

1 Mobility of daughter elements of  $^{238}\text{U}$  decay chain during leaching by In

2 Situ Recovery (ISR): New insights from digital autoradiography

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5 Abstract

6 In highly permeable sedimentary rock formations, U extraction by *in-situ* leaching techniques  
7 (ISR – In-Situ Recovery) is generally considered to have a limited environmental impact at  
8 ground level. Significantly, this method of extraction produces neither mill tailings nor waste  
9 rocks. Underground, however, the outcome for  $^{238}\text{U}$  daughter elements in aquifers is not well  
10 known because of their trace concentrations in the host rocks. Thus, understanding the *in-situ*  
11 mobility of these elements remains a challenge. Two samples collected before and after six  
12 months of ISR experiments (Dulaan Uul, Mongolia) were studied with the help of a digital  
13 autoradiography technique (DA) of alpha particles, bulk alpha spectrometry, and  
14 complementary petrographic observation methods. These techniques demonstrate that before  
15 and after leaching, the radioactivity is concentrated in altered and microporous Fe-Ti oxides.  
16 Most of the daughter elements of U remain trapped in the rock after the leaching process. DA  
17 confirms that the alpha activity of the Fe-Ti oxides remains high after uranium leaching, and  
18 the initial secular equilibrium of the  $^{238}\text{U}$  series for  $^{230}\text{Th}$  to  $^{210}\text{Po}$  daughter elements  
19 (including  $^{226}\text{Ra}$ ) of the fresh rocks is maintained after leaching. While these findings should  
20 be confirmed by more systematic studies, they already identify potential mechanisms  
21 explaining why the U-daughter concentrations in leaching water are low.

22 Keywords: uranium mining; autoradiograph; in-situ leaching; radium mobility

23

## 24 1. Introduction

25

26 In-Situ Recovery (ISR) is a primary method used to extract uranium (U) from porous  
27 and permeable rocks. ISR facilities are used to extract U from low-grade ores at lower cost  
28 than conventional mining and milling processes (Seredkin et al., 2016). The method consists  
29 of injecting leaching solutions (acidic and/or oxidizing) through a series of wells into the  
30 permeable U-mineralized body to dissolve the U-bearing minerals (Habib, 1981; World  
31 Nuclear Association, 2018). The leachate is then pumped out through recovery wells and  
32 transported to the treatment plant where U is extracted from the mineralized solution. In the  
33 absence of a significant amount of carbonate in the reservoir rocks, ISR proceeds by the  
34 injection of acidic (sulfuric acid, pH ~ 2) solutions and oxidizing solutions (Eh ~ 0.8 V/SHE)  
35 (Robin *et al.*, 2015; Lagneau *et al.*, 2019). This mining technique results in little surface  
36 disturbance and generates neither tailings nor waste rock. The restoration of the aquifer is  
37 usually performed by ‘treat and pump’ solutions, in-situ treatment and natural attenuation so  
38 as to return it to its initial water classification/quality. Natural attenuation relies on the buffer  
39 capacities of the aquifer to attenuate the main contaminants of concern (U, <sup>226</sup>Ra and pH)  
40 through geochemical processes such as sorption, reduction and precipitation (WoldeGabriel et  
41 al., 2014; Gallegos et al., 2015; Robin et al., 2017; Dangelmayr et al., 2018). Currently very  
42 few peer-reviewed publications on groundwater restoration at ISR uranium mines are  
43 available, especially when acid is used as the leachate (Yazikov and Zabaznov, 2002;  
44 Kayukov, 2005; Jeuken et al., 2009; Dong et al., 2016).

45 The ISR method is based on the geochemical behaviour of uranium which is highly  
46 mobile under oxidizing and acidic conditions U(VI) and poorly mobile under reducing  
47 conditions U(IV) (Langmuir, 1978; Bourdon et al., 2003). As well as generating the  
48 production of a sulfate-rich plume which can contaminate the groundwater beyond the

49 mineralized zones, the use of sulfuric acid as a leachate produces a strong radioactive  
50 disequilibrium state in the leached rocks (Lagneau et al., 2019). This disequilibrium is due to  
51 the almost total depletion by chemical extraction of the U isotopes which belong to the  $^{238}\text{U}$   
52 natural decay chain. Daughter elements are very difficult to investigate due to their very low  
53 concentration (ppb-ppt). Understanding the mobility of these radio-elements is an important  
54 environmental issue in the post-mining ISR context. While previous works highlighted the  
55 retention of  $^{226}\text{Ra}$  by celestine ( $\text{SrSO}_4$ ), ilmenite ( $\text{TiFeO}_3$ ), barite ( $\text{BaSO}_4$ ) and clay minerals  
56 (Robin *et al.*, 2017; Lestini et al., 2019; Heberling et al., 2018; Boulesteix et al., 2019; Billon  
57 et al., 2020), the geochemical behaviour of U-daughter elements is still poorly understood in  
58 an acidic context (Déjeant et al., 2016; Déjeant et al., 2014; Chautard et al., 2017; Ballini et  
59 al., 2020), in which other important isotopes in the  $^{238}\text{U}$  series are  $^{230}\text{Th}$ ,  $^{222}\text{Rn}$  and polonium  
60 isotopes ( $^{218}\text{Po}$ ,  $^{214}\text{Po}$ ,  $^{210}\text{Po}$ ). As of today, the geochemical studies of U and its daughter  
61 elements are based on sequential leaching of the bulk material, which is an expensive,  
62 destructive and complex method which is also difficult to interpret (Blanco et al., 2004;  
63 Bacon and Davidson, 2008; Menozzi et al., 2016).

64 A new autoradiographic method for the mapping of alpha particle emissions in  
65 geomaterials has been developed very recently (Sardini et al., 2016; Angileri et al., 2018). It is  
66 based on the use of a real-time Digital Autoradiograph (DA) device called BeaQuant™. This  
67 was initially designed to produce images of beta emissions from medical or biological  
68 samples (Donnard et al., 2009a, 2009b, 2009c). More recently, DA has also been employed to  
69 map beta emitters in geomaterials (Billon et al., 2019a,b, 2020; Muuri et al., 2019). Compared  
70 to existing autoradiographic methods (Illic and Durrani, 2003; Durrani and Illic, 1997;  
71 Amgarou, 2002; Siitari-Kauppi, 2002; Cole et al., 2003; Koarashi et al., 2007; Schmidt et al.,  
72 2013; Sardini et al., 2015), this digital autoradiograph device provides new type of data.  
73 Concerning geomaterials, it is able to spatialize and determine the radioactive equilibrium

74 state of the  $^{238}\text{U}$  decay chain on cm-mm scale samples, with a spatial resolution of  $\sim 20\ \mu\text{m}$ .  
75 The principle is to compare the alpha activity map made by DA and the U-content maps  
76 obtained from microprobe analysis (Angileri et al., 2018). The U maps are converted into a  
77 theoretical alpha activity map assuming secular equilibrium. Comparing the activities of both  
78 the theoretical and the experimental maps allows us to determine the equilibrium state  
79 distribution, and to allocate it in a petrographic framework.

80 This study is focused on understanding the effects of the mobility of U-series elements  
81 in the sands of the geological aquifer at Duulan Uul (Mongolia) after U extraction by the ISR  
82 process. In this study we performed a coupled radiometric and mineralogical analysis of two  
83 core samples which were extracted from the industrial-scale pilot mining site at Dulaan Uul  
84 after a six months of in-situ acidic leaching tests carried out by the ORANO Group (Cardon et  
85 al., 2016; de Boissezon et al., 2017). The roll-front mineralization is hosted in Upper  
86 Cretaceous sands deposited in a fluvial to lacustrine environment. One sample is  
87 representative of the untreated uranium ore whereas the second one was sampled in the  
88 uranium ore which had been subjected to six months of leaching tests.

89 Investigations were performed by combining bulk alpha spectrometry and multi-scale  
90 imaging techniques. On fresh and leached sands, multiscale observations were needed to  
91 establish the relationship between the alpha activity and the sand mineralogy. At the scale of  
92 the thin section ( $3 \times 4.5\ \text{cm}^2$ ), DA was the key technique for the quantitative mapping of  
93 alpha activity, and was combined with mineral mapping using QEMSCAN (Quantitative  
94 Evaluation of Minerals by SCANNing electron microscopy). SEM (Scanning Electron  
95 Microscopy) and an electron microprobe were employed at the scale of the primary mineral  
96 grains, and TEM (Transmission Electron Microscopy) at the nanometric scale.

97 Following on from previous studies devoted to ISR process optimization (Bonnaud et al.,  
98 2014; Regnault et al., 2014), the main aim of this contribution is to better understand the

99 reactive transport of ultra-trace radioelements of the  $^{238}\text{U}$  decay series by combining multi-  
100 scale imaging methods of radioactivity and mineralogy.

101

## 102 2. Material and Methods

103

### 104 2.1 Samples

105 The studied samples were selected after six months of ISR experiments (12/2010 to 06/2011)

106 performed in the U-mineralized sands of the Dulaan Uul site (Mongolia). It consisted of the

107 continuous injection-pumping of a sulphuric acid solution through a pilot extraction cell.

108 During this process, the fluid continuously circulates between the injection and pumping wells

109 in a loop both underground and at the surface. U is extracted from the pumped fluid, whose

110 pH is monitored and readjusted before reinjection in order to maintain its ability to dissolve U

111 in the rock (see Lagneau et al., 2019 for further details). A summarised description of the ISR

112 test is available in Cardon et al. (2016) and de Boissezon et al. (2017). The goal of this

113 experiment was to collect most of the environmental data (variations in pH, water chemistry,

114 mineralogy) needed to determine the effect of the acidic plume in the surrounding aquifer up

115 to several years after the end of acid injection (de Boissezon et al. 2017).

116 The core samples investigated in this study were collected from two different boreholes

117 drilled at the end of the ISR experiment. Sample F (fresh) was extracted from a depth of

118 113.10 m and is representative of the uranium ore zone unaffected by the acidic plume.

119 Sample L (leached) was extracted from a depth of 110.80 m and is representative of the

120 uranium ore zone after six months of leaching by acidic solution. This sample came from the

121 same mineralized layer, but the lateral distance between the two core samples is

122 approximatively 30 m (de Boissezon et al. 2017). Such a distance was chosen to guarantee a

123 non-acidic zone. The samples were protected from the atmosphere using airtight bags filled

124 with nitrogen. For both samples, bulk U concentrations were obtained from chemical analysis,

125 and gamma radioactivity was provided by a portable gamma field counter (SPP –  
126 Scintillomètre Portatif Prospectif). The data is shown in the “Results” section. Both samples  
127 are mineralogically similar, but we emphasize here that the initial U content of sample L is  
128 not accurately known.

## 129 2.2 Alpha spectrometry

130 Alpha spectrometry is a bulk method used here to determine which alpha emitters are present  
131 in the studied samples. Measurements were obtained using a CANBERRA A450 PIPS®  
132 model with a 450 mm<sup>2</sup> detector and intrinsic energy resolution (FWHM – Full Width at Half  
133 Maximum) of 32 and 26 keV (Radiochemistry Laboratory, University of Helsinki, Finland).  
134 The data acquisition and analysis were done with MAESTRO for Windows® Model A65-332  
135 software. The energy calibration was performed with a reference sample containing <sup>237</sup>Np (E  
136 = 4788 keV, I = 47 %), <sup>241</sup>Am (E = 5486 keV, I = 84.5 %) and <sup>244</sup>Cm (E = 5805 keV, I = 76.4  
137 %). The distance from the source to the detector was  $8.40 \pm 0.21$  mm. The number of energy  
138 channels was 1024. The distance between the sample and the detector window (23.9 mm  
139 diameter) was  $8.8 \pm 0.2$  mm. The acquisition time of both samples was set to about one week  
140 (614,000 s).

141 Alpha spectra of thin sections show step-like shapes. This shape is due to the progressive  
142 energy loss of the alpha particles emitted through the sample thickness (~30µm); therefore, a  
143 well-designed simulation is crucial for analyzing these step-like spectra produced by thick  
144 samples. The experimental spectra were adjusted using the ‘Advanced Alpha Spectrometry  
145 Simulation’ (AASI) software (Siiskonen and Pöllänen, 2005). The resulting data enabled the  
146 evaluation of the activity of each radionuclide present in the sample. Secular equilibrium is  
147 confirmed for a given decay chain if all alpha emitters are present and have the same activity.

148

### 2.3 Digital Autoradiography– BeaQuant™

149 Autoradiography is an imaging technique which provides the spatial distribution of  
150 radioactive emissions emerging from a surface. In this contribution, we employed  
151 BeaQuant™, which is a real-time digital autoradiograph (DA) system developed by Ai4R  
152 SAS (Nantes, France). Compared to older autoradiograph techniques that use films (FA)  
153 (Siitari-Kauppi, 2002; Robinet et al., 2015) or phosphor screens (PSA) (Koarashi et al., 2007;  
154 Sardini et al., 2015), this device counts particles.

156 BeaQuant™ is based on the use of micromesh structures such as parallel ionization  
157 multipliers working in a proportional mode in a gaseous chamber (PIM - MPGD) (Donnard et  
158 al., 2009a, 2009c; Thers et al., 2003). This device was initially designed for analyzing charged  
159 particles having a low penetrating power, such as low-energy beta particles emitted by  $^3\text{H}$ .  
160 The gaseous chamber is divided into three parts: amplification, diffusion and reading anode.  
161 In these parts are three different electric fields limited by the sample surface, two of  
162 micromesh, and the reading anode. Particles emitted by the sample circulate in the gas  
163 chamber and interact with the gas, producing electron avalanches. These avalanches occur  
164 mainly in the amplification stage and near the sample surface, and they drift into the diffusion  
165 part. Amplified avalanches induce sufficiently high voltages above the electronic threshold to  
166 be detected by the reading anode.

167 Contrary to FA or PSA, particles are detected one by one, each particle position being first  
168 reconstructed in 2D and then assembled into a raster image. In a given pixel, the intensity  
169 represents the number of particles recorded during the exposure time. The acquisition  
170 software combined with BeaQuant™ enables the real-time reconstruction and visualization of  
171 the amount of radioactive emissions. The chosen amplification system ensures a good spatial  
172 resolution; 20  $\mu\text{m}$  for tritium (Donnard et al., 2009b) as well as for alpha particles. The  
173 sensitivity of the detector is  $5 \times 10^{-4}$  cpm/mm<sup>2</sup> ( $^3\text{H}$ ), and the maximum counting rate is  $3 \times 10^4$

174 cps in the whole mapped area. Finally, the device is insensitive to X- and gamma rays, which  
175 is a benefit compared to FA and PSA. It is possible to select alpha or beta particles separately  
176 by adjusting the BeaQuant™ amplification gains.

177 The present study used only the alpha mapping capabilities of the BeaQuant™, not the beta  
178 ones. In a thick sample containing <sup>238</sup>U-series radioelements, the emitted alpha particles are  
179 more energetic than the beta particles, which are emitted with very variable and lower energy.  
180 Along their path in the gas chamber, alpha particles interact strongly with the gas, mainly in  
181 the amplification part. Beta particles also interact mainly in the amplification part, but their  
182 energy deposition is significantly lower than for alpha ones. In a previous study, it was  
183 estimated that 82% of alpha particles were detected by BeaQuant™ compared to the alpha  
184 spectrometry counts (Sardini et al., 2016). As suggested by these authors, a correction factor  
185 of  $1.22 \pm 0.03$  was applied to the BeaQuant™ counts. Digital autoradiographs were obtained  
186 from two polished petrographic thin sections of F and L samples. These sand samples being  
187 homogeneous, just one thin section was sufficient to represent the rock before and after  
188 leaching. The total acquisition time was set to 515,200 seconds (~143 h) for both samples.  
189 This duration was chosen to ensure the stability of the counting rate in low-activity regions,  
190 regardless of the acquisition time. The chosen pixel size for the alpha maps was  $20 \times 20 \mu\text{m}^2$   
191 which represents a good approximation of the alpha particle range emitted in matter by <sup>238</sup>U  
192 series emitters. Alpha maps cover the whole thin-section surface for both studied samples.

193 The alpha emission autoradiographs obtained for both studied samples contain areas of high  
194 and concentrated alpha activity, referred to as “hotspots” hereafter. Areas of low activity (the  
195 matrix between the hotspots) are referred to as “diffuse areas” hereafter (see section 3.1).  
196 Angileri et al. (2018) observed similar patterns from crushed ore and fresh uranium mill  
197 tailings. Because hotspots are related to the mineralogy of the sand (see section 3.1), we made  
198 a special focus on the characterization of hotspot activity at the thin-section scale. The total



199 activity of the hotspots and diffuse areas was determined; we were also able to analyze the  
200 hotspots individually by processing the autoradiographic images, using segmentation (Figure  
201 S1, supplementary material), and a spot-by-spot analysis. The latter consists of (1) the  
202 determination of total alpha activity emitted by each spot and (2) the determination of the area  
203 of each spot in 2D. The total activity of a given spot is obtained by superimposing the binary  
204 image of the spots onto the raw alpha map, and by integration of the spot activity. The area of  
205 a given spot is equal to its number of pixels multiplied by the pixel size (here  $20 \times 20 \mu\text{m}^2$ ).  
206 Image processing and analysis procedures were performed using the imaging software  
207 Aphelion™.

208

#### 209 2.4 Mineral distributions

210 SEM-EDS QEMSCAN, a non-destructive Scanning Electron Microscopy (SEM) method  
211 using Energy Dispersive X-Ray Spectroscopy (EDS), was used to produce 2D elemental and  
212 mineralogical maps of the thin sections. The acquisitions were performed using an FEI FEG-  
213 SEM QEMSCAN 650F electron microscope (Total S.A., Pau, France) with an accelerating  
214 voltage of 15 kV and a beam current of 10 nA. The main aim here was to clarify the  
215 relationship between the mineralogy and the alpha activity hotspots using mineral maps  
216 acquired at the same scale as the alpha maps. Firstly, SEM-EDS QEMSCAN provided the  
217 Back-Scattered Electrons (BSE) images and Elementary maps (Na, Mg, Al, Si, P, S, K, Ca,  
218 Ti, Mn, Fe, Zr, Ba, U) of the carbon-coated thin sections. The pixel size of the EDS analyses  
219 was about 15  $\mu\text{m}$ . BSE images were acquired with a resolution of 586 nm. The 2D SEM-EDS  
220 elemental maps were then post-treated using a dedicated Spectral Analysis Engine (SAE)  
221 developed by FEI, called Nanomin, allowing the automatic 2D quantification of the  
222 mineralogy by the deconvolution of the mixed X-ray spectra of each analyzed pixel using up

223 to three reference mineral spectra. The reference mineral spectra are selected from a dedicated  
224 database or measured on pure mineral grains by a specialist.

225 SEM-EDS QEMSCAN's chemical and mineralogical maps were manually superimposed onto  
226 Beaver™ alpha activity maps to locate the activity spots in the SEM-EDS QEMSCAN  
227 images. Any global SEM-EDS QEMSCAN map is made of several smaller sub-images which  
228 are easier to handle than a larger global map, which is in fact a large composite image. A total  
229 of six (sample F) and eleven (sample L) spots were randomly selected as ROI (Regions of  
230 Interest) in the alpha maps and located on the related mineralogical maps. SEM-EDS  
231 QEMSCAN elementary maps are 8-bit raster images whose intensities are proportional to the  
232 atomic percentage. In the present study, the thin-section scale maps from SEM-EDS  
233 QEMSCAN were only used for a qualitative mineral recognition of the hotspots. The purpose  
234 here was not to extract mass contents from the EDS analyses, which would require tedious  
235 calibration with reference quantitative mineralogical analyses performed on the crushed  
236 samples (Fialips et al., 2018).

237 To accurately determine the mass contents, an electron microprobe analysis was used, in point  
238 analysis mode or mapping mode. Because this analysis technique is more cumbersome, the  
239 microprobe mapping analyses were performed locally in the thin sections, at the scale of 0.1  
240 to 1 mm. These analyses were focused on the hotspots. Microchemical analyses were  
241 performed using an electron microprobe equipped with a wavelength dispersive spectrometer  
242 (model CAMECA SX-FIVE) in the CAMPARIS facility, Pierre et Marie Curie University,  
243 Paris. An acceleration voltage of 15 keV, a count time of 180-240 seconds, and a probe  
244 current of 15 nA were selected for Si, P, Ca, Fe, Ti, Al, Mg, Na, K, Mn, and Pb. Note that Ra  
245 mapping is not possible using either QEMSCAN or microprobe, as the Ra content is  $3 \times 10^6$   
246 lower than the  $^{238}\text{U}$  content (it is an ultra-trace element). The probe current was fixed at 150

247 nA for U and Th, the detection limit was estimated as 100–200 ppm, with the interaction  
248 volume of the beam around 5  $\mu\text{m}$  (Goldstein et al., 2007). The bulk U content of the F and L  
249 samples (180 and 6 ppm respectively) is concentrated in mineral grains having an internal  
250 content of U which is higher than the provided detection limit. The chemical maps were  
251 acquired at 15 keV with a probe current of 298 nA. Chemical mapping acquisition was made  
252 using a 2  $\mu\text{m}$  step length, a dwell of 0.1 second, and the detection limit of U was estimated to  
253 be around 0.2% (2000 ppm).

254

## 255 2.5 Small scale observations

256 Thin cross-sections for TEM analysis were prepared by the FIB/SEM (Focused ion beam /  
257 Scanning electron microscope) method with a FEI-HELIOS dual-beam G3 using the standard  
258 lift-out method (Giannuzzi and Stevie (1999), Langford and Clinton (2004)). This instrument,  
259 available at the PPrime Institute, incorporates electron- and ion-beam columns. The liquid-  
260 metal ion source (LMIS) is gallium. Four thin cross-sections were prepared, two for each  
261 sample. Their size is approximatively  $15 \times 10 \mu\text{m}^2$  with a thickness lower than 150 nm for  
262 specific EDS analysis. We observed and analyzed the mineral heterogeneity of the hotspots at  
263 high resolution.

264 FIB is equipped with an EDS detector from EDAX SDD (Silicon Drift Detector); a 15 keV  
265 beam was used to detect all the elements present in the samples. At this acceleration voltage  
266 the probe size is smaller than 10 nm, which results in a very good spatial resolution during the  
267 EDS analysis. We used those chemical analyses to end-point the position of the lamella for  
268 the TEM analysis.

269 Chemical analysis and petrographic observations were made using high-angle annular dark-  
270 field scanning transmission electron microscopy (HAADF-STEM). HAADF-STEM imaging  
271 is a mapping technique based on the detection of incoherent electrons elastically scattered by

272 the sample at a high angle. The resulting image contrast is related to the atomic number and  
273 provides a chemical analysis of the nano-particles (Howie, 1979; Pennycook and Jesson,  
274 1991). HAADF-STEM observation and analysis were performed with a Jeol 2200FS FEG  
275 TEM operating at 200keV. The microscope is equipped with a Bruker EDS SDD detector.

276

277

### 278 3. Results and Discussion

279

#### 280 3.1 Petrographic observations and digital autoradiograph of alpha activity

281 The core samples are poorly-consolidated to unconsolidated, medium- to coarse-grained  
282 arkosic sands. Each core sample consists of poorly sorted angular material made of lithic  
283 fragments and detrital minerals. Lithic fragments are composed of granitoids (granite,  
284 pegmatite) with subordinate volcanic rocks (rhyolite, andesite). The detrital mineral  
285 assemblage comprises quartz, alkali feldspars (microcline, orthoclase and albite) and  
286 phyllosilicates, which are made up of white micas, chlorite, biotite and smectite. Accessory  
287 minerals were mainly pyrite, epidote, tourmaline, zircon and polycrystalline grains consisting  
288 of various types of Fe-Ti minerals (ilmenite, Ti-magnetite, rutile, anatase and titanite). The  
289 primary porosity of the sandy sediments is partly filled by a fine-grained polycrystalline  
290 sedimentary matrix having the same mineralogical composition as the coarse-grained detrital  
291 assemblage. At a higher magnification, all the detrital grains (except the quartz) present  
292 evidence of dissolution and partial replacement by clay minerals (montmorillonite). In the F  
293 sample, U-mineralization consists mainly of uraninite with two specific crystal habits: (1)  
294 minor amounts of individual uraninite crystals distributed within the lithic fragments and (2) a  
295 covering of the dissolution surface of Fe-Ti and Ti minerals (Ti -magnetite, ilmenite, rutile,  
296 titanite, anatase) with large amounts of uraninite nanograins (50 to 100 nm in diameter) and a  
297 partial infilling of the residual pore space with montmorillonite (Figure 1). TEM observations

298 show that uraninite nanograins are polycrystalline, and made up of aggregates of uraninite  
299 nanocrystals (Figure 1).

300 From a mineralogical point of view, the sands of the L sample differs from those of the F  
301 sample by the total disappearance of uraninite and a strong dissolution of pyrite (Figure 2).

302 An SEM/EDX analysis on both samples of the Fe-Ti minerals (Figure S2, supplementary  
303 material) and a detailed TEM observation of the latter's alteration sites confirms the total  
304 disappearance of uraninite nanograins and the absence of crystallization of secondary  
305 minerals at any scale of observation (Figure 2).

306 A bulk characterization of the samples in terms of U-concentration and Ra/U activity ratio  
307 was first performed. A U-concentration of 383 ppm and a Ra/U activity ratio of 0.7 indicating  
308 the radioactive equilibrium of the  $^{238}\text{U}$  series were measured in the bulk sample F ( $^{226}\text{Ra}$   
309 activity is 3.34 Bq/g). A very low U-concentration (6 ppm) and a very high Ra/U activity ratio  
310 (29) were measured in bulk sample L, indicating a strong radioactive disequilibrium of the  
311  $^{238}\text{U}$  series after uranium leaching ( $^{226}\text{Ra}$  activity is 2.18 Bq/g). The persistence of radio-  
312 elements of the  $^{238}\text{U}$  decay chain in the leached mineralized sands is confirmed by the field  
313 gamma counter analysis which indicates that despite almost complete leaching of the uranium  
314 (6 ppm in sample L vs 383 ppm in sample F), the radioactivity remains high in sample L after  
315 the leaching test (100 cps for L sample against 133 cps for F sample, respectively).

316 Digital alpha autoradiographs acquired for both samples display a similar heterogeneous  
317 spatial distribution of alpha activity, presenting scattered hotspots (Figure 3). However, larger  
318 hotspots were observed in the F sample. For the L sample, considering the very low residual  
319 uranium content (6 ppm) and the total dissolution of uraninite nanograins after acidic  
320 leaching, finding hotspots in the images is an unexpected result which indicates the  
321 persistence of a significant alpha activity of alpha-emitting radionuclide(s) other than  
322 uranium.

323 From the superimposition of the mineralogical maps obtained by QEMSCAN onto the alpha  
324 map of the same area obtained by DA (Figure S3, supplementary material), we see that the  
325 hotspots identified in both samples are mostly located in the aggregates of Fe-Ti minerals as  
326 described above.

327 Such observations have already been made in the same geological context (namely the South  
328 Tortkuduk roll-front deposit in Kazakhstan) (Boulesteix et al., 2019). Chemical maps of Fe-Ti  
329 minerals of the L sample obtained from microprobe analysis (WDS X-ray spectrometry)  
330 confirm the almost total depletion of uranium after acidic leaching (Figure S4, supplementary  
331 material). The uranium content never exceeds 0.2 wt% in the leached Fe-Ti minerals of  
332 sample L while it commonly exceeds 30 wt% in unleached Fe-Ti minerals. The only  
333 significant traces of uranium persisting locally within the leached aggregates of Fe-Ti  
334 minerals (0.2 wt%) are potentially related to minute grains of zircon. For both samples the  
335 presence of light chemical elements such as Al, Si, Na and Mg is related to smectite minerals  
336 which do not seem particularly well dissolved after the acidic leaching process (Robin et al.,  
337 2016; Robin et al., 2020).

### 338 339 3.2 Alpha spectrometry

340 Alpha spectrometry analyses were also performed to confirm the equilibrium state of the  $^{238}\text{U}$   
341 decay chain in both samples. Because alpha emission occurs in the thickness of the samples,  
342 alpha spectra are “step-like”. Table 1 shows the calculated contribution of each radionuclide  
343 in the alpha simulated spectra using AASI (Advanced Alpha Spectrometry SIMulation)  
344 software (Siiskonen and Pöllänen, 2005).

345 The spectrum of the F sample shows the presence of alpha emitters of the whole  $^{238}\text{U}$  decay  
346 chain (Figure 4). All emitters present the same contribution in the simulation, indicating  
347 secular equilibrium for this sample ( $\text{Ra}/\text{U} \sim 1$ ). The L sample shows the absence of  $^{238}\text{U}$  and

348  $^{234}\text{U}$  energy peaks, indicating global disequilibrium of the decay chain. Moreover, the AASI  
349 simulation shows the same activity contribution for the remaining daughter elements,  
350 indicating local equilibrium in the decay chain from  $^{230}\text{Th}$  to  $^{210}\text{Po}$ . The low activity of the L  
351 sample makes the spectrum quite noisy. Accurate determination of Ra/U ratio is not possible  
352 here because the U steps are below the detection limit.

353

### 354 3.3 Bulk alpha activity from alpha autoradiography

355 Previous work shows that alpha maps acquired by BeaQuant™ device are quantitative  
356 (Sardini et al., 2016). The alpha activity of the leached sample ( $2.3 \times 10^{-4}$  cps/mm<sup>2</sup>) is around  
357 four times lower than in the fresh sample ( $9.3 \times 10^{-4}$  cps/mm<sup>2</sup>). For both samples a theoretical  
358 activity assuming secular equilibrium was calculated based on their bulk U content (see  
359 section 3.1). The theoretical activities of the F and L samples are  $7 \times 10^{-4}$  cps/mm<sup>2</sup> and  $1.3 \times 10^{-5}$   
360 cps/mm<sup>2</sup>, respectively. The ratio  $R = \text{theoretical alpha activity} / \text{measured alpha activity}$  is  
361 0.77 and 0.055 for the F and L samples, respectively. These ratios indicate a secular  
362 equilibrium for the fresh sample ( $R \sim 1$ ), and a strong disequilibrium, with a lack of U ( $R \ll 1$ )  
363 for the leached sample. Such a calculation enables an approximation of the bulk equilibrium  
364 state of both samples without using spectrometry. When alpha spectrometry and BeaQuant™  
365 are combined, estimations of  $^{226}\text{Ra}$  activities give 8.6 and 2.8 Bq/g in samples F and L  
366 respectively. These two activities are close to the ones estimated by bulk methods (see section  
367 3.1), but the  $^{226}\text{Ra}$  activity of the F sample measured in the studied thin section is larger.

368

### 369 3.4 Analysis of hotspot activity

370 The alpha map observation enables us to identify and spatialize the alpha activity (Figure 3).  
371 Total activities are normalized to the related window area. For the F and L samples, 131 and  
372 111 spots were analyzed, and the area of the spots was measured to be 1.2% and 0.8% of the

373 total area of the ROIs, respectively. So the spot areas are quite low compared to the total ROI  
374 area.

375 On the F sample, the alpha activity emitted by the hotspots is  $1.81 \times 10^{-2}$  cps/mm<sup>2</sup> (total spot  
376 activity divided by total spot area). On the L sample, the total activity emitted from the  
377 hotspots is  $1.23 \times 10^{-2}$  cps/mm<sup>2</sup>. The hotspot activity is quite comparable before and after  
378 leaching. We emphasize that this hotspot activity is high compared to the bulk, as it  
379 corresponds to 25% and 28% of the whole sample's activity, respectively for the F and L  
380 samples. These contributions are calculated taking into account the total area of the hotspots.  
381 The average activity emitted by a hotspot (total spot activity [cps] divided by spot number) is  
382  $1.17 \times 10^{-3}$  cps for the F sample, and  $0.49 \times 10^{-3}$  cps for the L sample. These activities are  
383 determined from all hotspots, regardless of spot size.

384 After segmentation of the hotspots, it was possible to extract the size (mm<sup>2</sup>) and the activity  
385 (cps) of each spot, so as to perform an individual analysis of each hotspot. Figure 5 is a plot  
386 diagram where each spot is shown using its own size and activity, one point representing one  
387 spot. The expected behaviour was that the larger the spot, the higher its activity. Such an  
388 expectation was verified (Figure 5). However, several important additional observations can be  
389 made: (1) for a given spot size, there is no difference of activity between both samples, and (2)  
390 the F sample contains larger spots than the L sample, seven spots of the F sample having an  
391 activity higher than  $4 \times 10^{-3}$  cps.

392 Moreover, there is a good correlation between the size and the activity of the spot in both  
393 samples. On a log-log scale, a linear trend between spot activity and spot size is observed for  
394 both samples. If the big spots of the F sample are excluded, the adjustment of the point cloud  
395 gives a similar result for both samples:  $A = A_0 \times \text{size}^m$ . Such a linear behaviour indicates that  
396 spot activity and spot size are linked by a power law. The  $A_0$  term represents the activity for a  
397 grain size = 1 mm<sup>2</sup> ( $A_0$  is nearly 0.03 cps here for both samples).  $m$  is the power factor of the



398 adjustment law. The obtained power factors are very similar for both samples ( $m \sim 1.3$ ). This  
399 relationship suggests a kind of “fractal behaviour” of the alpha activity according to the  
400 hotspot size. Determination of the Fe-Ti oxide masses linked to each spot would certainly  
401 have enabled a better understanding of the relationship. However, the fractal behaviour  
402 suggests an effect of fractal geometry of the grains. This will be investigated in further  
403 studies.

### 404 405 3.5 Implication for the mobility of $^{238}\text{U}$ daughters elements

406 The use of the ISR method is increasing in the mining industry, especially for U extraction.  
407 This is mainly due to its capability to drastically reduce production costs and its low impact  
408 on the surface environment compared to conventional mining methods (Seredkin et al., 2016).  
409 Nevertheless, important questions persist about the global/underground environmental impact  
410 of this technique. The main goal of this work was to develop a new quantitative approach  
411 coupling complementary and multiscale mapping methods to better understand the influence  
412 of the mineral framework on the mobility of radioactive elements.

413 Petrographic observations reveal that the alpha activity of spots which persist after almost  
414 total leaching of uranium from the bulk rock is located in aggregates of altered Fe-Ti minerals  
415 (ilmenite, anatase, rutile, titanite) with a large internal and open porosity (with a pore size  
416 observed by TEM ranging from micrometer to nanometer). STEM-HAADF analysis of  
417 ultrathin sections showed the chemical complexity of these mineral assemblages with quite  
418 varying Fe and Ti contents, and the presence of smectite in the microporous network.

419 DA indicates that leaching has a limited influence on spot activity, because, comparing the F  
420 and L samples: (1) the contribution of spot activity to total activity is similar, and (2) the  
421 activities of spots having the same size are similar. As only two U isotopes were removed,  
422 spots of the leached sample would emit three quarters of the initial spot activity in the fresh

423 sample. We did not observe such a difference in spot activity in the two samples: for a given  
424 spot size, we measured a comparable activity (Figure 4). Such a discrepancy may be due to  
425 the difference of initial U concentrations of spots in the two samples: the fresh sample can be  
426 considered as an initial state of the leached one, but only from a mineralogical point of view.  
427 Finally, the most important fact to remember here is the low variation of individual spot  
428 activity, suggesting that the leaching process of U was homogeneous in the sand but that  
429 daughter elements from  $^{230}\text{Th}$  to  $^{210}\text{Po}$  still persist in the Fe-Ti minerals after leaching. A  
430 similar conclusion can be proposed for the radioactively diffuse area. The activity of the  
431 diffuse area is not attributed to a specific mineralogy, but corresponds to the whole  
432 mineralogy of the sample. It was not possible to link this diffuse activity to the mineralogy,  
433 because this activity is spread across this region, without any “clustering”. Possibly, in the  
434 fresh rock, this activity comes from tiny uraninite grains dispersed in the sand. In the bulk  
435 leached rock, the activity of the diffuse area comes also from  $^{230}\text{Th}$  to  $^{210}\text{Po}$ , but contrary to  
436 hotspots, the mineral phase(s) are not detected. The weak and dispersed activity in this region  
437 prevents us from assigning a mineral phase for these radio-elements. However, the ratio of  
438 spot activity to global activity is similar for both samples (nearly 25%), suggesting no  
439 selectivity of the leaching in hotspots and in the diffuse area. The absolute difference of  
440 activity between the F and L samples could be explained by a variation of the initial U content  
441 on both samples, affecting hotspots and diffuse area activities similarly.

442 The alpha spectrometry results support these conclusions, because the initial secular  
443 equilibrium of the  $^{238}\text{U}$  chain (in sample F) is measured and maintained for  $^{230}\text{Th}$  to  $^{210}\text{Po}$   
444 daughter elements in sample L. Such observations agree with the environmental data survey  
445 for  $^{226}\text{Ra}$  (de Boissezon et al., 2017; Lagneau et al., 2019). It appears that Fe-Ti minerals  
446 constitute an efficient trap for the “undetectable” U daughters. Such an observation seems  
447 consistent considering the reactivity of an altered ilmenite surface such as hydrous ferric

448 oxides, known for their retention capacities of  $^{226}\text{Ra}$  (Ames et al., 1983; Sajih et al., 2014) and  
449 the high cation exchange capacity of the smectites (Robin et al., 2017) located in the  
450 microporous space.

451  
452 4. Conclusion  
453

454 In the ISR context, this study managed to develop a new quantitative multi-scale  
455 approach by combining complementary methods in order to better understand the influence of  
456 mineralogy on the mobility of radioactive elements which are difficult to detect. A digital  
457 autoradiography technique was employed; it is a relatively inexpensive and straightforward  
458 imaging technique that can be easily combined with mineralogical and petrographical  
459 investigations. Our findings suggest a limited migration of the U decay product from the ISR  
460 cell of the Dulaan Uul site, consistent with a natural attenuation process. Potential  
461 mechanisms were identified, explaining why the U-daughter concentrations in leaching water  
462 are low. To evaluate the environmental impact of these results, further studies are however  
463 required, by investigating more statistically the leaching of the sand, by increasing the number  
464 of studied samples, and by following the hydro-chemistry of water near the ISR cells. More  
465 generally, this work provides a new approach for understanding the mobility of the U decay  
466 products which could be applied to U-mining sites worldwide and to leaching lab experiments  
467 where initial conditions are better controlled.

468  
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676 Figure Captions

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678 Figure 1: Bright field TEM of the thin section (Sample F) part showing UO<sub>2</sub> ilmenite and  
679 montmorillonite (a). HRTEM micrograph showing the fine microstructure of the particle, in  
680 inset the corresponding fast Fourier transform showing the ring pattern (b and 3). The particle  
681 diameter is around 100nm. In inset, the corresponding selected area diffraction shows ring  
682 pattern characteristic of a polycrystalline UO<sub>2</sub> particle. The size of the nanocrystals is around  
683 a few ten of nanometers.

684 Figure 2: Bright field TEM of the thin section (Sample L) part showing ilmenite and smectite  
685 (a). HRTEM micrograph showing the fine microstructure of the smectite, in inset the  
686 corresponding fast Fourier transform showing the ring pattern (b and 3). The particle diameter  
687 is around 100nm. The corresponding fast Fourier transform is shown in inset with  $d\{001\} \sim$   
688 10.4 Å.

689 Figure 3: Alpha map of (a) F and (b) L samples. Alpha activity is represented in grey scale.  
690 Black colour corresponds to a null alpha activity. In both samples the alpha activity is  
691 heterogeneous in spatial repartition, with hot spots of activity and areas of diffuse and null  
692 activity.

693 Figure 4: Alpha spectra of F (a) and L (b) samples. Grey line corresponds to the experimental  
694 alpha spectra and the black line is the simulation computed with AASI software

695 Figure 5: Plot diagram of size (X axis) versus activity (Y axis) for every hot spots on fresh (F,  
696 blue) and leached (L, red) samples.

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