger part of the isotopes is integrated into the sample under the  $\text{D}_2^{18}\text{O}$   
462 form by substitution in the syngenite molecular water. There is nevertheless some evidence that  $^{18}\text{O}$   
463 was present without D in some alteration phases, suggesting its integration to sulphates, most likely  
464 through the precipitation of new alteration phase in the system.

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

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

475

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480

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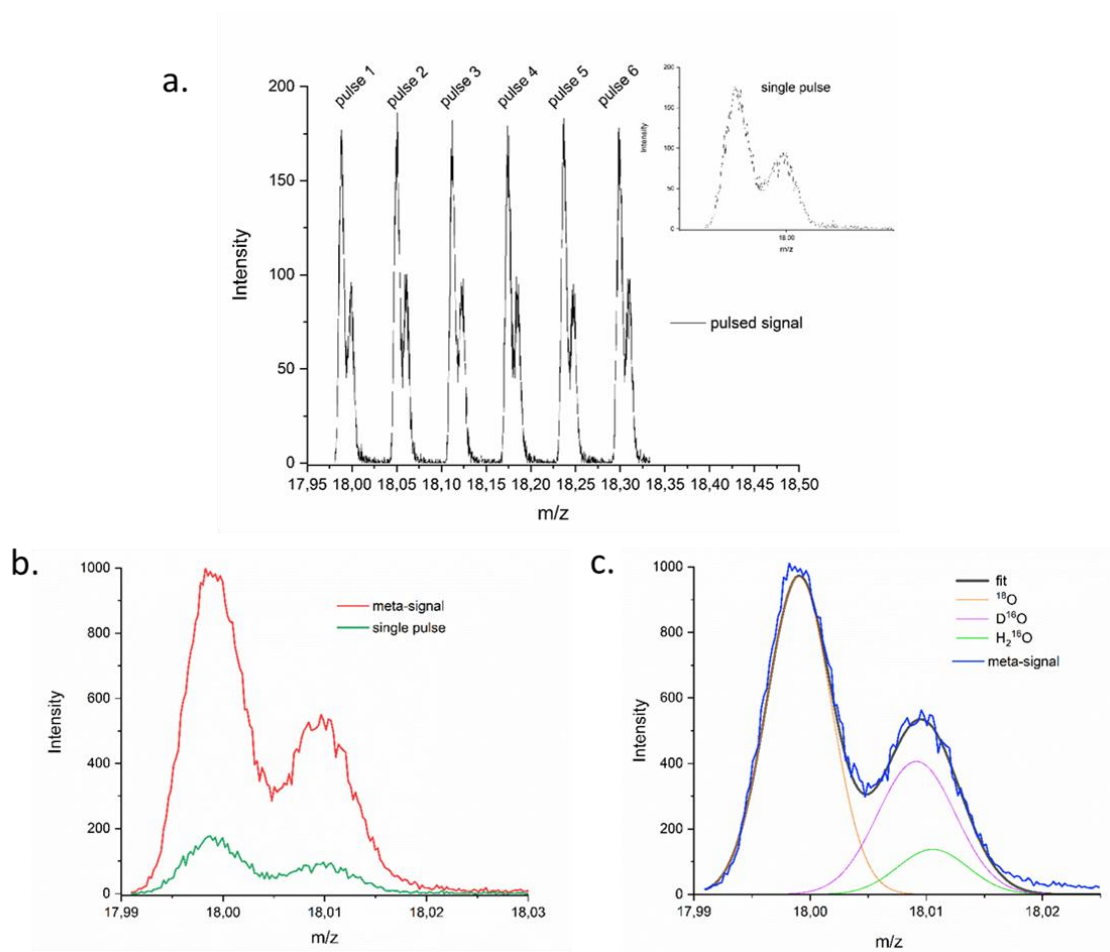
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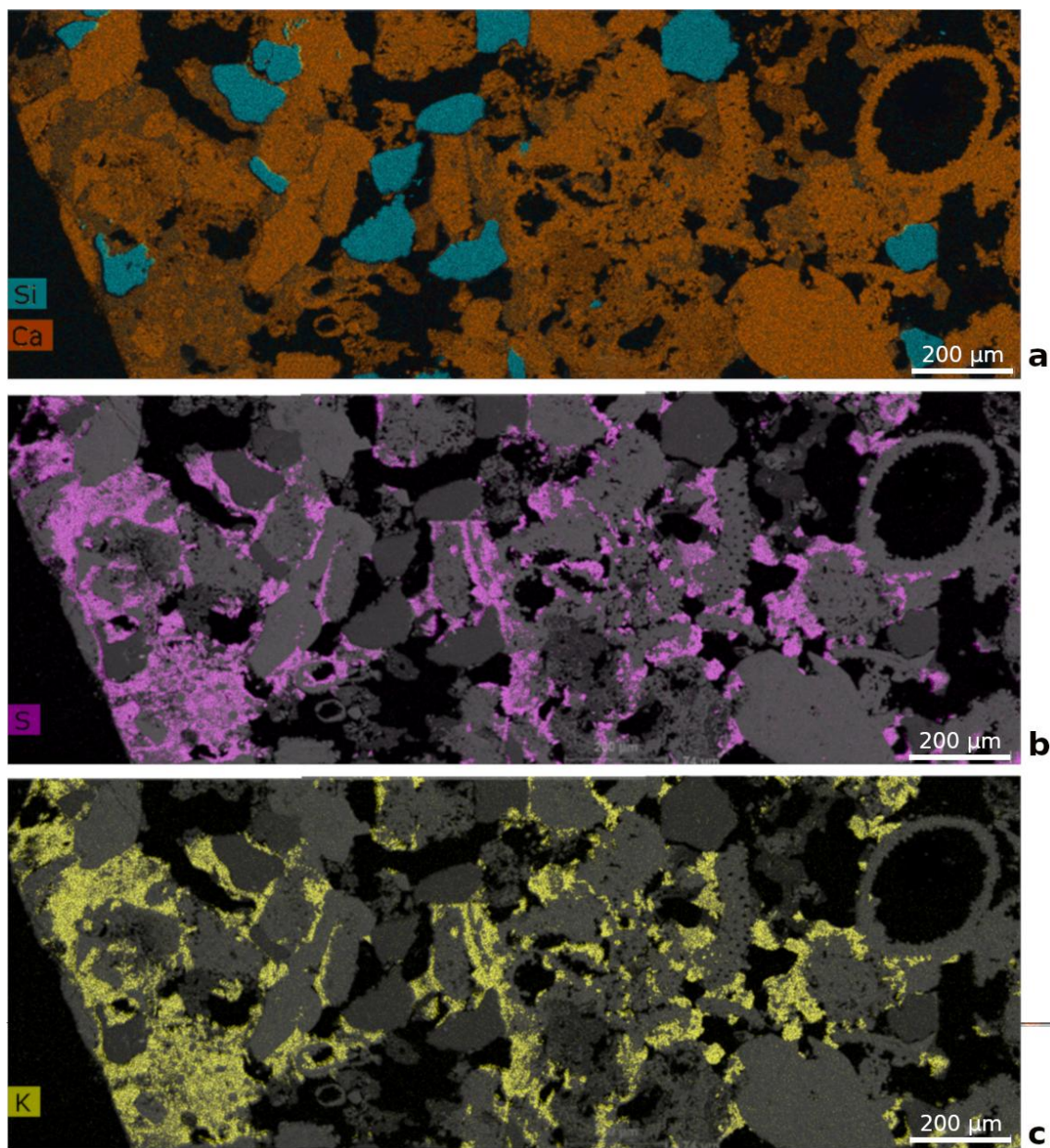
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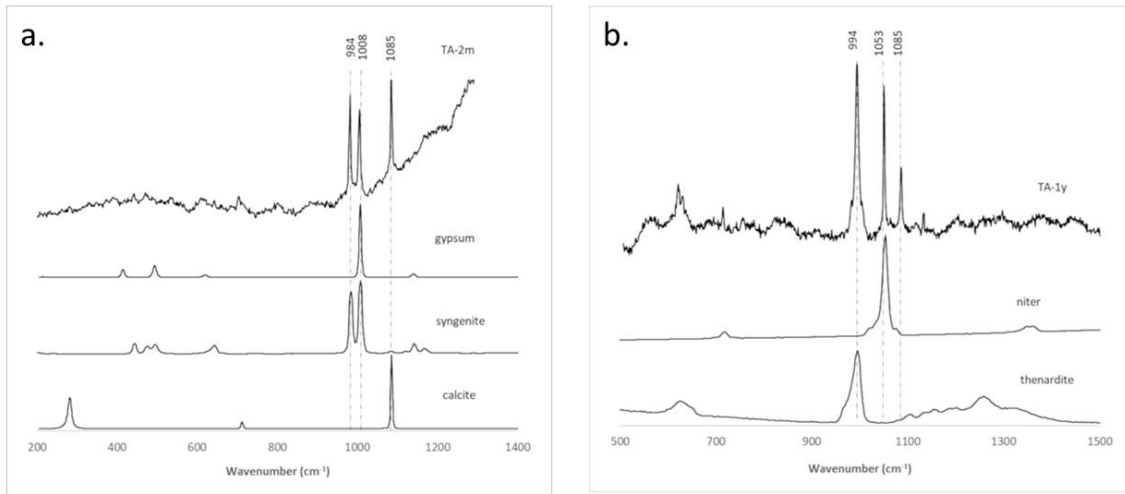
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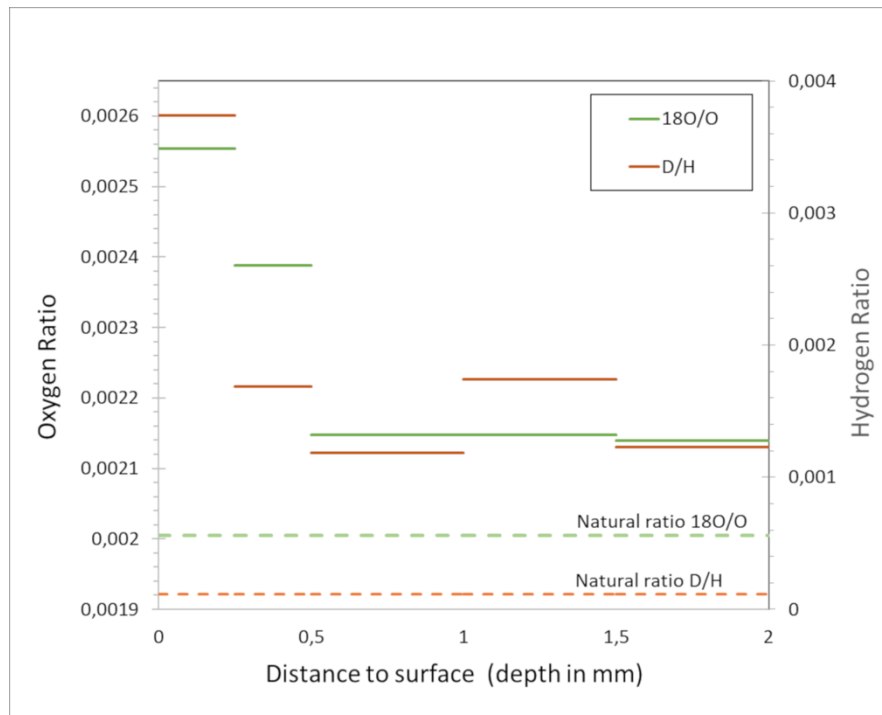
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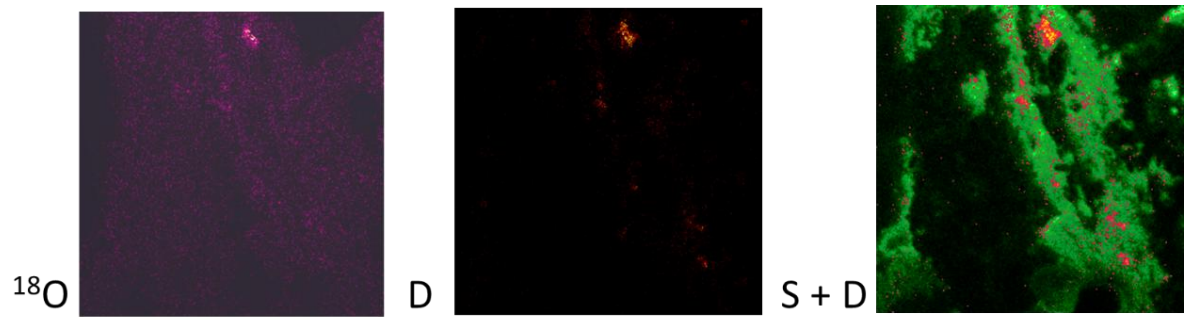
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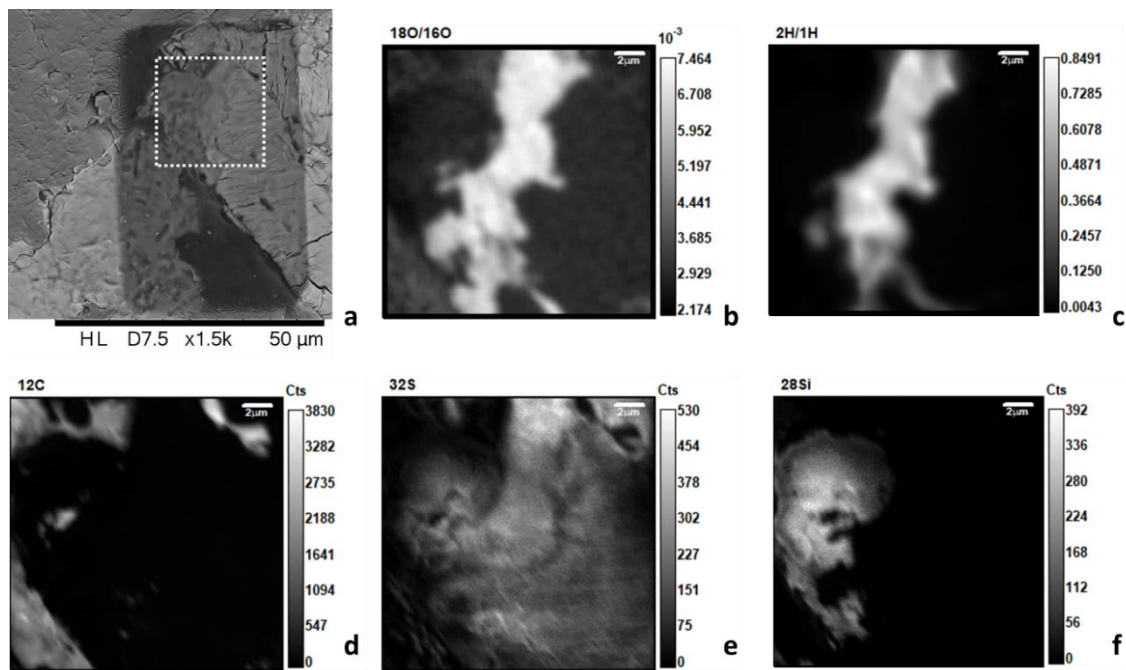
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653 Table 1: Isotopic fraction and enrichment factor compared to the natural abundance for D and <sup>18</sup>O.

	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
<sup>18</sup> 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/ <sup>18</sup> 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: