



HAL
open science

In situ Raman monitoring of studtite formation under alpha radiolysis in ^{18}O -labeled water

Aurélien Perrot, Aurélien Canizares, Sandrine Miro, Laurent Claparede, Renaud Podor, Thierry Sauvage, Sylvain Peugeot, Christophe Jegou, Nicolas Dacheux

► **To cite this version:**

Aurélien Perrot, Aurélien Canizares, Sandrine Miro, Laurent Claparede, Renaud Podor, et al.. In situ Raman monitoring of studtite formation under alpha radiolysis in ^{18}O -labeled water. Journal of Nuclear Materials, 2024, 600, pp.155267. 10.1016/j.jnucmat.2024.155267 . hal-04704283

HAL Id: hal-04704283

<https://hal.science/hal-04704283v1>

Submitted on 30 Sep 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Public Domain

1 In situ Raman monitoring of studtite formation under alpha radiolysis
2 in ¹⁸O-labeled water

3

4 Aurélien Perrot^a, Aurélien Canizares^b, Sandrine Miro^{a,*}, Laurent Claparede^c, Renaud Podor^c,
5 Thierry Sauvage^b, Sylvain Peugeot^a, Christophe Jegou^a, Nicolas Dacheux^c

6

7 ^a CEA, DES, ISEC, DPME, Univ Montpellier, Marcoule, France

8 ^b CEMHTI, Univ d'Orléans, Orléans, France

9 ^c ICSM, Univ Montpellier, CNRS, CEA, ENSCM, Site de Marcoule, Bagnols/Cèze, France

10

*sandrine.miro@cea.fr

11 **Abstract**

12 Studtite [(UO₂)(O₂)(H₂O)₂].2(H₂O) is a secondary phase precipitating during the alteration of uranium-
13 bearing materials. The mechanistic link between the formation of uranyl and peroxide bonds in the
14 solid and the nature of the oxidizing species produced by water radiolysis remains to be elucidated. In
15 order to improve our understanding of these mechanisms, an original experimental methodology in
16 the presence of ¹⁸O isotopes and Raman spectroscopy has been developed. It appears that there is a
17 direct chemical relationship between the peroxy ligands inside studtite and the peroxide entities of
18 H₂O₂ molecule into the solution. The link between H₂O₂ formation mechanism in solution by the
19 radiolysis of water, the nature of the radiation and the isotopy of the peroxy ligands inside studtite has
20 been described thanks to a coherent set of experimental data. For the uranyl UO₂²⁺ ions, the
21 characterization of its isotopy allows to specify the mechanism of oxidation at the UO₂ /water
22 interface. The isotopic configurations observed for the uranyl ion inside studtite, can be explained by
23 assuming an oxidation mechanism of UO₂ involving both a simple transfer of electrons by interaction
24 with H₂O₂ and the incorporation of oxygen atoms from the solution into the fluorite structure via OH°
25 radicals.

26 **Keywords:** Nuclear fuel; Oxidative dissolution; Uranium dioxide; Irradiation; Hydrogen peroxide;
27 Spectroscopy

28

29 1. Introduction

30 Water in interaction with heterogeneous nuclear materials such as spent fuel (UO_2 or $(\text{U,Pu})\text{O}_2$ based
31 ceramic), fuel debris or molten nuclear fuel (corium) produces hydrogen peroxide by radiolysis [1-4].
32 Interaction between the surface and hydrogen peroxide induces oxidative dissolution of uranium oxide
33 and the precipitation of U(VI) secondary phases such as studtite $[(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$, a common
34 uranium peroxide that generally forms under strongly oxidizing conditions. It has been the subject of
35 important studies over the past 20 years as it can potentially incorporate radionuclides, play a
36 protective role during spent fuel alteration or even control uranium solubility in solution [3-9]. Studtite
37 has also been observed in natural deposits such as barite solid solutions incorporating ^{226}Ra and
38 associated with other uranyl minerals such as rutherfordine or uranophane [10]. The crystallographic
39 structure of this uranium peroxide is well known [11]. It is composed of ribbons of U-coordination
40 polyhedra with shared edges, which are composed of O_2^{2-} bridging peroxo ligands.

41 There are also numerous studies on the stability of uranium peroxides as a function of solution
42 chemistry, irradiation conditions and temperature [12-16]. For example, with regard to solution
43 chemistry, the presence of carbonate ligand and H_2O_2 in groundwater increase studtite dissolution and
44 uranium (U) release [12]. The stability under γ and α irradiation of studtite, and more generally of
45 uranyl peroxide-based solid materials, with various structural topologies, has also been studied by XRD
46 and Raman spectroscopy [13, 14]. Studtite is particularly affected by α irradiation which induces the
47 formation of amorphous uranyl peroxide [14]. In addition, an increase in temperature leads to the loss
48 of water molecules and the formation of metastudtite $(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2$, or even that of an amorphous
49 compound [15, 16].

50 Despite of all these studies, the link between the radiolytic products of water (i.e. radicals and
51 molecular species) and the formation of the uranyl ion and peroxo ligands within studtite needs to be
52 better understood, requiring further investigation. Recently, a study coupling Raman spectroscopy
53 with γ irradiation of ^{18}O labelled water has shown the possibility of linking the formation of radiolysis
54 products to the main structural entities of studtite, namely peroxo ligands and uranyl ion [17]. The goal
55 of the present work is to perform this study under α irradiation by monitoring studtite precipitation
56 using in-situ Raman spectroscopy and ^{18}O labelled water irradiated by 5 MeV He^{2+} particles. This can
57 be achieved using the in-situ irradiation Raman set-up implemented at the CEMHTI cyclotron
58 beamline, which has already been used in previous studies [18, 19]. The originality of this work lies in
59 the use of ^{18}O labelled water. Indeed, the gathering of Raman spectra coupled with solution analysis is
60 expected to provide new insights to propose studtite formation mechanisms. The respective roles of
61 hydrogen peroxide and radicals in the formation of peroxo and uranyl bonds will be particularly
62 evaluated. The nature of isotopic exchanges under irradiation will provide a better understanding of
63 the effects of Linear Energy Transfer (i.e. high or low LET effect) in studtite formation and, more
64 broadly, in the mechanism of oxidative dissolution of uranium dioxide.

65

66 2. Materials and methods

67 2.1. Sample preparation

68 The target used for the alpha radiolysis experiment came from a sintered pellet of depleted UO_2 ,
69 manufactured at CEA Cadarache, and was obtained after wire saw cutting and mirror polishing with
70 diamond paste. The resulting UO_2 disk measured 8 mm in diameter and was 277 μm thick, stored in
71 air within membrane storage boxes. Prior to leaching, three cycles of pre-leaching of the experimental
72 device (cell and pellet) were carried out in a water solution (MilliQ Water) in the presence of 10^{-3} mol.L⁻¹
73 NaHCO_3 , in order to ensure the stoichiometry at the sample surface by removing the pre-oxidized
74 surface layer. The pre-leaching steps lasted 1 hour, with the exception of the last one, which was
75 extended to 14 hours. This pre-leaching was followed by three washing stages in the presence of the
76 leaching cell, two washing stages were performed with pure water (MilliQ Water) and the last one was
77 performed with ^{18}O -labelled water.

78 In order to carry out a complementary experiment to study the alteration of UO_2 without irradiation
79 but in the presence of ^{18}O -labelled hydrogen peroxide, a second UO_2 sample was synthesized. This
80 sample was prepared according to the process described by Martinez et al., i.e. by precipitating
81 uranium (IV) in hydroxide form [20]. After washing, the precipitate obtained was deagglomerated then
82 heated at 700°C for 4h under Ar/ H_2 atmosphere. Finally, the powder was pelletized and sintered at
83 1550°C for 6h under Ar/ H_2 . The resulting sintered UO_2 pellet was fragmented. One of the fragments
84 was annealed under Ar/ H_2 atmosphere at 1100°C for 5h to ensure U/O stoichiometry. After synthesis
85 and prior to leaching, the sample was characterized by Raman spectroscopy. It then underwent a 4
86 stages pre-leaching cycle in the presence of 10^{-3} mol.L⁻¹ NaHCO_3 . Pre-leaching lasted 1 hour, with the
87 exception of the last one, which was extended for 12 hours. These steps were followed by two washing
88 stages with deionized water and a last one with ^{18}O labelled water.

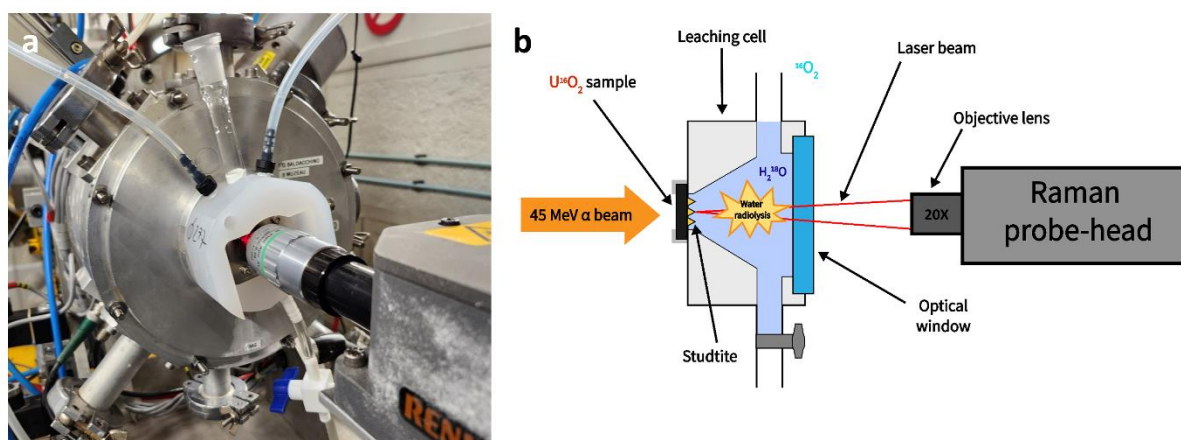
89 2.2. Leaching experiments

90 2.2.1. Leaching of UO_2 sample under α irradiation in presence of H_2^{18}O

91 **Irradiation conditions.** An external helium irradiation beam was used to irradiate the $\text{UO}_2/\text{H}_2^{18}\text{O}$
92 system. This irradiation was performed at the CEMHTI cyclotron, using 45 MeV $^4\text{He}^{2+}$ ions. The He^{2+} ion
93 beam was collimated to obtain a 6 mm diameter centred on the UO_2 target. The 277 μm thickness of
94 the UO_2 target was chosen according to the results of the SRIM software [21], which evaluated the
95 trajectory and the dissipated energy of ions passing through a material. The SRIM-calculated energy of
96 $^4\text{He}^{2+}$ ions at the UO_2 disk exit was 7.7 ± 0.9 MeV, with UO_2 density of 10.74 g.cm⁻³ (98 % theoretical
97 density) and taking into account the presence of three 26.8 μm -thick titanium foils at the beam
98 controller. Atom displacement energies have been set at 20 eV for oxygen and 40 eV for uranium,
99 based on calculation of Soullard et al. [22]. The calculated projected range of these 7.7 MeV $^4\text{He}^{2+}$ ions,
100 which induce water radiolysis in H_2^{18}O , was 71.8 ± 0.8 μm . The irradiation lasted 6 hours at an intensity
101 of 10 nA, only during the first 35 minutes, then the intensity was decreased to 5 nA to limit the
102 appearance of dihydrogen bubbles. The corresponding fluxes were 5.5×10^{10} α .cm⁻².s⁻¹ for 5 nA and
103 1.1×10^{11} α .cm⁻².s⁻¹ for 10 nA, to reach a final fluence of 1.3×10^{15} α .cm⁻². Based on fluence and SRIM
104 simulation data [21], the displacement per atom (dpa) within the uranium dioxide layer probed by
105 Raman spectroscopy (~ 1 μm) was calculated at 4.0×10^{-4} dpa. This value corresponds to a measure of
106 the number of atoms ejected from their initial position in the crystal lattice, following ballistic
107 collisions. It provides us a quantitative means of assessing the damage inflicted on the material by
108 irradiation. However, it does not take into account defect recombination.

109 **Experimental set-up in the irradiation chamber.** This set-up allowing in-situ Raman monitoring of the
110 $\text{UO}_2/\text{H}_2^{18}\text{O}$ interface during and after irradiation is presented in [Figure 1](#). It consists of a leaching cell,
111 manufactured in a polymer material resistant to radiolytic species attacks (PCTFE) in which the UO_2
112 target is placed and held in place by a system of screwed rings to ensure watertightness. The leaching

113 solution used was ^{18}O -enriched deionized water (97.17% ^{18}O , 0.34% ^{17}O , 2.49% ^{16}O , INNOVA-CHEM,
114 France). During irradiation, the α beam is transmitted through the UO_2 specimen inducing water
115 radiolysis. Finally, a 40 mm diameter quartz window located on the opposite side of the UO_2 sample
116 provides optical access for in-situ Raman monitoring of the $\text{UO}_2/\text{H}_2^{18}\text{O}$ interface.



117
118
119 **Figure 1.** *In situ experimental set-up combining a leaching cell under α - irradiation with Raman monitoring: a. picture of*
120 *the instrumental set-up; b. schematic diagram of the set-up, inspired from [18].*

121 **In-situ Raman spectroscopy.** Raman measurements were performed continuously on the direction
122 parallel to the $^4\text{He}^{2+}$ beam direction (Figure 1), using a Renishaw RA100 spectrometer equipped with a
123 He-Ne excitation laser (633 nm). The laser beam was delivered to the irradiation cell via a multimode
124 optical fiber and a Renishaw's RP10 probe, equipped with a Mitutoyo long working distance (30.5 mm)
125 objective which offers a 0.28 numerical aperture and with a 20x magnification. The 7 mW laser power
126 measured at the sample surface allows a very good compromise between UO_2 disk laser damage
127 resistance and Raman efficiency. The spectra were recorded with a 1800 groove/mm holographic
128 grating, allowing 4 cm^{-1} spectral resolution and offering simultaneous observation from 310 to 1244
129 cm^{-1} , and an accumulation time of 2 minutes for each spectrum. Raman monitoring was carried out
130 during a 21-hour leaching period, enabling the continuous observation of studtite precipitation,
131 including post-irradiation precipitation induced by radiolytic products remaining in solution after a 6-
132 hour irradiation period.

133 When the leaching test was stopped, the solution was drained, followed by 3 successive washes of the
134 cell with pure water. The pellet was then taken off and carefully dabbed with Kimtex© paper to remove
135 water and stop surface alteration, ensuring no rubbing occurred during the process.

136 2.2.2. Leaching of UO_2 in presence of $\text{H}_2^{18}\text{O}_2$

137 To understand the role of oxidizing species during water radiolysis, an additional leaching experiment
138 was carried out by replacing the presence of these radiolytic species produced in ^{18}O -labelled water
139 with a $\text{H}_2^{18}\text{O}_2$ solution. The $10^{-3}\text{ mol.L}^{-1}$ $\text{H}_2^{18}\text{O}_2$ solution was prepared from a commercial solution
140 (Sigma-Aldrich Hydrogen Peroxide - $^{18}\text{O}_2$ Solution - 2-3% in H_2O , 90 atom % of ^{18}O) diluted with H_2^{18}O
141 water. The H_2O_2 concentration was verified in the resulting solution by the Ghormley method [23]. The
142 sample was weighed and placed in a 10 mL leaching tube for 48 hours in the presence of 5 mL of 10^{-3}
143 mol.L^{-1} $\text{H}_2^{18}\text{O}_2$ solution. After leaching, the samples were characterized by Raman spectrometry, while
144 the leachates were filtered to 3 kDa by centrifugation before being analysed by ICP - OES.

145 2.3. Post-mortem characterization

146 **ESEM.** ESEM (Environmental Scanning Electron Microscopy) characterization was carried out to
147 observe the morphology of studtite precipitated on the pellet surface, using a ThermoFischer Scientific

148 Quattro S SEM. Micrographs were recorded using a voltage varying between 1 and 10 kV and a
149 pressure in the chamber between 10^{-3} and 10^{-4} Pa.

150 Following an initial observation of the pellet's surface, an analysis of its cross-section was conducted.
151 Prior to this second ESEM observation, the irradiated sample was vacuum-coated in resin, cut with a
152 Buehler IsoMet 1000 milling cutter, then polished with a Buehler Beta polishing machine using
153 diamond paste $1\ \mu\text{m}$ to achieve a mirror-polished surface. To prevent charge accumulation onto the
154 surface, the cross-section was coated with carbon prior to SEM observation.

155 **X-Rays Diffraction.** Structural analysis of the solids was carried out by X-ray diffraction (XRD) using a
156 Bruker D8 ADVANCE diffractometer (Cu- $K\alpha_1$ radiation, $\lambda = 1.5406\ \text{\AA}$, 40 kV, 40 mA, LinxEye detector).
157 XRD patterns were collected at room temperature over the $5\text{-}100^\circ$ (2θ) range, using a step size of
158 0.009° and a duration per step equal to 1 s.

159 **ICP-OES/ICP-MS.** Concentrations of uranium released in the leachate were first determined using a
160 iCAP 7000 series optical plasma emission spectroscopy (ThermoFischer Scientific). The analysis was
161 performed considering the results obtained at $\lambda = 385.958\ \text{nm}$. In a second step, solutions with uranium
162 concentrations below the limit of quantification by ICP-OES (LOQ (U) $\sim 100\ \text{ppb}$) were analysed by ICP-
163 MS (LOQ (U) $\sim 50\ \text{ppt}$). The elemental concentrations of uranium was calculated as the average of
164 three replicates. The instrument used was a ThermoFischer Scientific iCAP RQ. For all elemental
165 analyses, a calibration curve was produced using a range of diluted samples prepared from a certified
166 solution, framing the concentration range under consideration. All samples were diluted with $0.2\ \text{mol.L}^{-1}$
167 HNO_3 prior to analysis, to limit uranium adsorption onto the walls of the vials.

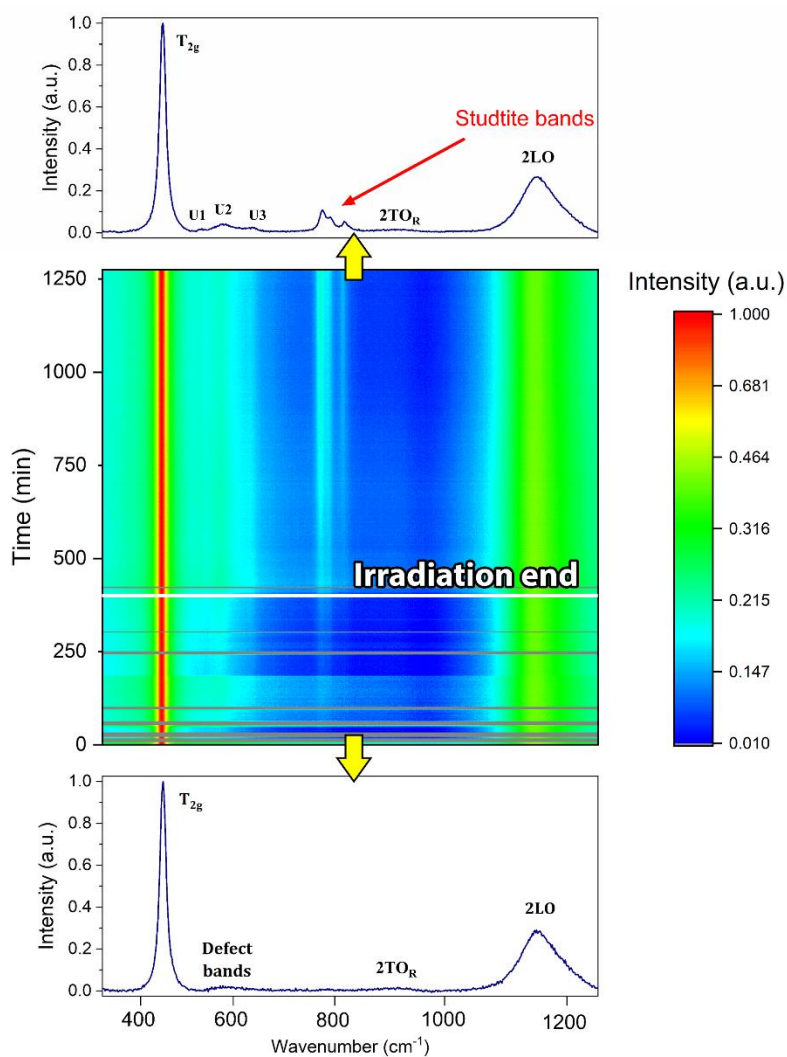
168 **Raman spectroscopy.** Post-mortem μ -Raman analyses were carried out using the LabRam ARAMIS
169 spectrometer (Horiba Jobin-Yvon) to study the alteration of UO_2 sample leached in $\text{H}_2^{18}\text{O}_2$ solution. The
170 instrument is equipped with He-Ne excitation laser ($632.8\ \text{nm}$) and a Nd:YAG laser ($532\ \text{nm}$). The laser
171 beam was focused onto the sample surface using an Olympus BX 41 microscope equipped with a $100\times$
172 SLMP objective. The resulting spot size was of the order of $1\ \mu\text{m}^2$. During spectra acquisitions, the laser
173 ($532\ \text{nm}$) was filtered down to $0.3\ \text{mW}$ (measured at the sample surface) to avoid any sample
174 modification. The spectra were recorded using the $1800\ \text{grooves.mm}^{-1}$ holographic grating and taking
175 into account accumulation time of 4 minutes per spectrum. These parameters were chosen to ensure
176 a good signal-to-noise ratio. For the sake of reproducibility, different remote areas were analysed to
177 confirm the homogeneity of the sample surface. Once the spectra have been recorded, they were
178 processed using OriginPro (Version 2023b. OriginLab Corporation, Northampton, MA, USA) software.
179 A baseline correction was performed and the spectra were then normalized to the band of maximum
180 intensity.

181

182 3. Results

183 3.1. In-situ Raman monitoring of studtite precipitation under alpha irradiation

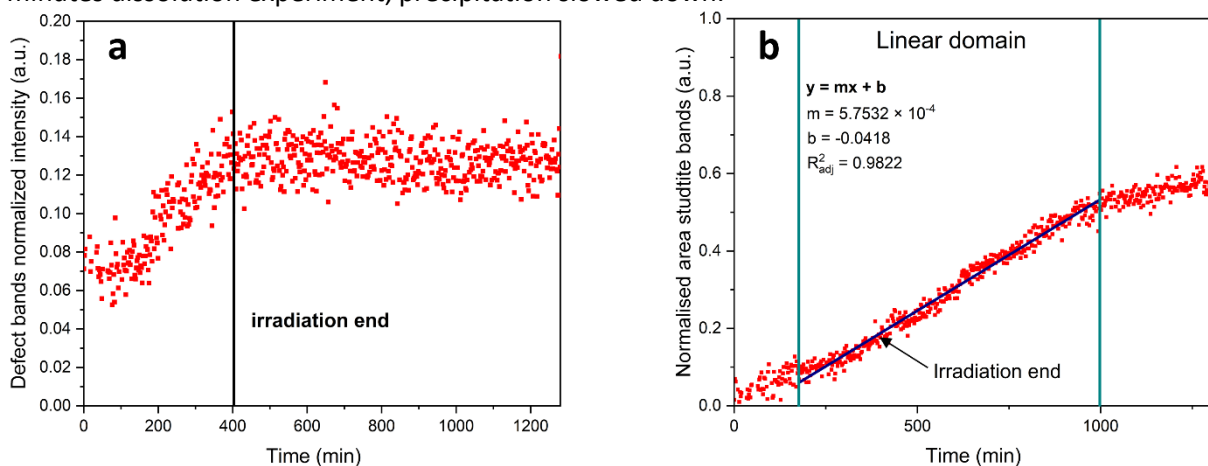
184 Uranium dioxide presents a fluorite-type crystal structure (CaF_2), characterized by a space group
185 $Fm\bar{3}m (O_h^5)$. In this structure, the U^{4+} cations adopt a face-centred cubic (f.c.c.) arrangement, while
186 the anions (O^{2-}) occupy the tetrahedral positions [24]. In accordance with group theory, a triply
187 degenerate Raman-active vibrational mode at 445 cm^{-1} is observed in the initial Raman spectrum. This
188 band, called T_{2g} , results from the antiphase oscillation of stretching oxygen atoms around uranium
189 [25]. The initial spectrum admits other bands, including defect bands between 500 and 700 cm^{-1} (Figure
190 2). A broad band is also observed at 1150 cm^{-1} . This band has been assigned to a second-order
191 longitudinal optic phonon (2LO) [24]. Finally, a band at 911 cm^{-1} was also identified, generally
192 attributed to the 2TO_R mode [24, 26]. All spectra recorded during the leaching test were normalized in
193 intensity with T_{2g} and then used to acquire a temporal Raman map (Figure 2). During the first few
194 minutes of irradiation, dihydrogen was produced by radiolysis of water within the cell. This led us to
195 make short interruptions of the irradiation at 10 nA to evacuate the bubbles present and to lower the
196 beam intensity. During these stops, the recording of Raman spectra were stopped. These stops
197 correspond to the grey lines observed in Figure 2.



198

199 **Figure 2.** 2D time-resolved Raman spectra alteration with the pristine UO_2 signal (bottom) and the final spectrum showing
200 studtite precipitation (top).

201 The characteristic bands of the UO_2 compound were observed in all the Raman spectra recorded during
 202 the entire experiment. The final spectrum was still composed of the UO_2 fingerprint, in which no
 203 position and FWHM variation was detected in the T_{2g} and 2LO bands compared to the initial spectrum.
 204 No significant evolution of the FWHM was also observed by Gutierrez et al. for a dpa lower than 0.03
 205 [27]. However, a significant evolution of the band associated with defects was observed between 500
 206 and 700 cm^{-1} . The intensity of this defect band composed of three contributions: U_1 , U_2 and U_3 is
 207 reported in **Figure 3a**. The increasingly pronounced appearance of these three defect bands during
 208 irradiation is clearly evidenced. Their growth was due to the ballistic impact of the He^{2+} ions in the
 209 fluorite structure. The latter is composed of 3 defect bands: Firstly, the U_1 band is present at 530 cm^{-1} ,
 210 which assignment is still discussed [18, 28]. Indeed, it is sometimes associated with the distortion of
 211 the cubic lattice by interstitial oxygen. Secondly, the U_2 band at 577 cm^{-1} , which is assigned to the first-
 212 order longitudinal optical phonon (1LO) mode, active in IR and observable in Raman in the presence of
 213 defects in the fluorine structure, due to loss of symmetry. This loss of symmetry resulted from the
 214 appearance of oxygen clusters and the change in ionic radius between U (IV) and U (V) during oxidation
 215 [29, 30]. Lastly, the U_3 band at 634 cm^{-1} which is characteristic of the presence of oxygen cuboctahedra,
 216 is observed [28, 29, 31]. When irradiation was stopped, the increase of bands intensity stopped and
 217 the phenomenon was not reversible. No saturation appeared to have been reached before the end of
 218 irradiation. This observation is in good agreement with the results obtained by G. Guimbretière et al.
 219 Indeed, saturation was not yet observed for fluence values of $1.3 \times 10^{15}\text{ }\alpha\text{.cm}^{-2}$ [32]. The displacement
 220 per atom (dpa) previously calculated tells us that alpha particles are transmitted with a very low impact
 221 on UO_2 , revealing the extreme sensitivity of defect bands to irradiation-induced damages. In addition,
 222 in **Figure 2**, the growth of 3 bands at 774 , 790 and 817 cm^{-1} can be noted. These bands correspond to
 223 the $[(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2]\cdot 2(\text{H}_2\text{O})$ studtite compound and were already detected on ^{18}O labelled studtite
 224 [11, 17]. The observation of this phase under our conditions is consistent with the results obtained by
 225 Corbel et al. [33]. The intensity of the studtite characteristic bands is plotted against time in **Figure 3b**.
 226 The increase in their intensity clearly shows the formation of this phase from the very beginning of the
 227 experiment, and its subsequent growth during the experiment. The evolution of the Raman response
 228 of this phase allowed us to establish that studtite precipitation occurred according to a linear kinetic.
 229 It was observed that the linear evolution of the Raman response continues while the pellet is no longer
 230 irradiated, until around 1000 minutes. This result is in good agreement with the observations by R.
 231 Mohun who has reported that studtite kept growing despite the stop of irradiation [34]. After 1000
 232 minutes dissolution experiment, precipitation slowed down.



233
 234 **Figure 3.** Monitoring the time-dependent Raman response of bands normalized with T_{2g} during the leaching time. Evolution
 235 of the area of defect bands (a) and evolution of band area associated with studtite (b).

236 3.2. Analysis of the solutions and post-mortem characterization of the studtite layer

237 The study of UO₂ alteration by water radiolysis is well documented in the literature [4, 17, 33, 35].
 238 Consequently, studtite precipitation under these experimental conditions can be anticipated and
 239 should occur as soon as saturation of this phase in solution is reached. To correlate uranium release
 240 with studtite precipitation, the concentration of uranium in solution during the leaching test was
 241 measured. First, the pre-leaching steps ensured that the oxidized surface layer of the UO₂ pellet was
 242 removed. Thus, the effectiveness of the washing steps carried out after this pre-leaching stage was
 243 monitored, verifying that all the uranium present in the leach cell was recovered. This then enabled a
 244 balance to be drawn up for the uranium in solution. For all these reasons, the uranium concentration
 245 was determined after each stage (Table 1).

246 A low concentration of uranium released during the pre-leaching stage was noted, indicating a weak
 247 pre-existing oxidized layer of U(VI). This observation seems to be in agreement with the initial Raman
 248 response of the pellet, which did not show significant defect bands (in particular the U₃ band).

249 After the leaching test, the uranium concentration of the leaching solution was measured at (1.1 ± 0.1)
 250 $\times 10^{-4}$ mol.L⁻¹, from which a quantity of uranium released into solution equal to $(5.9 \pm 0.5) \times 10^{-7}$ mol
 251 was deduced. These release values are in agreement with the release previously obtained by Corbel et
 252 al. [33].

253 A speciation calculation was carried out using CHESS software [36] and the ThermoChimie database
 254 [37]. At the end of the leaching stage, the saturation index in uranium was determined to be 2.58 at a
 255 pH of 3. This value confirms that the conditions in the solution were oversaturated with respect to
 256 studtite during leaching, resulting in the precipitation of this phase.

257 The thickness of the studtite layer was estimated using the data reported by Corbel et al. under similar
 258 conditions [33]. Knowing the output energy of the alpha particles (7.7 MeV) and the fluence at the end
 259 of the experiment (1.3×10^{15} α.cm⁻²), it can be calculated that the total energy deposited in the solution
 260 is 456 J. Corbel et al. have established a relationship between this deposited energy and H₂O₂
 261 concentration, allowing us to estimate that the H₂O₂ concentration present at the end of irradiation
 262 was $C_{H_2O_2} \approx 6 \times 10^{-3}$ mol · L⁻¹ [33]. From the H₂O₂ concentration and a second relationship
 263 established by Corbel et al, a layer growth rate of 100 nm.h⁻¹ was able to be estimated, enabling the
 264 determination of the precipitated studtite layer's thickness at 2.1 μm. With the knowledge of studtite's
 265 density (3.64 g.cm⁻³) [38], it can be deduced that the mass of studtite that was precipitated on the
 266 pellet's surface amounts was approximately 1 mg.

267 **Table 1.** Uranium concentration determination in solution during pre-leaching, washing and leaching stages when leaching
 268 UO₂ irradiated with α particles

Sample	Duration (h)	Solution	Volume (mL)	C _U (mol.L ⁻¹)
Pre-leaching 1	1	NaHCO ₃	4.5 ± 0.1	$(1.7 \pm 0.1) \times 10^{-7}$
Pre-leaching 2	1			$(1.5 \pm 0.1) \times 10^{-8}$
Pre-leaching 3	14			$(1.8 \pm 0.1) \times 10^{-9}$
Washing 1	--	H ₂ O	4.5 ± 0.1	$(1.6 \pm 0.1) \times 10^{-8}$
Washing 2	--			$(2.0 \pm 0.3) \times 10^{-10}$
Washing 3	--			H ₂ ¹⁸ O
Leaching	21	H ₂ ¹⁸ O + α*	5.5 ± 0.1	$(1.1 \pm 0.1) \times 10^{-4}$

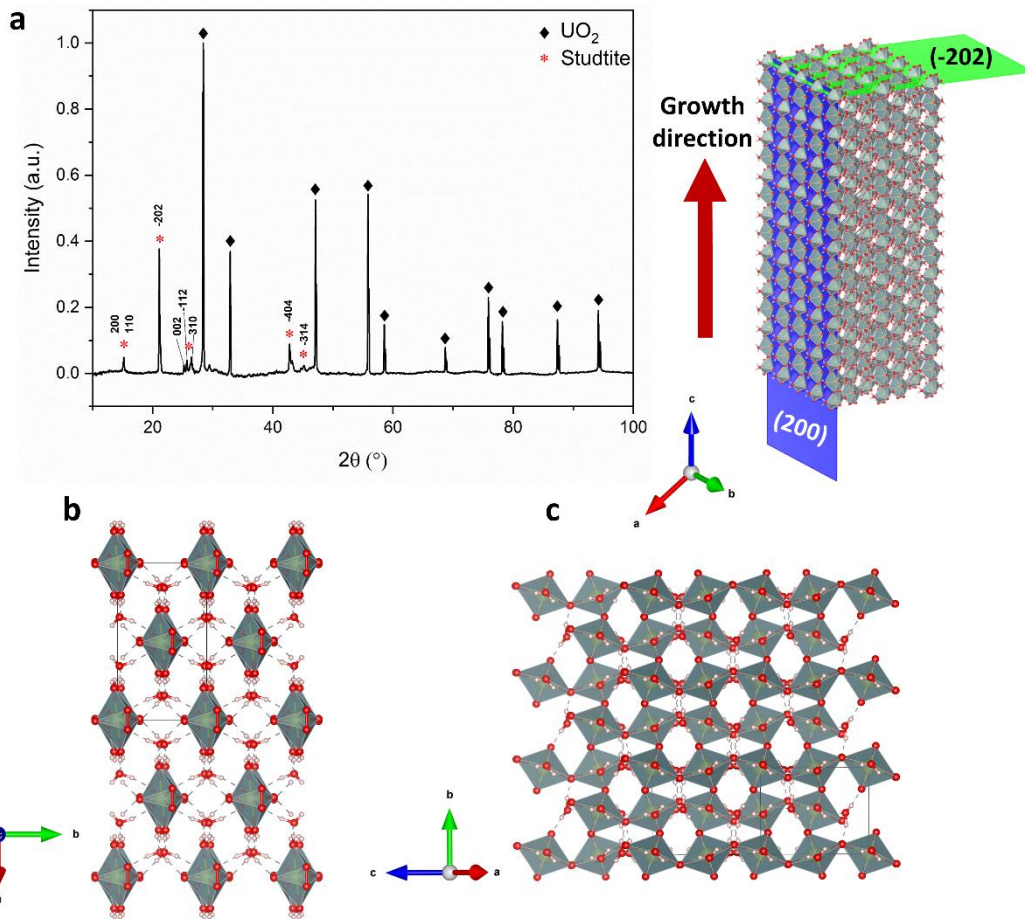
269 *6 hours of irradiation

270 Once the radiolysis experiment was completed, the UO₂ disk was first characterized by X-ray diffraction
 271 (XRD) to identify crystal phases. The X-ray pattern obtained (Figure 4) in reflectivity mode with normal
 272 incidence, revealed the coexistence of two different phases: UO₂ and studtite

273 $[(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$. This compound crystallizes in a monoclinic structure with space group C2/c
274 [11].

275 The recorded diffractogram is compared with the studtite diffractogram reported by Burns et al. [11].
276 Thus, the XRD diffractogram revealed a strong anisotropy in the intensity of the lines, marked by a
277 crystal growth surface favoured along the (-202) plane, associated with a position of 21.12° (2θ). The
278 ratio of peak amplitudes (1,1,0)/(-2,0,2) is ~ 5.34 , whereas it is ~ 0.13 for our sample [11]. Thus, it can
279 be deduced, as shown in **Figure 4**, that studtite chains are oriented parallel to the axis of needle
280 growth, this axis corresponding to the c-axis. The orientation of studtite within a needle is illustrated
281 in **Figure 4a**, where the (-202) plane (**Figure 4b**) is arranged perpendicular to the growth direction while
282 the (200) plane (**Figure 4c**) is aligned parallel along the growth axis. The work of Corbel et al. did not
283 identify any preferential orientation in the formation of studtite under alpha irradiation [33], however,
284 our results are consistent with the observations of Schlegel and Jegou who reported the presence of a
285 preferential orientation of crystal growth along (-202) in the case of precipitation without irradiation
286 [39]. Two hypotheses may be put forward to explain this contradiction. On the one hand, if irradiation
287 does indeed inhibit studtite formation with preferentially oriented textures, our finding could result
288 from the fact that, in our experiments, studtite growth mainly occurred in the absence of irradiation,
289 during the last part of the experiment, when the beam was off. This could lead to a diffractogram that
290 is predominantly representative of studtite that grew without the influence of irradiation. On the other
291 hand, it's important to point out that studtite growth duration reported by Corbel et al. was
292 significantly shorter than that observed in our study, with a maximum of 6h for continuous irradiation.
293 However, research by Schlegel and Jegou has shown that the orientation effect along the (-202) plane
294 is only perceptible after six hours of precipitation [39]. This time difference could therefore play a
295 crucial role in whether or not orientation effects are observed, providing a second hypothesis to
296 explain the observed contradiction.

297



298

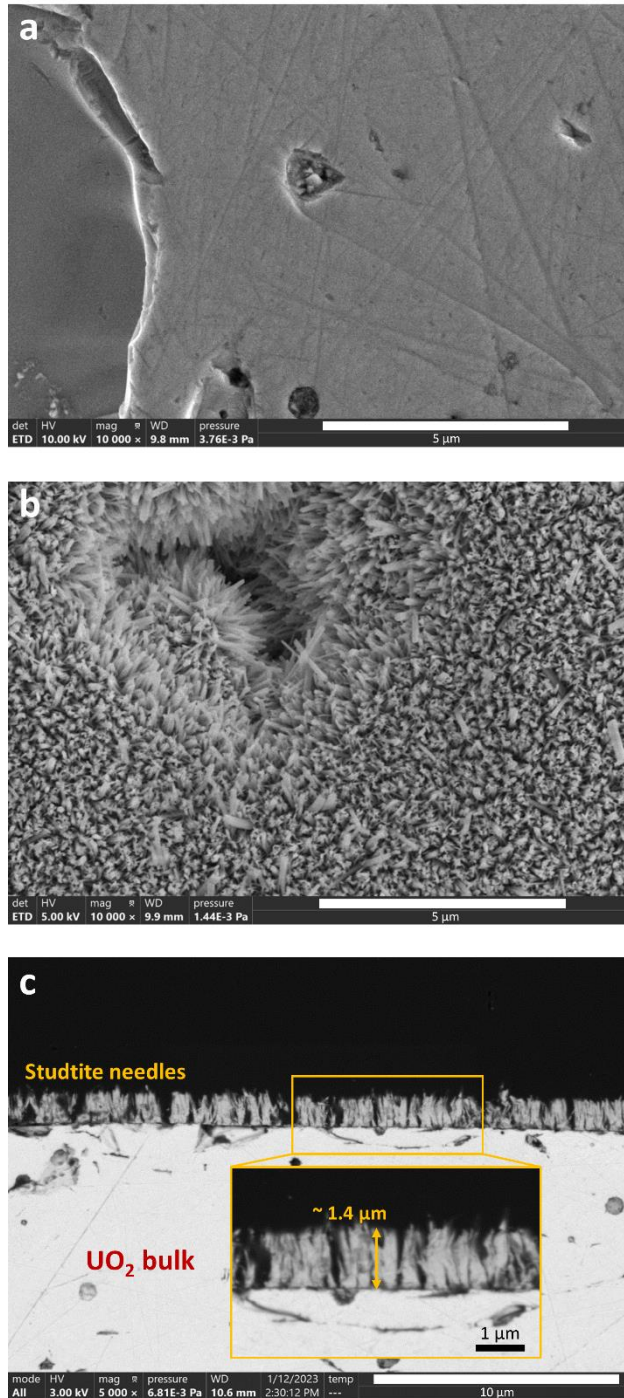
299

300 **Figure 4.** XRD diagram and structural analysis of studtite growth: a. XRD pattern of UO_2 pellet after leaching, showing the
 301 formation of studtite at the solid/solution interface (left) and schematic illustration of the structure of studtite
 302 during crystal growth (right); uranium atoms being at the center of the coordination polyhedra; b. View of the
 303 plans (-202) and (-404) ; c. View of the plan (200)

304 ESEM observations of the UO_2 disk reported in **Figure 5**, confirmed the formation of a homogeneous
 305 crystalline layer characteristic of the studtite phase formed during the oxidative dissolution of UO_2 in
 306 presence of H_2O_2 [33]. The area that was not in contact with the solution (**Figure 5a**) does not show
 307 any secondary phase or alteration marks on the surface. Only marks due to the polishing process
 308 such as scratches and grain tears are observed, whereas a layer covered with needle-like studtite
 309 crystals was formed on the area in contact with the solution (**Figure 5b**).

310 In addition, the observation of the cross-section of the pellet (**Figure 5c**) allowed us to image the
 311 alteration layer and to determine the morphology of the crystal growth. A single homogeneous layer
 312 of studtite, formed by needles grown perpendicularly to the UO_2 surface, with an average height of
 313 about $1.4 \mu\text{m}$, was observed. The studtite thickness measured is in accordance with that which has
 314 been previously estimated by leachate analysis (i.e. $2.1 \mu\text{m}$).

315 The SEM observations of the studtite layer clearly indicate that the needles have grown according to a
 316 preferential orientation. This result is in good accordance with XRD data, where a texture marked by
 317 preferential orientation of crystal growth was observed (**Figure 4**).



318
319
320
321

Figure 5. ESEM micrographs of UO₂ leached pellet: a. Non-leached peripheral zone; b. Altered surface covered with a layer of studtite needle-like crystals; c. Cross-section of the pellet.

322 3.3. Analysis of studtite isotopic enrichment

323 The use of ¹⁸O enriched water and Raman spectroscopy offer a precise method to determine the origin
324 of the oxygen present in studtite and to deduce its formation mechanisms. In order to analyse the
325 enrichment of the different bonds in studtite, it was first necessary to determine the different Raman
326 band positions of ¹⁸O enriched studtite. To evaluate the theoretical vibration frequencies and deduce
327 the wavenumber associated with each ¹⁸O enriched studtite bond, it was considered that an

328 intramolecular stretching vibration can be described by a harmonic oscillator model in which the
 329 binding force is described by the Hooke's law [40].

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (1)$$

330
 331 where $\tilde{\nu}$ is the wavenumber (in cm^{-1}), c is the speed of light (in $\text{cm}\cdot\text{s}^{-1}$), k is the binding force constant
 332 (in $\text{kg}\cdot\text{s}^{-2}$) and μ corresponds to the reduced mass (in kg). There is a direct relationship between mass
 333 and bond vibration frequency. Isotopic labelling thus induces a shift in the Raman bands by modifying
 334 the mass of the original atoms. To determine the position of the bands after isotopic enrichment, the
 335 experimental position of the isotopically unlabelled bands was used and then the calculated shift was
 336 applied [17].

337 In the case of studtite, its response to isotopic labelling is characterized by a behaviour similar to that
 338 of a free molecule, where each possible isotopic configuration is associated with a specific Raman
 339 response. This is in contrast to solids, which generally show a single band per bond, integrating the
 340 different contributions [17]. The calculated vibration frequencies associated with each of the different
 341 oxygen configurations within the peroxide and uranyl bonds of studtite are presented in **Table 2**.

342
 343 *Table 2. Calculated Raman band positions associated with the contribution of the various bonds for O^{18} enriched H_2O_2 ,
 344 studtite and UO_2^{2+}*

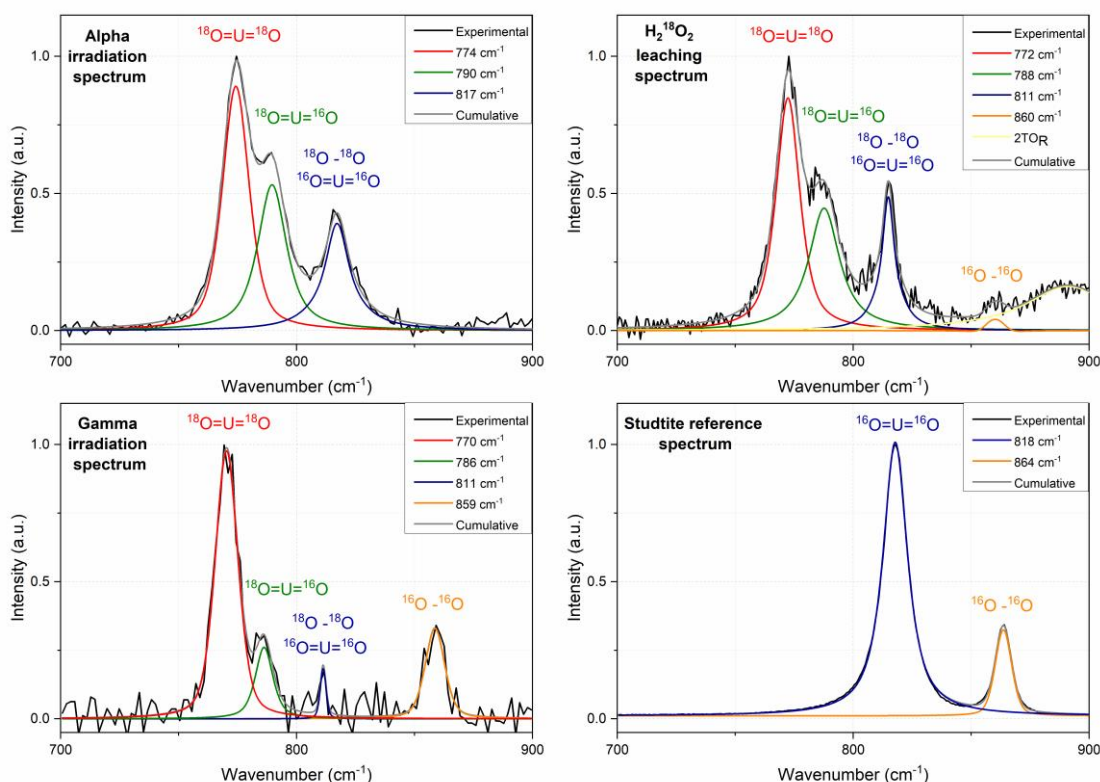
Bond	Compound	Configuration	Experimental position (cm^{-1}) [17]	Calculated Raman band position for ^{18}O enriched compound (cm^{-1})
Peroxyde	H_2O_2	$^{16}\text{O}-^{16}\text{O}$	876 (1)	
		$^{16}\text{O}-^{18}\text{O}$		851
		$^{18}\text{O}-^{18}\text{O}$		826
	Studtite	$^{16}\text{O}-^{16}\text{O}$	863 (1)	
		$^{16}\text{O}-^{18}\text{O}$		838
		$^{18}\text{O}-^{18}\text{O}$		814
Uranyl	UO_2^{2+}	$^{16}\text{O} = \text{U} = ^{16}\text{O}$	870 (3)	
		$^{16}\text{O} = \text{U} = ^{18}\text{O}$		845
		$^{18}\text{O} = \text{U} = ^{18}\text{O}$		820
	Studtite	$^{16}\text{O} = \text{U} = ^{16}\text{O}$	817 (2)	
		$^{16}\text{O} = \text{U} = ^{18}\text{O}$		793
		$^{18}\text{O} = \text{U} = ^{18}\text{O}$		770

345
 346 **Figure 6** shows the Raman spectra of studtite from three leaching experiments together with the
 347 reference spectrum of studtite. Pseudo-Voigt function fits of the Raman spectra presented in **Figure 6**
 348 were performed on the bands present between 700 and 900 cm^{-1} associated with studtite, in order to
 349 assign the corresponding bonds to each band (**Table 2**) and thus deduce the isotopic enrichment of
 350 studtite.

351 As mentioned above, the Raman spectrum of pellet subjected to leaching by alpha irradiated labelled
 352 water shows a cluster of 3 bands between 700 and 900 cm^{-1} (**Figure 6a**). The first band at 774 cm^{-1} is

353 associated with the uranyl bond composed of two ^{18}O oxygen ($^{18}\text{O} = \text{U} = ^{18}\text{O}$). The second band at 790
 354 cm^{-1} is associated with the uranyl bond composed of one ^{18}O and one ^{16}O ($^{16}\text{O} = \text{U} = ^{18}\text{O}$). Finally, the
 355 third band at 817 cm^{-1} is attributed to the sum of the contributions of the uranyl bond composed of
 356 two ^{16}O oxygen ($^{16}\text{O} = \text{U} = ^{16}\text{O}$) and the peroxide bond composed of two ^{18}O oxygen ($^{18}\text{O} - ^{18}\text{O}$). No
 357 bands at 840 cm^{-1} and 860 cm^{-1} attributed respectively to the peroxide bond $^{18}\text{O} - ^{16}\text{O}$ and $^{16}\text{O} - ^{16}\text{O}$
 358 were observed despite the presence of ^{16}O (3 atom %) present in water.

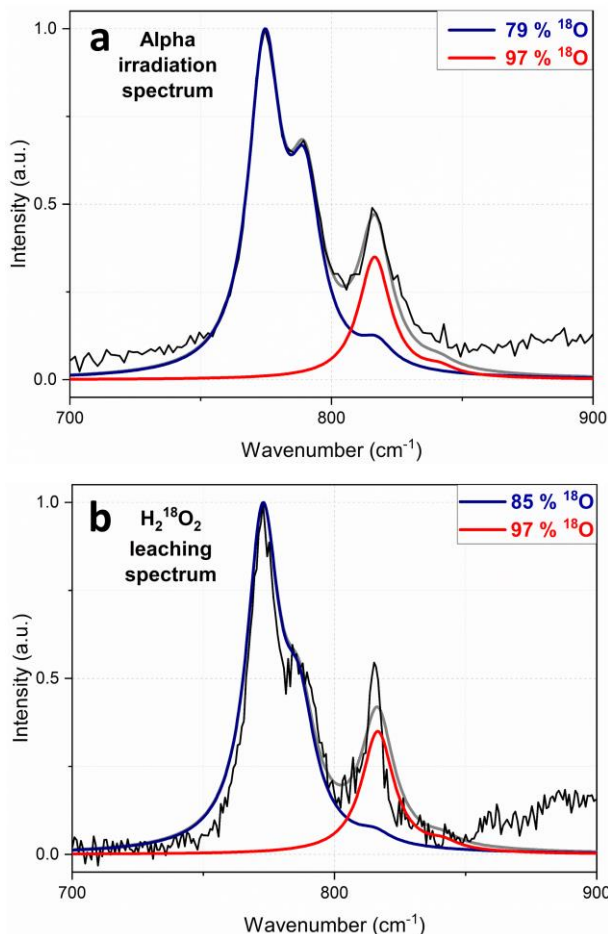
359 For the stoichiometric UO_2 pellet submitted to a leaching by a $1\text{mM H}_2^{18}\text{O}_2 + \text{H}_2^{18}\text{O}$ solution (Figure
 360 6b), the Raman spectrum showed a band at 772 cm^{-1} , corresponding to the uranyl $^{18}\text{O} = \text{U} = ^{18}\text{O}$ bond.
 361 A second band was seen at 788 cm^{-1} , corresponding to the uranyl $^{16}\text{O} = \text{U} = ^{18}\text{O}$ bond. Finally, a last
 362 band located at 811 cm^{-1} was associated with the contribution of the uranyl $^{16}\text{O} = \text{U} = ^{16}\text{O}$ bond, but
 363 also with that of the peroxide $^{18}\text{O} - ^{18}\text{O}$ bond. A slight band at 860 cm^{-1} attributed to the peroxide ^{16}O
 364 $- ^{16}\text{O}$ bond seemed to be present. This band is confused with the noise and the 2TO_R band at 925 cm^{-1}
 365 and was expected in these proportions due to the presence of ^{16}O (10 atom% ^{16}O) in the $\text{H}_2^{18}\text{O}_2$
 366 enrichment. Sarrasin had noted for a pellet having undergone leaching by a gamma-irradiated labelled
 367 water (Figure 6c) the presence of a significant band associated with the $^{16}\text{O} - ^{16}\text{O}$ peroxide bond while
 368 the band at 817 cm^{-1} was weak [17]. Finally, the reference spectrum of studtite without isotopic
 369 labelling (Figure 6d) showed two bands at 817 cm^{-1} and 860 cm^{-1} corresponding to the uranyl ($^{16}\text{O} = \text{U}$
 370 $= ^{16}\text{O}$) bond and the peroxide ($^{16}\text{O} - ^{16}\text{O}$) bond, respectively.



371
 372 **Figure 6.** Results of deconvolution of studtite Raman spectra recorded for UO_2 after 1 day of α radiolysis (a), UO_2 after 2
 373 days of leaching with $\text{H}_2^{18}\text{O}_2$ (b) UO_2 after 1 day of γ radiolysis, based on the results of [17] (c) and studtite without
 374 any isotopic labeling (d)

375 In order to quantify the isotopic proportion of each band, the method proposed by Sarrasin was carried
 376 out [17], which results are presented Figure 7. The model proposed by Sarrasin is a binomial
 377 distribution in which x corresponds to the isotopic abundance of ^{16}O while $1 - x$ corresponds to the
 378 isotopic abundance of ^{18}O . Thus, for the uranyl bond, the respective probabilities of the different

379 configurations are as follows: x^2 for $^{16}\text{O}=\text{U}=\text{O}$, $2x(1-x)$ for $^{16}\text{O}=\text{U}=\text{O}$ and $(1-x)^2$ for $^{18}\text{O}=\text{U}=\text{O}$.
 380 The intensity of the three uranyl peaks is directly proportional to the probability of a given isotopic
 381 configuration. By knowing the probabilities of the configurations, the isotopic abundance can be
 382 determined from the intensity ratios of the uranyl bands. Applying this model at the end of the leaching
 383 test of the UO_2 sample under α irradiation in H_2^{18}O , an isotopic fraction of 79% ^{18}O in the uranyl bond
 384 and 97% ^{18}O in the peroxide bond was obtained. Refinement of the recorded spectrum of studtite
 385 precipitated on stoichiometric UO_2 in the presence of $\text{H}_2^{18}\text{O}_2$, gave an isotopic fraction of 85% ^{18}O in
 386 the uranyl bond and 97% ^{18}O in the peroxide bond. No $^{16}\text{O}-^{18}\text{O}$ band was found at 840 cm^{-1} . For these
 387 experiments, the process of studtite formation seems to have produced only oxygen groups of
 388 identical isotopy, and this feature has persisted over time.

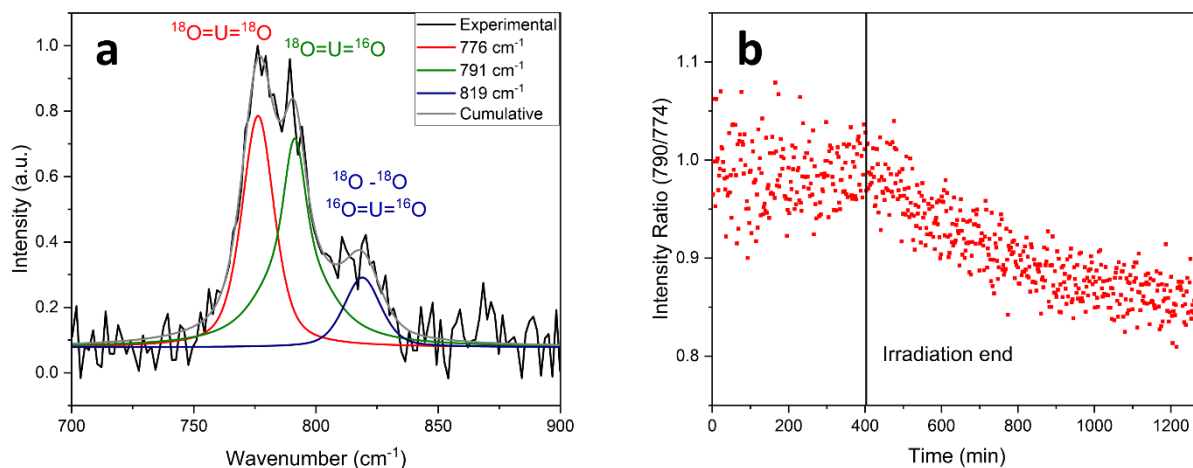


389
 390 **Figure 7.** Isotopic labeling fit of studtite bands by Lorentzian function: a. UO_x after 1 day with α radiolysis; b. UO_2 after 2
 391 days of leaching with $\text{H}_2^{18}\text{O}_2$. The isotopic enrichment of uranyl (blue) and peroxide (red) bonds is shown on each
 392 graph.

393 During leaching, a significant change in the isotopic ratio of the uranyl bond was observed, as shown
 394 in **Figure 8**. During irradiation, a band corresponding to $^{18}\text{O}=\text{U}=\text{O}$ was observed, with an intensity
 395 comparable to that of the band associated with the $^{18}\text{O}=\text{U}=\text{O}$ bond (**Figure 8a**). When irradiation was
 396 stopped, a change in the isotopic response occurred: the $^{18}\text{O}=\text{U}=\text{O}$ band became progressively
 397 weaker compared to that of the $^{18}\text{O}=\text{U}=\text{O}$ band (**Figure 8b**). The observation of an isotopic change
 398 when the beam is stopped suggests an evolution in studtite formation mechanism, with or without
 399 irradiation, which will be discussed later. The shape of the curve showing a gradual isotopic transition
 400 following the end of the irradiation can be attributed to the fact that the studtite layer as a whole
 401 influences the Raman response. As a result, the isotopic impact of studtite formed under irradiation
 402 remains despite the beam being stopped. The result is a direct link between the curve profile and the

403 kinetics of studtite growth after the beam is stopped (**Figure 3b**). Thus, the inflexion observed in the
404 curve after 1000 minutes can either be interpreted as the attainment of a spectrum characteristic of
405 studtite formed without irradiation, or as the result of a slowdown in precipitation.

406 Finally, it was not possible to obtain a satisfactory fit with the binomial distribution model, suggesting
407 the existence of a mechanism for the formation of the specific uranyl bond during alpha irradiation.
408 This mechanism seems to favour the formation of the $^{18}\text{O}=\text{U}=\text{}^{16}\text{O}$ bond during irradiation. The peroxide
409 bond, on the other hand, is not affected by these changes during leaching.



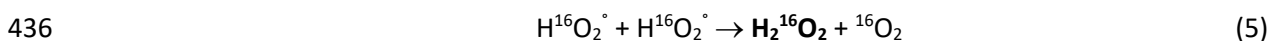
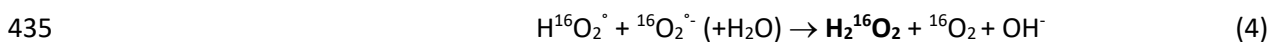
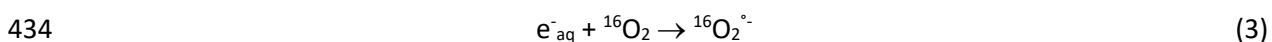
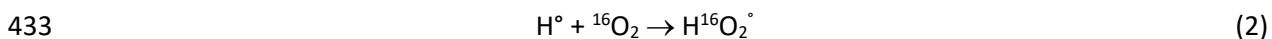
410

411 **Figure 8.** Evolution of uranyl bond isotopy during leaching experiment a. spectrum recorded at the end of irradiation; b.
412 intensity ratio of 790 cm⁻¹ ($^{18}\text{O}=\text{U}=\text{}^{16}\text{O}$) to 774 cm⁻¹ ($^{18}\text{O}=\text{U}=\text{}^{18}\text{O}$) bands.

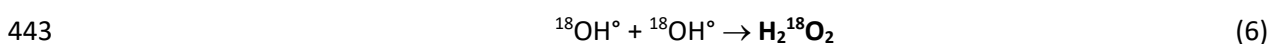
413 4. Discussion

414 In light of the results obtained, the first open question is to understand the chemical relationship
 415 between the peroxide bond of the H₂O₂ radiolytic product and the bridging peroxo ligand inside
 416 studtite.

417 Firstly, the reference leaching experiment of the UO₂ pellet in the presence of H₂¹⁸O₂ shows that there
 418 is isotope exchange with the solution and secondly that the isotopy of the bridging peroxo ligand in
 419 studtite is directly linked to that of H₂O₂ in solution. Indeed, **Figure 7b** shows that in the presence of
 420 H₂¹⁸O₂, the bridging peroxo ligand in studtite is predominantly ¹⁸O-¹⁸O. In other words, the stability of
 421 the peroxo ion is important and the peroxide bond is not broken when studtite precipitation occurs.
 422 Based on this observation, it is interesting to discuss the isotopy of the peroxide bond in studtite in
 423 relation to the radiolytic processes leading to the formation of H₂O₂ in solution under high and low LET
 424 radiation. **Figure 6** clearly shows that under alpha irradiation (high LET) the peroxide bond is
 425 predominantly ¹⁸O-¹⁸O, whereas it is mainly ¹⁶O-¹⁶O under gamma irradiation (low LET). Under water
 426 radiolysis, primary hydrogen peroxide is produced mainly by recombination of OH° radicals during the
 427 heterogeneous chemistry step (< 10⁻⁶ s) in the spurs generated by the energy deposition of alpha
 428 particles and gamma rays. However, under gamma irradiation, over longer periods and during the
 429 homogeneous chemistry stage (> 10⁻⁶ s), dissolved oxygen (¹⁶O₂) in solution controls the final H₂O₂
 430 concentration at steady state and is strongly involved in its formation processes [41-45]. Under gamma
 431 irradiation, dissolved oxygen leads to the formation of H₂¹⁶O₂ by scavenging the H° radical and the
 432 aqueous electron according to the following reaction scheme:



437 This process, related to the presence of dissolved oxygen, has been the subject of several comparisons
 438 between radiolysis calculations and experimental measurements and is now well known and reported
 439 in the literature [41-45]. Under alpha irradiation, the primary production of H° radicals and aqueous
 440 electron is much lower than under gamma irradiation, therefore the production of H₂O₂ is not very
 441 sensitive to the presence of dissolved oxygen in the homogeneous solution. The main process of H₂O₂
 442 formation in H₂¹⁸O labelled water remains the recombination of two ¹⁸OH° radicals according to:



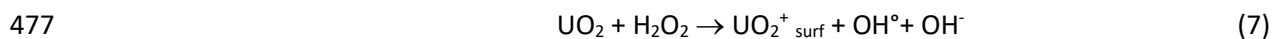
444 The isotopic signatures of the peroxo ligands in studtite for the experiments carried out under alpha
 445 and gamma irradiation are therefore fully consistent with the formation processes of hydrogen
 446 peroxide in solution. A ¹⁶O-¹⁶O chemical bond is observed under gamma irradiation, whereas an ¹⁸O-
 447 ¹⁸O bond is favoured under alpha irradiation. The presence of a peroxo ¹⁸O-¹⁸O bond under alpha
 448 irradiation also confirms the stability of water with respect to isotopic exchange over the duration of
 449 the experiment, which is consistent with the long-term studies conducted by Bonales [46].

450 The second objective is to obtain some information on the oxidative dissolution mechanism from the
 451 use of isotopes. For the uranyl bond, the isotopic composition of the oxygen atoms inside UO₂²⁺ ions
 452 can provide information on the oxidative dissolution mechanisms of uranium dioxide. However, in
 453 order to ensure that the actinyl species keeps the memory of the dissolution mechanism, the residence

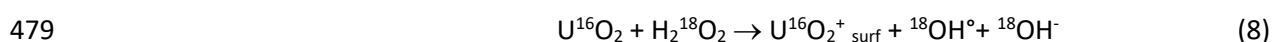
454 time of the oxygen atoms on the UO_2^{2+} ions must be long enough since its release from the surface to
 455 the studtite to be analysed by Raman spectroscopy. The isotopic exchange of oxygen atoms within the
 456 uranyl ion has been studied since the early 1960's. These studies [47, 48] have shown that the uranyl
 457 ion does not exchange its oxygen atoms with the solution for a period of 2000 hours, much longer than
 458 the duration of the experiments presented in this work. Similarly, studies of the nature of isotopic
 459 exchange between studtite and ^{18}O -enriched water have shown the absence of exchange with the
 460 peroxo and uranyl bonds within studtite [47]. These bonds are strong and not very sensitive to
 461 isotopic exchange. The only fast exchanges are with the water molecules of studtite. Therefore, it is
 462 reasonable to assume that the oxygen isotope of the uranyl ion provides relevant information about
 463 the nature of the oxidative dissolution mechanism at the UO_2 / water interface.

464 The reference leaching experiment of the UO_2 pellet in the presence of $\text{H}_2^{18}\text{O}_2$ clearly shows that the
 465 uranyl bond contains a significant amount of ^{16}O (15%) while the peroxo bond mainly contains ^{18}O
 466 (97%) (Figure 6). The uranyl bond well integrates oxygen ^{18}O coming from the labelled water (H_2^{18}O +
 467 $\text{H}_2^{18}\text{O}_2$ media), but also ^{16}O . The latter certainly comes from the solid and reflects an oxidation
 468 mechanism at the surface of the pellet. Indeed, the hypothesis of an initial release of the U^{4+} ion from
 469 the surface into the solution, followed by oxidation in the solution (H_2^{18}O + $\text{H}_2^{18}\text{O}_2$ system), would have
 470 led to an ^{18}O enrichment close to 100%. Furthermore, $^{16}\text{O}_2$ coming from the air is 5 times less
 471 concentrated than $\text{H}_2^{18}\text{O}_2$ and its kinetic oxidation constant is 200 times lower [49], which does not
 472 support its participation in the uranium oxidation process.

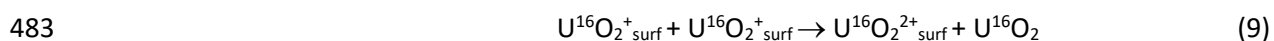
473 With regard to the surface oxidation process in the presence of H_2O_2 , it is generally described in two
 474 stages, with the formation of U(V) first, followed by the formation of the uranyl ion. A plausible
 475 mechanism proposed by Ekeröth and Jonsson [50] for the reaction between UO_2 and H_2O_2 is a primary
 476 slow one-electron transfer stage producing U(V) and OH° radicals according to the following reaction:



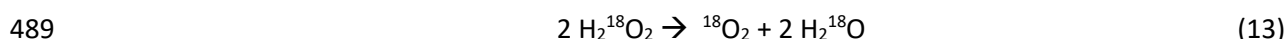
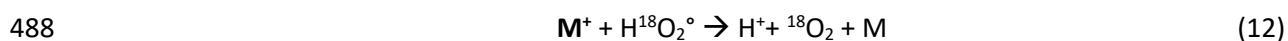
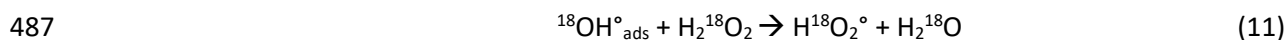
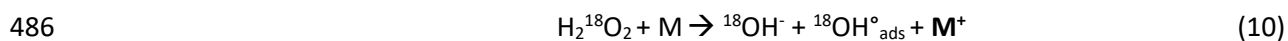
478 Which becomes by taking into account the isotopy of the studied system:



480 According to such a process, the formation of U(V) from H_2O_2 would not necessarily involve the
 481 incorporation of oxygen atoms into the fluorite structure. The formation of the uranyl ion can then be
 482 written [50]:

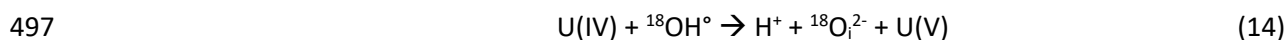


484 As the ${}^{18}\text{OH}^\circ$ radicals formed, they can contribute to catalytic decomposition of H_2O_2 according to the
 485 following mechanism [51-53]:



490 They can even oxidize the UO_2 surface. The relative contribution of these two processes (catalytic
 491 decomposition versus oxidation) depends in particular on the amount of OH° radicals scavenged by
 492 hydrogen peroxide [52]. Sunder [54] has proposed an interaction process between OH° and the surface

493 involving the incorporation of oxygen atoms into the fluorite structure. OH° radicals, produced during
494 the first oxidation step with H₂O₂ are smaller in size than the H₂O₂ molecule and can also oxidize the
495 surface. The UO₂ surface can incorporate oxygen atoms in an interstitial position according to the
496 following process [54]:



498 The interstitial ¹⁸O oxygen atom can therefore also contribute to the formation of UO₂⁺_{surf} and UO₂²⁺_{surf}
499 ions. More recently, studies on the interaction between water plasma and a UO₂ surface mention the
500 incorporation of oxygen atoms into the fluorite structure, resulting in a decrease of the U4f/O1s
501 surface area ratio measured by XPS [55]. Thus, the formation of the uranyl ion in the presence of H₂¹⁸O₂
502 alone (H₂¹⁸O + H₂¹⁸O₂ media), with both ¹⁸O and ¹⁶O isotopic contributions, is fully compatible with an
503 oxidation mechanism involving both electronic transfer and incorporation of interstitial oxygen from
504 the solution.

505 Therefore, it is interesting to discuss the isotopy of the uranyl bond for the alpha and gamma
506 irradiation experiments. For the gamma irradiation experiment, the uranyl bond is highly enriched up
507 to 95% in ¹⁸O. The primary yields of OH° radicals for gamma radiation (low LET radiation) are high [35]
508 and these highly reactive species can rapidly interact with the UO₂ surface. The high reactivity of these
509 ¹⁸OH° radicals produced by radiolysis of labelled water (H₂¹⁸O) would lead to a massive incorporation
510 of ¹⁸O at the surface and explain the low ¹⁶O content of the uranyl ion. On the other hand, under alpha
511 irradiation, H₂O₂ peroxide remains a major product of water radiolysis and the primary production of
512 OH° radicals is 10 times lower than under gamma irradiation. Furthermore, the ¹⁸O enrichments
513 obtained for the uranyl bond for the reference experiment with simple addition of H₂¹⁸O₂ and for the
514 experiment under alpha irradiation with ¹⁸O labelled water are very similar (figure 6). This observation
515 clearly argues for a predominant role of H₂¹⁸O₂, especially after the beam has been cut. It is then
516 consistent to find the two isotopes (¹⁸O and ¹⁶O) of oxygen in the uranyl bond if processes involving
517 both electronic transfer and surface incorporation occur simultaneously under alpha irradiation.

518 It should be noted that under alpha irradiation and before the beam is cut off, the ¹⁸O enrichment in
519 the uranyl bond is lower and the ¹⁶O content is higher than after the beam is cut. This point may reflect
520 an increased mobility of oxygen atoms (¹⁶O) in the solid due to the continuous creation of defects, but
521 will require additional development in the future. Another hypothesis is that the high local content of
522 hydrogen peroxide in the first seventy microns under alpha irradiation induces strong scavenging of
523 ¹⁸OH° radicals.

524

525 5. Conclusion

526 An original experimental approach combining Raman spectroscopy to the use of H₂¹⁸O labelled water
527 was developed to better understand the oxidizing dissolution of UO₂ and studtite precipitation
528 mechanisms under alpha radiolysis of water. Two static leaching experiments were performed: the
529 first involved the alteration of a UO₂ pellet under alpha radiolysis in the presence of ¹⁸O-labelled water
530 with in-situ Raman monitoring of the altered layer, and the second one involved the alteration of UO₂
531 in the presence of ¹⁸O-labelled hydrogen peroxide. In these experiments, the precipitation of a studtite
532 layer on the surface of the pellet was observed. It is clear that the bridging peroxo ligands in studtite
533 originate from the peroxo species within the hydrogen peroxide molecule, which is itself produced by
534 the radiolysis of water. Under alpha irradiation, the isotopic composition of the peroxide bond in
535 studtite is essentially ¹⁸O-¹⁸O and originates from the H₂¹⁸O₂ molecule formed by recombination of
536 ¹⁸OH° radicals in solution.

537 For the uranyl bond of the UO₂²⁺ ions, the presence of both ¹⁶O and ¹⁸O isotopes is observed. This can
538 be explained by allowing an oxidation process involving both a simple electron transfer by interaction
539 with H₂O₂ and the incorporation of oxygen atoms coming from the solution into the fluorite structure
540 due to oxidation by OH° radicals. The production of ¹⁸OH° radicals, particularly by catalytic
541 decomposition of hydrogen peroxide H₂¹⁸O₂ on the surface of UO₂, remains a preferred route leading
542 to the insertion of oxygen atoms into the material structure at the surface.

543 Moreover, these results are consistent with previous studies, this time carried out under gamma
544 irradiation and in aerated conditions. The chemical relationship between the peroxide bond of H₂O₂
545 and the O-O bridging bond in studtite is also confirmed, as is the important role of OH° radicals in the
546 insertion of oxygen atoms into the fluorite structure.

547 In the future, it will be useful to further investigate the role of atomic defects in the dynamics of
548 isotopic exchange at the reaction interface. In this context, the use of a solid doped with ¹⁸O, which
549 allows the study of exchange dynamics within the solid under irradiation, would be relevant and is
550 currently under extensive investigation.

551

552 Acknowledgments

553 The authors would like to express their gratitude to William Hate, Dominique Baux and Paul Sigot,
554 members of the CEMHTI particles beams platform, for their technical support in this study. We are
555 grateful to acknowledge Rachele Omnée from CEMHTI and Stéphanie Szenknect from ICSM for their
556 technical assistance. We would also like to thank Véronique Broudic from LMPA, Nicolas Clavier from
557 ICSM and David Chaulin from CEMHTI for organizing the transport of the sample as well as Joseph
558 Lautru from ICSM for the SEM analyses and Maxime Lanyi for his careful proofreading. Finally, the
559 authors would like to thank the project Transport & Entreposage of the French Institut Tripartite CEA-
560 EDF-Framatome for supporting this study.

561

562

563 CRediT

564 **Aurelien Perrot:** Writing – original draft, Methodology, Software, Formal analysis, Data curation,
565 Investigation, Resources.

566 **Aurelien Canizares:** Methodology, Formal analysis, Data curation, Investigation, Resources, Writing –
567 Review & Editing.

568 **Sandrine Miro:** Conceptualization, Validation, Formal analysis, Data curation, Investigation, Writing –
569 original draft, Writing – Review & Editing, Visualisation, Supervision, Project administration, Funding
570 acquisition.

571 **Laurent Claparede:** Conceptualization, Validation, Writing – Review & Editing, Visualisation,
572 Supervision.

573 **Renaud Podor:** Methodology, Formal analysis, Data curation, Investigation, Resources, Writing –
574 Review & Editing.

575 **Thierry Sauvage:** Conceptualization, Project administration, Writing – Review & Editing.

576 **Sylvain Puget:** Writing – Review & Editing, Project administration, Funding acquisition.

577 **Christophe Jegou:** Conceptualization, Validation, Writing – original draft, Writing – Review & Editing,
578 Visualization, Supervision, Project administration, Funding acquisition.

579 **Nicolas Dacheux:** Conceptualization, Validation, Writing – original draft, Writing – Review & Editing,
580 Visualization, Supervision, Project administration, Funding acquisition.

581

582 **References**

- 583 [1] Burns, P.C., R.C. Ewing, and A. Navrotsky, *Nuclear fuel in a reactor accident*. Science, 2012.
584 **335**(6073): p. 1184-1188 DOI: <https://doi.org/10.1126/science.1211285>.
- 585 [2] Ewing, R.C., *Long-term storage of spent nuclear fuel*. Nature Materials, 2015. **14**: p. 252-257
586 DOI: <https://doi.org/10.1038/nmat4226>.
- 587 [3] Hanson, B.D., et al., *Corrosion of commercial spent nuclear fuel. 1. Formation of studtite and*
588 *metastudtite*. Radiochimica Acta, 2005. **93**(3): p. 159-168 DOI:
589 <https://doi.org/10.1524/ract.93.3.159.61613>.
- 590 [4] Jégou, C., et al., *Oxidizing dissolution of spent MOX47 fuel subjected to water radiolysis:*
591 *Solution chemistry and surface characterization by Raman spectroscopy*. Journal of Nuclear
592 Materials, 2010. **399**(1): p. 68-80 DOI: <https://doi.org/10.1016/j.jnucmat.2010.01.004>.
- 593 [5] McNamara, B., et al., *Corrosion of commercial spent nuclear fuel. 2. Radiochemical analyses*
594 *of metastudtite and leachates*. Radiochimica Acta, 2009. **93**: p. 169-175 DOI:
595 <https://doi.org/10.1524/ract.93.3.169.61615>.
- 596 [6] Giménez, J., et al., *Cesium sorption on studtite (UO₂O₂·4H₂O)*. Radiochimica Acta, 2010. **98**(8):
597 p. 479-483 DOI: <https://doi.org/10.1524/ract.2010.1742>.
- 598 [7] Kubatko, K.A.H., et al., *Stability of Peroxide-Containing Uranyl Minerals*. Science, 2003.
599 **302**(5648): p. 1191-1193 DOI: <https://doi.org/10.1126/science.1090259>.
- 600 [8] Clarens, F., et al., *The oxidative dissolution of unirradiated UO₂ by hydrogen peroxide as a*
601 *function of pH*. Journal of Nuclear Materials, 2005. **345**(2-3): p. 225-231 DOI:
602 <https://doi.org/10.1016/j.jnucmat.2005.06.002>.
- 603 [9] Magnin, M., et al., *Oxidizing dissolution mechanism of an irradiated MOX fuel in underwater*
604 *aerated conditions at slightly acidic pH*. Journal of Nuclear Materials, 2015. **462**: p. 230-241
605 DOI: <https://doi.org/10.1016/j.jnucmat.2015.03.029>.
- 606 [10] Forbes, T.Z., et al., *Alteration of dehydrated schoepite and soddyite to studtite,*
607 *[(UO₂)(O₂)(H₂O)₂](H₂O)₂*. American Mineralogist, 2011. **96**(1): p. 202-206 DOI:
608 <https://doi.org/10.2138/am.2011.3517>.
- 609 [11] Burns, P.B. and K.-A. Hughes, *Studtite, [(UO₂)(O₂)(H₂O)₂](H₂O)₂: The first structure of a*
610 *peroxide mineral*. American Mineralogist, 2003. **88**(7): p. 1165-1168 DOI:
611 <https://doi.org/10.2138/am-2003-0725>.
- 612 [12] Kim, J., et al., *Dissolution of studtite [UO₂(O₂)(H₂O)₄] in various geochemical conditions*.
613 Journal of Environmental Radioactivity, 2018. **189**(October 2017): p. 57-66 DOI:
614 <https://doi.org/10.1016/j.jenvrad.2018.01.010>.
- 615 [13] Rey, A., et al., *Stability of uranium (VI) peroxide hydrates under ionizing radiation*. American
616 Mineralogist, 2009. **94**(2-3): p. 229-235.
- 617 [14] Fairley, M., et al., *Stability of Solid Uranyl Peroxides under Irradiation*. Inorganic Chemistry,
618 2019. **58**(20): p. 14112-14119 DOI: <https://doi.org/10.1021/acs.inorgchem.9b02132>.
- 619 [15] Rey, A., et al., *Effect of temperature on studtite stability: Thermogravimetry and differential*
620 *scanning calorimetry investigations*. Journal of Nuclear Materials, 2009. **385**(2): p. 467-473
621 DOI: <https://doi.org/10.1016/j.jnucmat.2008.12.045>.
- 622 [16] Thompson, N.B.A., et al., *The thermal decomposition of studtite: analysis of the amorphous*
623 *phase*. Journal of Radioanalytical and Nuclear Chemistry, 2021. **327**(3): p. 1335-1347 DOI:
624 <https://doi.org/10.1007/s10967-021-07611-4>.
- 625 [17] Sarrasin, L., et al., *Studtite Formation Assessed by Raman Spectroscopy and ¹⁸O Isotopic*
626 *Labeling during the Oxidative Dissolution of a MOX Fuel*. Journal of Physical Chemistry C,
627 2021. **125**(35): p. 19209-19218 DOI: <https://doi.org/10.1021/acs.jpcc.1c04392>.
- 628 [18] Canizarès, A., et al., *In situ Raman monitoring of materials under irradiation: Study of*
629 *uranium dioxide alteration by water radiolysis*. Journal of Raman Spectroscopy, 2012. **43**(10):
630 p. 1492-1497 DOI: <https://doi.org/10.1002/jrs.4088>.

- 631 [19] Guimbretière, G., et al., *Characterization of nuclear materials in extreme conditions: Raman*
632 *spectroscopy approach*. IEEE Transactions on Nuclear Science, 2014. **61**(4): p. 2045-2051 DOI:
633 <https://doi.org/10.1109/TNS.2014.2311166>.
- 634 [20] Martinez, J., et al., *An original precipitation route toward the preparation and the sintering of*
635 *highly reactive uranium cerium dioxide powders*. Journal of Nuclear Materials, 2015. **462**: p.
636 173-181 DOI: <https://doi.org/10.1016/j.jnucmat.2015.03.053>.
- 637 [21] Ziegler, J.F., M.D. Ziegler, and J.P. Biersack, *SRIM - The stopping and range of ions in matter*
638 *(2010)*. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions
639 with Materials and Atoms, 2010. **268**(11-12): p. 1818-1823 DOI:
640 <https://doi.org/10.1016/j.nimb.2010.02.091>.
- 641 [22] Soullard, J. and A. Alamo, *Etude du ralentissement des ions dans une cible diatomique*.
642 *Radiation Effects*, 1978. **38**(3-4): p. 133-139 DOI:
643 <https://doi.org/10.1080/00337577808233221>.
- 644 [23] Charlot, G., *Les méthodes de la chimie analytique: analyse quantitative minérale*. 5rd ed,
645 Masson, Editor. 1966.
- 646 [24] Livneh, T. and E. Sterer, *Effect of pressure on the resonant multiphonon Raman scattering in*
647 *UO₂*. Physical Review B - Condensed Matter and Materials Physics, 2006. **73**(8): p. 1-9 DOI:
648 <https://doi.org/10.1103/PhysRevB.73.085118>.
- 649 [25] Allen, G.C., I.S. Butler, and T. Nguyen Anh, *Characterisation of uranium oxides by micro-*
650 *Raman spectroscopy*. Journal of Nuclear Materials, 1987. **144**(1-2): p. 17-19 DOI:
651 [https://doi.org/10.1016/0022-3115\(87\)90274-1](https://doi.org/10.1016/0022-3115(87)90274-1).
- 652 [26] Elorrieta, J.M., et al., *Temperature dependence of the Raman spectrum of UO₂*. Journal of
653 *Nuclear Materials*, 2018. **503**: p. 191-194 DOI:
654 <https://doi.org/10.1016/j.jnucmat.2018.03.015>.
- 655 [27] Gutierrez, G., et al., *Effect of ballistic damage in UO₂ samples under ion beam irradiations*
656 *studied by in situ Raman spectroscopy*. Nuclear Instruments and Methods in Physics
657 *Research, Section B: Beam Interactions with Materials and Atoms*, 2018. **434**(April): p. 45-50
658 DOI: <https://doi.org/10.1016/j.nimb.2018.08.010>.
- 659 [28] Jegou, C., et al., *Raman micro-spectroscopy of UOX and MOX spent nuclear fuel*
660 *characterization and oxidation resistance of the high burn-up structure*. Journal of Nuclear
661 *Materials*, 2015. **458**: p. 343-349 DOI: <https://doi.org/10.1016/j.jnucmat.2014.12.072>.
- 662 [29] Lv, J., et al., *Raman scattering from phonons and electronic excitations in UO₂ with different*
663 *oxygen isotopes*. Journal of Raman Spectroscopy, 2015. **47**(3): p. 345-349 DOI:
664 <https://doi.org/10.1002/jrs.4785>.
- 665 [30] He, H. and D. Shoesmith, *Raman spectroscopic studies of defect structures and phase*
666 *transition in hyper-stoichiometric UO_{2+x}*. Physical Chemistry Chemical Physics, 2010. **12**(28): p.
667 8108-8117 DOI: <https://doi.org/10.1039/b925495a>.
- 668 [31] Lee, J., et al., *Raman spectroscopic study of the structural change of uranium–thorium-mixed*
669 *oxides before and after oxidation*. Journal of Radioanalytical and Nuclear Chemistry, 2018.
670 **316**(3): p. 1295-1300 DOI: <https://doi.org/10.1007/s10967-018-5829-x>.
- 671 [32] Guimbretière, G., et al., *In situ Raman monitoring of He²⁺ irradiation induced damage in a*
672 *UO₂ ceramic*. Applied Physics Letters, 2013. **103**(4): p. 2-6 DOI:
673 <https://doi.org/10.1063/1.4816285>.
- 674 [33] Corbel, C., et al., *Addition versus radiolytic production effects of hydrogen peroxide on*
675 *aqueous corrosion of UO₂*. Journal of Nuclear Materials, 2006. **348**(1-2): p. 1-17 DOI:
676 <https://doi.org/10.1016/j.jnucmat.2005.05.009>.
- 677 [34] Mohun, R., *Raman spectroscopy for the characterization of defective spent nuclear*. PhD
678 *thesis, Université Aix-Marseille*, 2017. Available from:
679 <https://www.theses.fr/2017AIXM0288.pdf>.
- 680 [35] Lucchini, J.-F., *Influence de la radiolyse a de l'eau sur l'alteration de la matrice UO₂ du*
681 *combustible nucléaire usé*. PhD thesis, Université Paris XI, 2001. Available from:
682 <https://inis.iaea.org/collection/NCLCollectionStore/Public/46/131/46131462.pdf>.

- 683 [36] Van der Lee, J., et al., *Module-oriented modeling of reactive transport with HYTEC*.
684 Computers and Geosciences, 2003. **29**(3): p. 265-275 DOI: [https://doi.org/10.1016/S0098-](https://doi.org/10.1016/S0098-3004(03)00004-9)
685 [3004\(03\)00004-9](https://doi.org/10.1016/S0098-3004(03)00004-9).
- 686 [37] Giffaut, E., et al., *Andra thermodynamic database for performance assessment*:
687 *ThermoChimie*. Applied Geochemistry, 2014. **49**: p. 225-236 DOI:
688 <http://dx.doi.org/10.1016/j.apgeochem.2014.05.007>.
- 689 [38] Kurt, W., *On Studtite and Its Composition*. American Mineralogist, 1974. **59**(1-2): p. 166-171.
- 690 [39] Schlegel, M.L. and C. Jegou, *Uraninite alteration by H₂O₂ solutions and formation of*
691 *secondary phases: An in situ microRaman spectroscopy and synchrotron X-ray diffraction*
692 *study*. Journal of Nuclear Materials, 2022. **572**: p. 154056 DOI:
693 <https://doi.org/10.1016/j.jnucmat.2022.154056>.
- 694 [40] Lu, G., A.J. Haes, and T.Z. Forbes, *Detection and identification of solids, surfaces, and*
695 *solutions of uranium using vibrational spectroscopy*. Coordination Chemistry Reviews, 2018.
696 **374**: p. 314-344 DOI: <https://doi.org/10.1016/j.ccr.2018.07.010>.
- 697 [41] Sunder, S. and H. Christensen, *Gamma Radiolysis of Water Solutions Relevant to the Nuclear*
698 *Fuel Waste Management Program*. Nuclear Technology, 1993. **104**(3): p. 403-417 DOI:
699 <https://doi.org/10.13182/NT93-A34900>.
- 700 [42] Hiroki, A., S.M. Pimblott, and J.A. LaVerne, *Hydrogen Peroxide Production in the Radiolysis of*
701 *Water with High Radical Scavenger Concentrations*. J. Phys. Chem. A, 2002. **106**(40): p. 9352–
702 9358 DOI: <https://doi.org/10.1021/jp0207578>.
- 703 [43] Jégou, C., et al., *Effect of external gamma irradiation on dissolution of the spent UO₂ fuel*
704 *matrix*. Journal of Nuclear Materials, 2005. **341**(1): p. 62-82 DOI:
705 <https://doi.org/10.1016/j.jnucmat.2005.01.008>.
- 706 [44] Joseph, J.M., et al., *A combined experimental and model analysis on the effect of pH and*
707 *O_{2(aq)} on γ -radiolytically produced H₂ and H₂O₂*. Radiation Physics and Chemistry, 2008. **77**(9):
708 p. 1009-1020 DOI: <https://doi.org/10.1016/j.radphyschem.2008.06.001>.
- 709 [45] Iwamatsu, K., S. Sundin, and J.A. LaVerne, *Hydrogen peroxide kinetics in water radiolysis*.
710 Radiation Physics and Chemistry, 2018. **145**: p. 207-212 DOI:
711 <https://doi.org/10.1016/j.radphyschem.2017.11.002>.
- 712 [46] Bonales, L.J., et al., *Oxygen diffusion coefficient and characterization of leachant in UO₂*
713 *corrosion studied by new methods*. Solid State Ionics, 2022. **380**(April): p. 1-8 DOI:
714 <https://doi.org/10.1016/j.ssi.2022.115922>.
- 715 [47] Lonadier, F.D. and J.E. Boggs, *Isotope exchange studies on the uranium(VI) oxide hydrates*
716 *and uranium peroxide*. J. Less-Common Met., 1963. **5**(2): p. 112-116 DOI:
717 [https://doi.org/10.1016/0022-5088\(63\)90003-1](https://doi.org/10.1016/0022-5088(63)90003-1).
- 718 [48] Berger, P., *Etude du mécanisme de La dissolution par oxydoreduction chimique et*
719 *electrochimique des bioxydes d'actinides (UO₂, NpO₂, PuO₂, AmO₂) en milieu aqueux acide*.
720 PhD thesis, Paris VI, 1990. Available from: <https://theses.fr/1988PA066073>.
- 721 [49] Ekeroth, E., O. Roth, and M. Jonsson, *The relative impact of radiolysis products in radiation*
722 *induced oxidative dissolution of UO₂*. Journal of Nuclear Materials, 2006. **355**(1-3): p. 38-46
723 DOI: <https://doi.org/10.1016/j.jnucmat.2006.04.001>.
- 724 [50] Ekeroth, E. and M. Jonsson, *Oxidation of UO₂ by radiolytic oxidants*. journal of Nuclear
725 Materials, 2003. **322**(2-3): p. 242-248 DOI: <https://doi.org/10.1016/j.jnucmat.2003.07.001>.
- 726 [51] Jonsson, M., *An Overview of Interfacial Radiation Chemistry in Nuclear Technology*. Israel
727 Journal of Chemistry, 2014. **54**(3): p. 292-301 DOI: <https://doi.org/10.1002/ijch.201300119>.
- 728 [52] Fidalgo, A.B., Y. Kumagai, and M. Jonsson, *The role of surface-bound hydroxyl radicals in the*
729 *reaction between H₂O₂ and UO₂*. Journal of Coordination Chemistry, 2018. **71**(11-13): p.
730 1799-1807 DOI: <https://doi.org/10.1080/00958972.2018.1466287>.
- 731 [53] Maier, A.C., E.H. Iglebaek, and M. Jonsson, *Confirming the Formation of Hydroxyl Radicals in*
732 *the Catalytic Decomposition of H₂O₂ on Metal Oxides Using Coumarin as a Probe*.
733 Chemcatchem, 2019. **11**(22): p. 5435-5438 DOI: <https://doi.org/10.1002/cctc.201901316>.

- 734 [54] Sunder, S., et al., *Oxidation of UO₂ fuel by the products of gamma radiolysis of water*. Journal
735 of Nuclear Materials, 1992. **190**: p. 78-86 DOI: [https://doi.org/10.1016/0022-3115\(92\)90078-
737 \[55\] El Jamal, G., et al., *Time-dependent surface modification of uranium oxides exposed to water
738 plasma*. Dalton Transactions, 2021. **50**\(14\): p. 4796-4804 DOI:
739 <https://doi.org/10.1039/D1DT00486G>.](https://doi.org/10.1016/0022-3115(92)90078-
736 Y)
- 740