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**U- and Th- series disequilibria in separated soil mineral fractions: insight into the
mechanism and timescale of U, Th and Ra redistribution**

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1 **Abstract**

2 In recent decades, U- and Th- series nuclides have been successfully used to determine weathering
3 rates in soils and regoliths. However, the redistribution of the nuclides within secondary minerals
4 and/or organic matter may interfere with the recorded U- and Th-series weathering signals and can
5 result in inaccurate and/or poorly constrained weathering rate determinations. In addition, the
6 migration of radionuclides in the environment represents a major current issue. The objective of this
7 study, therefore, was to evaluate the meaning of bulk soil data for weathering investigations and to
8 assess the processes and timescales of U, Th and Ra redistribution in a forested-soil profile, both at
9 the bulk soil scale level and for separated mineral fractions. This study was carried out at the INRAE-
10 Andra experimental beech-forested site of Montiers (Meuse, France), which was developed on acidic
11 detrital sediments inherited from tropical paleosoils erosion. U- and Th-series activity nuclides were
12 measured in bulk soil samples and in separated Fe nodules and clay-size (<2 µm) fractions.
13 Furthermore, the analyses of atmospheric particles allow discussing the potential influence of
14 atmospheric inputs.

15 While bulk soil disequilibria suggested negligible to moderate mobility of the nuclides, an important
16 transfer between mineral fractions was highlighted; this resulted in contrasting redistributions of U,
17 Th and Ra within soil fractions. Fe-oxide nodules controlled the overall mobility of U on the bulk soil
18 scale, while the fine < 2 µm fraction controlled the mobility of Ra. A capture of ²³⁴U by Fe-oxide
19 nodules (mainly comprised of goethite) was observed within the entire soil profile, most likely
20 occurring for several hundred ky. In the shallow soil layers, a leaching of U from the < 2 µm fraction
21 that was not re-adsorbed onto Fe-oxides occurred. In contrast, Fe-oxides appeared to retain all U
22 mobilized from the < 2 µm fraction in the deep soil layers, resulting in negligible U mobility and an
23 apparent “closed-system” at the bulk soil scale. This transfer, however, seemed to occur over shorter
24 timescale than the one in the shallowest soil layers. No mobility of ²²⁶Ra was observed at the bulk soil
25 scale, despite the large release of this nuclide from Fe-oxides. The measured (²¹⁰Pb/²²⁶Ra) activity
26 ratios suggested that up to 50% of ²²⁶Ra in Fe-oxides is available for desorption. However, the < 2 µm
27 fraction strongly re-adsorbed the released Ra and prevented the loss of this nuclide at the bulk soil
28 scale. Considering the short half-life of ²²⁶Ra, such transfer from Fe-oxides to the < 2 µm fraction
29 occurred over a significantly shorter timescale than U mobilization. In addition, the analysis of the
30 short-lived ²²⁸Ra isotope emphasized the flux involved in the biological cycle and the potential impact
31 of vegetation on the soil radionuclide redistribution over a short timescale.

32 Our results suggest that the fine < 2 μm fractions might be suitable for probing the residence time of
33 clay minerals in soils by the U-series dating method, if the soil profile can be assumed to consist of
34 homogenous inherited clays.

35

36 **Key words:** U-series, Th- series, soil weathering, ferruginous nodule, clay, radionuclide mobility.

37

38

39 1. Introduction

40 Uranium, thorium and radium belong to the Naturally Occurring Radioactive Materials (NORMs).
41 Their behavior in soils is of substantial concern in risk assessment since their mobility or retention
42 may lead to concentration in foodstuffs or waters, which has increased risks for humans (e.g.:
43 Miekeley *et al.*, 1992; Hakam *et al.*, 2001; Isam Salih *et al.*, 2002; Vera Tome *et al.*, 2003;
44 Asaduzzaman *et al.*, 2014). In addition to naturally occurring production from rocks weathering,
45 many industrial activities including milling and mining of uranium ores, production of coal, oil and gas
46 or phosphate industry produce residues containing U, Th and their decay products (IAEA, 2014). In
47 addition to its high mobility in a number of common environmental conditions, the tendency of Ra
48 and its short-lived progeny to accumulate in bones also leads to increased risk concern for this
49 nuclide (IAEA, 2014). The geochemical properties of these elements have been reviewed in detail by
50 Ivanovich and Harmon (1992), Bourdon *et al.* (2003) and Chabaux *et al.* (2008). Briefly, in a
51 supergene environment, Th is generally less soluble than U or Ra. The difference in solubility
52 between U and Th is mainly explained by different oxidation states. Tetravalent U and Th ions have
53 strong ionic potential and form insoluble hydroxyl complexes that tend to adsorb quickly onto
54 surfaces. While tetravalent oxidation state is the only stable state for Th, U is capable of reaching
55 hexavalent oxidation state to form soluble uranyl UO_2^{2+} ions (Langmuir, 1978). The alkaline earth Ra
56 is generally more mobile than U or Th, although it can adsorb onto negatively charged clays, mineral
57 coatings, and/or particulate organic matter (Langmuir and Riese, 1985; Ames *et al.*, 1983c). The
58 interaction of these three nuclides with inorganic ligands (such as carbonate, phosphate and sulfate)
59 or organic matter can significantly modify their mobility (Benes *et al.*, 1982; LaFlamme and Murray,
60 1987; Lin *et al.*, 1996; Langmuir and Herman, 1980). Several approaches have been used to specify
61 the mobility of these nuclides in underground and surface environments, including studies of former
62 mining sites or contaminated areas (Blanco *et al.*, 2002; Allard *et al.*, 2007; Thiry and Van Hees, 2008;
63 Hu *et al.*, 2014), of radionuclides – minerals binding at atomic scale (Allard *et al.* 1999; Bargar *et al.*,
64 2000; Duff *et al.*, 2002), of radionuclides distribution in soil-vegetation pairs from uncontaminated
65 fields (Greenman *et al.*, 1999; Vandenhoven *et al.*, 2009; review in IAEA, 2014), of
66 sorption/desorption characterization in laboratory experiments (e.g.: Ames *et al.*, 1983a,b, c,d; Wang
67 *et al.*, 1993; Rihs *et al.*, 2004; Reinoso-Maset and Ly, 2016) and/or of modeling (Gustafsson *et al.*,
68 2009; Sajih *et al.*, 2014; Robin *et al.*, 2017). The observation of radioactive disequilibria in U- and Th-
69 series in soils may also help to assess radionuclide mobility (Latham and Schwarcz, 1987; Greeman *et*
70 *al.*, 1999; Rezzoug *et al.*, 2009; Rihs *et al.*, 2011; Gontier *et al.*, 2015; Rihs *et al.*, 2016; Pourcelot *et*
71 *al.*, 2017).

72 On the other hand, radioactive disequilibria of U- and Th-series have proved to be useful
73 chronometers of weathering rates for regoliths and soils over various timescales (Chabaux et al.,
74 2003a, 2003b, 2013; Dequincey et al., 1999, 2002; Dosseto et al., 2008, 2012, 2019; Keech et al.,
75 2013; Ma et al., 2010, 2013; Pelt et al., 2008; Rihs et al., 2011, 2020; Suresh et al., 2013, Gontier et
76 al., 2015; Ackerer et al., 2016; Schoonejans et al., 2016). The use of these nuclides as weathering
77 chronometers is based on the radioactive equilibrium reached between the members of the
78 following decay series:

79 ^{238}U (T= 4.47×10^9 y) \rightarrow ^{234}U (T= 2.45×10^5 y) \rightarrow ^{230}Th (T= 7.57×10^4 y) \rightarrow ^{226}Ra (T= 1600y) \rightarrow ...

80 ^{232}Th (T= 1.41×10^{10} y) \rightarrow ^{228}Ra (T= 5.75y) \rightarrow ...

81 (Note that some short-lived daughters were omitted for clarity purpose). The rate of decay of the
82 parent nuclide controls the activity of the whole decay series until the activities of all daughters are
83 equal to that of the parent. The radioactive equilibrium therefore corresponds to the point at which
84 the activity ratios among all members equal 1. During weathering, chemical and physical
85 fractionation occurring between a parent nuclide and its daughter breaks this equilibrium, leading to
86 a "radioactive disequilibrium" state. The duration of weathering processes is deduced from the
87 modeled evolution of the U- and Th-series activity ratios by assuming a continuous gain or loss of
88 nuclides, in addition to the radioactive decay, over time (Dequincey *et al.*, 2002, Dosseto *et al.*,
89 2008). However, concerns may arise regarding this approach in soil profiles because water-rock
90 interaction signatures can be disrupted over short time-scale by biological activity (Rihs *et al.*, 2016)
91 or because the soil is the result of a complex mixture of bedrock-derived-minerals and secondary
92 minerals with possible external inputs that could introduce uncertainties in the model. The
93 mechanisms and, even more importantly, the timescales of the U, Th and Ra redistribution processes
94 between the different soil fractions need to be assessed to improve the accuracy of weathering rate
95 estimations.

96 The objective of this study was to investigate the processes and timescales of U- and Th-series
97 nuclides redistributions - including the short-lived ^{226}Ra and ^{228}Ra - that may occur between mineral
98 fractions of a forested soil and to evaluate the meaning of bulk soil data for determination of
99 weathering rates. U- and Th-series disequilibria were therefore measured in bulk soil samples of a
100 beech-forested profile and in the separated iron oxide nodules and fine < 2 μm fractions, as well as in
101 some related atmospheric dust particles.

102

103 **2. Material and methods**

104 2.1. Site and sampling

105 The study was carried out at the Montiers-sur-Saulx ecosystem research site
106 (<https://www6.nancy.inrae.fr/bef/Moyens-analytiques/Montiers>), located in northeastern France in
107 the Meuse Department (48° 31' 54" N, 5° 16' 08" E) (Fig. 1). This beech-forested experimental site
108 was jointly implemented in 2010 by the ANDRA-OPE and INRAE-BEF teams. The local climate is
109 semicontinental, with mean annual precipitation of 1100 mm and an average temperature of 12.6°C
110 over the last ten years (Calvaruso *et al.*, 2017). The vegetation is dominated by 60-year-old beech
111 trees.

112 The lithology of the site consists of Tithonian limestone overlain by heterogeneous marine
113 Valanginian detrital sediments inherited from lower-Cretaceous weathering episodes of lateritic
114 formations (Marteau *et al.*, 2004). These sediments are mainly composed of quartz, clay minerals
115 and Fe nodules, and are characterized by some cross-stratification (Calvaruso *et al.*, 2017).
116 Pedogenesis of these sediments yields a southwest exposure soil sequence over approximately 73 ha
117 at an elevation ranging from 340 to 386 m above sea level, with an overall mean slope of 4.25%. The
118 soil properties vary along the soil sequence in relation to the thickness of the Valanginian sediment
119 layer, from superficial calcic to deep acidic soils (Rendzic Leptosol, Eutric Cambisol and Dystric
120 Cambisol, FAO, 2014). Three experimental stations were implemented on each soil type. The present
121 study focuses on the Dystric Cambisol near the S1 experimental station, located on the flat top of the
122 hill slope (Fig. 1). This slightly acidic soil is developed to a mean depth of 2 m, with 90% of tree fine
123 roots located in the superficial 0-30 cm layer (Kirchen *et al.*, 2017). A profile was sampled in
124 December 2015. The pit was dug by a compact excavator and samples weighing between 1 and 2 kg
125 were collected within an increment ranging from 5 to 20 cm down to 170 cm depth (Table 1).

126 To estimate the present-day atmospheric input flux, atmospheric particles were sampled using a
127 high-volume sampler at an average flow rate of 335 m³ h⁻¹. This sampler belongs to the OPERA-air
128 network (IRSN), which is dedicated to the routine monitoring of radionuclides at trace levels in
129 France. The flow rate was regulated and thus kept constant during weekly sampling periods
130 regardless of the ambient dust load. The sampler is located in Houdelaincourt (48.5623 N; 5.5055 E),
131 approximately 15 km east of the soil sampling site at nearly the same altitude (395 m above sea
132 level) (Fig. 1.). Air was sampled at 1.8 m above ground level. Air filtration was performed using 4-
133 layer polypropylene fiber filters (JPE 13160, Jonell Inc., USA). These filters exhibit a minimum
134 collection efficiency of approximately 95 % for particles with an aerodynamic diameter of 30 nm, and
135 can thus be considered very efficient for the size spectrum of ambient aerosols. Two samples (AD-1
136 and AD-2) were collected from the 7th to 13th and from the 14th to 20th of March, 2016, respectively.

137

138 2.2. Sample preparation and separation of mineral fractions

139 2.2.1. Bulk soil sample preparation

140 The bulk sampled soil was dried at 40°C for 7 days. In this soil, the coarse > 2 mm fraction (gravels
141 and blocks) represents less than 4 % at depth above 60 cm and approximately 35 % of the total soil
142 fraction (Kirchen, 2017, Turpault et al., 2018). To ensure complete subsequent dissolution, the
143 samples were crushed to less than 50 µm (Bosia et al., 2016). A grinding procedure involving several
144 steps used to progressively crush the samples to a smaller size was developed to ensure the
145 representativeness of the final chemical analyses from 100 mg of sample (Blaes, 2013). The minimum
146 amount of sample to be processed and analyzed to obtain a representative analysis depends on the
147 average grain size of the sample (Gy, 1992). Thus, 1 to 2 kg of total bulk soil samples (including the
148 coarse > 2mm fraction) were first crushed to less than 2mm. Then, 250 g of this first coarse powder
149 were crushed to less than 250 µm using an agate disk mill. Approximately 10 g of this powder were
150 finally crushed to less than 50 µm using an agate ball mill.

151

152 2.2.2 Mineral fractions separation

153 Based on the bulk soil analyses and some previous results from a variety of nearby soils that suggest
154 a strong retention of ²²⁶Ra by fine particles (< 2µm) (Pourcelot *et al.*, 2017), the < 2 µm fractions as
155 well as iron oxide nodules were extracted from the < 250 µm crushed fraction of five selected soil
156 layers.

157 Approximately 100 to 150 g of bulk soil samples milled at < 250 µm were sieved at 50 µm without
158 further grinding. The < 2 µm fraction was then extracted from the sieved < 50 µm fraction, following
159 the procedure published by Rihs et al. (2017) that leads to reduced U-series fractionation during clay
160 extraction, especially during organic matter removal. First, organic matter was removed by
161 calcination at 450°C and then the < 2 µm fraction was separated following the sedimentation Stokes
162 law from 50 g of sample dispersed in 700 ml of Milli-Q water and 1 ml of (NaPO₃)₆ at 110 g/l. In
163 addition, a specific extraction of the < 2 µm fraction, in which organic matter was removed with H₂O₂
164 oxidation (to avoid structural modifications induced by calcination), was performed for mineralogical
165 determination. Fe nodules were extracted from the remaining fraction larger than 50 µm. A Frantz
166 isodynamic magnetic separator was used to separate Fe nodules from the nonmagnetic fraction of
167 the bulk soil. Repeated separations were performed to obtain a purified Fe nodule fraction, which
168 was checked first by binocular microscopy and then by XRD analysis. Non-magnetic fractions
169 comprised more than 98 % quartz and feldspars. No clay minerals were detected in either fraction.

170 Before elemental and isotopic analyses, the Fe-oxides and nonmagnetic fractions were crushed
171 following the procedure described above (section 2.2.1); however the Fe-oxide fraction extracted
172 from the 150 – 170 cm soil sample was not treated in this way, owing to the very low amount
173 retrieved in this case. Consequently, mineralogical analysis was not performed for this sample.

174 Considering the operated separation, the bulk soil hereafter represents a mixture of three different
175 fractions, namely the Fe nodules, the <2 µm fraction and the residue fractions, the last of these
176 contains all other minerals and organic matter.

177

178 2.2.3. Atmospheric dusts

179 The atmospheric dust collected on polypropylene filters was fired in a muffle furnace, along with the
180 filters, at 550 °C (Masson et al., 2015). The calcination protocol was designed to ensure full
181 combustion of the organic matter and minimize the volatilization of trace elements. To this end, the
182 furnace temperature was gradually increased (20°C/hour up to 550°C after a 4h stage at 300°C), and
183 care was taken to ensure good oxygenation during combustion. Samples were weighed before and
184 after calcination so as to calculate mass loss. The contribution of the filter mass was deducted from
185 the mass loss. Analyses of the resulting ashes were performed. Analysis of a clean filter was also
186 performed for chemical blank determination.

187

188 2.3. Mineralogical, elemental and isotopic analyses

189 2.3.1 Mineralogical analyses

190 The mineral composition of powders milled at < 250 µm of the bulk soil samples, the Fe nodule
191 fractions, the residual nonmagnetic fractions as well as the < 2 µm fractions were determined using
192 X-ray diffraction (XRD) spectroscopy (Brücker D5000) with Cu-Kα radiation (40kV/30mA) and 3s
193 counting time per 0.02°/ 2θ interval for the < 2 µm samples or 10s counting time per 0.04°/ 2θ
194 interval for other samples. For oriented powders clay mineral determination, the following diagnostic
195 treatments were achieved before analysis: ethylene glycol, hydrazine solvation overnight and heating
196 at 490°C for 4h.

197

198 2.3.2. pH and major element analyses

199 The pH of the bulk soil samples was measured in H₂O, using 5g of sample in 25 ml of water (914
200 pH/Conductometer, Metrohm). Major elements concentrations were determined in bulk soil samples

201 and separated fractions, i.e. Fe-oxides, non-magnetic fraction and <2 μm fraction, using ≈ 100 mg of
202 powder (<50 μm). Major element concentrations were measured after lithium tetraborate fusion by
203 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The precision and accuracy of
204 the analyses were assessed by the replicate analyses of rock standards (BE-N, WSE, GH and DRN)
205 (Govindaraju, 1994). The resulting analytical uncertainty (2SD) is better than 3%, except for Zr (7 %).

206 Due to the low amount of available sample, the major elements concentrations of the 150 – 170 cm
207 Fe-oxide fraction as well as of atmospheric dusts were analyzed from an aliquot of the acid digestion
208 procedure used for U-series analysis. SiO_2 content was therefore not measured in these samples.

209

210 2.3.3. U- and Th-series and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio analyses

211 Measurements of U, Th and ^{226}Ra concentrations and U, Th and Sr isotopic compositions were
212 performed from an aliquot of ≈ 100 mg of the < 50 μm crushed samples, except for the 150 – 170 cm
213 Fe-oxide fraction, and the two atmospheric dust samples for which only 14 mg (non-crushed), 35 mg
214 and 31 mg (ashes) were available for analyses respectively. The powdered (or ashes) samples were
215 spiked with a ^{233}U - ^{229}Th tracer and a ^{228}Ra tracer purified from ^{232}Th salt. The concentration of the
216 ^{233}U - ^{229}Th tracer was calibrated using the gravimetric standard solutions NIST SRM 3164 and 3159
217 and the ^{228}Ra concentration with the AThO rock standard, using the ^{226}Ra concentration from Peate
218 *et al.* (2001).

219 The sample-spike mixture was then dissolved using a three-step digestion procedure with HNO_3 -HF
220 acids, HClO_4 and HCl - H_3BO_3 acids (Pelt *et al.*, 2008; Chabaux *et al.*, 2013; Pelt *et al.*, 2013). Separation
221 and purification of U and Th fractions were achieved using conventional anion exchange
222 chromatography (Dequincey *et al.*, 2002; Granet *et al.*, 2007). The mixed Sr-Ra fraction was collected
223 during the first step of the U-Th separation procedure. The separation of Sr and Ra was achieved
224 during the first step of the Ra purification procedure, where the Sr fraction was eluted and collected
225 while Ra was retained in the resin. Separated Sr and Ra fractions were then further purified following
226 the classical procedure using SrSpec resin (e.g.,Lahd *et al.*, 2007) for Sr and the protocol developed
227 by Pelt *et al.* (2013) and adapted from previous works by Chabaux *et al.* (1994) and Ghaleb *et al.*
228 (2004) for Ra.

229 U and Th concentrations as well as $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{232}\text{Th}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios were measured
230 with a MC-ICP-MS Thermo-Scientific Neptune. ^{226}Ra concentration was measured by Thermal
231 Ionization Mass Spectrometry (TIMS) using a Thermo-Scientific Triton mass spectrometer. Uranium
232 and thorium concentrations were calculated from the measured $^{235}\text{U}/^{233}\text{U}$ and $^{232}\text{Th}/^{229}\text{Th}$ ratios,
233 respectively. A standard-sample-standard bracketing method was applied to correct raw data for

234 instrumental mass bias using the IRMM-184 standard solution for U measurements and a mixture of
235 IRMM-035 standard solution and ^{229}Th spike for Th measurements (see Pelt et al., 2008 or Jeambrun
236 et al., 2012 for details). The $^{232}\text{Th}/^{230}\text{Th}$ isotopic ratio proposed by Sims et al. (2008) for the IRMM-
237 035 standard was used (87873 ± 738 2SD) rather than the original certified value. The ^{232}Th tailing
238 over the ^{230}Th was corrected by an exponential law fitted on the signals measured in 229.6 and 230.6
239 masses.

240 Accuracy and reproducibility of measured isotopic ratios were controlled by analyzing the HU1
241 uranium and IRMM-036 thorium standard solutions, the BE-N and BCR-2 rock- standards, and the
242 isotopic ratio of the Ra spike measured before each sample series (Rihs et al., 2020). During the
243 period of data acquisition (2016-2017), average ($^{234}\text{U}/^{238}\text{U}$) activity ratios and $^{232}\text{Th}/^{230}\text{Th}$ isotopic
244 ratio measured in the HU1 and IRMM-036 standards were equal to 1.000 ± 0.002 (2SD, N = 10) and
245 $3.26 \pm 0.03 \times 10^5$ (2SD, N = 9) respectively, in agreement with previously published values for HU1
246 (Cheng *et al.*, 2000; Delanghe *et al.*, 2002) and IRMM-036 (Sims et al., 2008; Bosia et al., 2018). The
247 change in the Ra spike isotopic ratio observed over time due to ^{228}Ra decay was found to be
248 consistent with the theoretical decay within 0.7 % (2SD, N=12). The reproducibility and accuracy of
249 the U, Th and ^{226}Ra concentrations were checked by replicating analyses of the BE-N and BCR-2 basalt
250 standard (Govindaraju, 1994; Sims et al., 2008). Overall analytical uncertainties (2SD) are estimated
251 to be 1 % for U and Th, 1.5 % for ^{226}Ra concentrations, 0.5 % for ($^{234}\text{U}/^{238}\text{U}$), 1 % for ($^{230}\text{Th}/^{232}\text{Th}$), 1.5
252 % for ($^{230}\text{Th}/^{234}\text{U}$) and 2 % for ($^{226}\text{Ra}/^{230}\text{Th}$) (Rihs et al., 2020). For few samples holding a really low
253 amount of ^{226}Ra , the internal error of the ($^{228}\text{Ra}/^{226}\text{Ra}$) activity ratio measurement exceeded the usual
254 internal error of rock samples measurements, i.e. < 0.5%. In this case, the uncertainty was estimated
255 by summing internal and external errors (at 2SD level). The average measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the
256 SRM 987 standard was equal to 0.710249 ± 0.000003 (2SD, N= 25) over the study period.

257 The (^{228}Ra) and (^{210}Pb) activities were measured using an Ortec-Ametek gamma spectrometer with a
258 high efficiency well-type germanium detector (Rihs et al., 2011). Approximately 8 g of bulk soil
259 samples and between 1 to 4 g of Fe-oxides and <2 μm fractions were sealed in polyethylene tubes.
260 The (^{228}Ra) activity was determined by means of the ^{228}Ac emission at 338.3 and 911.1 keV and the
261 (^{210}Pb) activity by the ^{210}Pb emission at 46.5 keV. Uncertainties of the measured activities were
262 estimated at the 2SD level from the counting statistics achieved during the analyses of the samples
263 and of the rock standard used for the detector efficiency curve calibration. The counting time ranges
264 from 7 to 21 days to achieve more than 2000 counts for separated fractions or 5000 counts for bulk
265 soils for each photopeak of interest, yielding a counting statistics better than 6 % (2 SD) for (^{228}Ra)
266 activity in bulk soil sample and in most of the separated fractions. Counting statistics for (^{210}Pb)
267 activity was better than 10 % (2 SD) in bulk soil samples, but can rise up to 30 % in separated

268 fractions due to the low amount of available material. Self-absorption of γ -rays inside the sample
 269 matrix was corrected using the model proposed by Appleby *et al.* (1992) for each photopeak. The
 270 measured (^{228}Ra) activities were corrected for decay since the time of collection.

271

272 3. Results

273 3.1. Mineralogy and major element concentrations in bulk soil samples and separated 274 fractions

275 Chemical compositions of the analyzed samples are reported in Table 1. The pH_{water} of the bulk soil
 276 samples remains almost constant with depth, and range from 4.4 to 4.8. The major element
 277 concentrations normalized to Ti are shown in Fig. 2. The nearly constant Zr/Ti ratios throughout the
 278 study soil profile support the assumed immobility of Ti and Ti rather than Zr was used for
 279 normalization because of its lower analytical uncertainty.

280 Mineralogical compositions of bulk soil samples, Fe nodules and the $< 2 \mu\text{m}$ fractions were
 281 determined by powder XRD analysis. Bulk soils mainly comprise quartz, goethite and clay minerals
 282 (kaolinite, vermiculite and illite). Feldspar such as microcline and albite were found in the shallowest
 283 horizons of the soil profile ($< 70 \text{ cm}$) (Fig. A1 in the electronic annex). Fe nodule fractions are
 284 composed of more than 75 % of goethite, with the remaining 25% containing quartz impurities (Fig.
 285 A2 in the electronic annex). This fraction will therefore hereafter be called the Fe-oxide fraction. The
 286 $< 2 \mu\text{m}$ fractions comprise mostly kaolinite, in addition to vermiculite, illite/mica and some
 287 lepidocrocite, in the deepest horizons ($>70 \text{ cm}$). Some traces of quartz and goethite were detected
 288 (Fig. A3 in the electronic annex).

289 The mass proportions of Fe-oxide fractions and $< 2 \mu\text{m}$ fractions in the bulk samples were estimated
 290 by the following set of equations:

$$291 \left\{ \begin{array}{l} [\text{Fe}_2\text{O}_3]_{\text{Bulk}} = X_{\text{Fe-oxides}}[\text{Fe}_2\text{O}_3]_{\text{Fe-oxides}} + X_{<2 \mu\text{m}}[\text{Fe}_2\text{O}_3]_{<2 \mu\text{m}} + (1 - X_{\text{Fe-oxides}} - X_{<2 \mu\text{m}})[\text{Fe}_2\text{O}_3]_{\text{non magn.}} \\ [\text{Al}_2\text{O}_3]_{\text{Bulk}} = X_{\text{Fe-oxides}}[\text{Al}_2\text{O}_3]_{\text{Fe-oxides}} + X_{<2 \mu\text{m}}[\text{Al}_2\text{O}_3]_{<2 \mu\text{m}} + (1 - X_{\text{Fe-oxides}} - X_{<2 \mu\text{m}})[\text{Al}_2\text{O}_3]_{\text{non magn.}} \end{array} \right\} \text{ [Eqs. 1]}$$

292 where $[\text{Fe}_2\text{O}_3]_i$ and $[\text{Al}_2\text{O}_3]_i$ are the measured concentrations in the bulk, the Fe-oxides, the $< 2 \mu\text{m}$
 293 and the nonmagnetic fractions (Table 1) and X_i is the relative mass proportion of the Fe-oxides and
 294 $<2 \mu\text{m}$ fractions. The measured Fe_2O_3 and Al_2O_3 concentrations of the nonmagnetic and Fe-oxides
 295 extracted from the $> 50 \mu\text{m}$ fractions are assumed to be representative of the Fe_2O_3 and Al_2O_3
 296 concentrations in the whole $> 2 \mu\text{m}$ fraction. The resulting estimates are reported in Table 2 and are
 297 consistent with the mass of Fe-oxides retrieved during separation processes (correlation factor $R^2 =$
 298 0.94, Fig A-4 in the electronic annex).

299 Mass losses reached 82 and 92 % during the calcination of AD-1 and AD-2 atmospheric particles,
300 emphasizing the high content of organic matter present in these samples. Concentrations reported in
301 all the tables are nevertheless expressed per g of bulk particles, including organic and mineral
302 matter. Assuming that the missing fraction is related to the SiO₂ content of these particles (which
303 could not be directly measured due to the use of HF acid during the acid digestion procedure), the
304 mass budget allows us to estimate this content (i.e., 100 – sum of all the others including LOI) as
305 between 5 and 8 % relative to bulk particles, which corresponds to 43 to 60 % of the inorganic
306 fraction of the dusts.

307

308 **3.2. ⁸⁷Sr/⁸⁶Sr isotopic ratio**

309 ⁸⁷Sr/⁸⁶Sr isotopic ratios in the bulk soil, separated fraction and atmospheric dust are reported in Table
310 3 and Fig. 3. The ratios show only slight variations within the range 0.70752 – 0.70877 in bulk
311 samples, except in the deepest layer (150-170 cm) where this ratio reaches 0.71366. The ratios are
312 generally slightly lower in the Fe-oxides and < 2 μm fractions than in the corresponding bulk soil.
313 Atmospheric dust show a mean ⁸⁷Sr/⁸⁶Sr value of approximately 0.7102, which is significantly higher
314 than that of bulk soil and separated fractions from depth above 150 cm.

315

316 **3.3. U- and Th-series in bulk soil and separated fractions**

317 *3.3.1. Concentrations of U, Th and Ra in the bulk soil, separated fractions and atmospheric*
318 *particles.*

319 U- and Th- series data of bulk soil samples, extracted fractions and atmospheric dusts are given in
320 Table 3. The U, Th, ²²⁶Ra and ²²⁸Ra concentrations in bulk soil samples show only weak vertical
321 variations. These data are consistent with previously published values for U and Ra on nearby soil
322 profile (Pourcelot *et al.*, 2017), although ²²⁶Ra concentrations are slightly lower in the present study.

323 The U and Th concentrations of the Fe-oxides are higher than those in the bulk soil samples (Table 3).
324 The ²²⁶Ra concentrations in the Fe-oxides are lower than those in the bulk soil samples in the
325 shallowest horizons (< 70 cm) but increase with depth. Conversely, ²²⁶Ra concentrations in the < 2
326 μm fractions are higher than those in bulk soil samples and decrease with depth. U and Th
327 concentrations in the < 2 μm fractions are also higher than those in bulk soil. The ²²⁸Ra
328 concentrations of the Fe-oxides are higher than the bulk soil concentrations in the shallowest
329 horizons (< 70 cm) and are approximately equal to those in the deepest horizons. These

330 concentrations are significantly higher in the < 2 μm fractions than in the bulk soil samples and
331 exhibit weak variations with depth.

332 U, Th and ²²⁶Ra concentrations in the AD-1 and AD-2 atmospheric particles are equal to 0.16 - 0.25 μg
333 per g of bulk particles, 0.35 - 0.53 μg/g and 60 - 84 fg/g, respectively. When expressed per g of
334 inorganic matter, i.e., the refractory mass after calcination instead of bulk masses of particles, these
335 values reach 1.4 - 2 μg/g, 2.9 - 4.4 μg/g and 466 - 750 fg/g, respectively, similar to the concentrations
336 measured in the residual soil fraction (mainly composed of quartz).

337

338 3.3.2. Estimations of U- and Th-series nuclide concentrations in residue fractions

339 The concentrations of U- and Th-series nuclides in the residue fraction, i.e., all the minerals and
340 organic matter that are not included in Fe-oxides or < 2 μm fractions, hereafter named “residue”,
341 were calculated from mass balance, as follows:

$$342 \quad C_{i, \text{residue}} = \frac{C_{i, \text{bulk}} - X_{<2\mu\text{m}} \times C_{i,<2\mu\text{m}} - X_{\text{Fe-oxides}} \times C_{i,\text{Fe-oxides}}}{1 - X_{<2\mu\text{m}} - X_{\text{Fe-oxides}}} \quad [\text{Eq. 2}]$$

343 where X_j represents the mass fraction of the given separated j^{th} fraction calculated from Eq. 1 and $C_{i,j}$
344 is the concentration of element i of the j^{th} separated fraction. Uncertainties were estimated using a
345 Monte Carlo simulation (Anderson, 1976). The results are reported in Table 3. It should be noted that
346 this residual fraction does not rigorously correspond to the previous operationally-defined
347 nonmagnetic fraction that was extracted from the > 50 μm soil grain-size fraction.

348 The estimated U, Th and Ra concentrations of the residual fraction are lower than those of other
349 separated fractions or bulk soil samples (Table 3). The estimated ²²⁸Ra concentrations are close to
350 zero.

351

352 3.3.3. Activity ratios involving long-lived nuclides: (²³⁴U/²³⁸U), (²³⁰Th/²³⁴U) and (²³⁸U/²³²Th)

353 The activity ratios of the bulk soil samples, the separated fractions and the atmospheric particles are
354 reported in Table 3. The (²³⁴U/²³⁸U) activity ratios in the bulk soil samples decrease with depth, from
355 radioactive equilibrium at the surface to 0.954 in the deepest layer, except in two layers (50–70 cm
356 and 110–130 cm), where the (²³⁴U/²³⁸U) ratio remains close to radioactive equilibrium (Fig 4a). The
357 (²³⁴U/²³⁸U) ratio in the <2 μm-fraction also decreases with depth from 0.966 to 0.927 while this ratio
358 varies from 1.136 to 1.089 in Fe-oxides. Atmospheric particles exhibit a (²³⁴U/²³⁸U) ratio slightly
359 higher than 1 (1.012 - 1.040).

360 In the shallowest horizons (< 70 cm) the ($^{230}\text{Th}/^{234}\text{U}$) ratio is higher than 1 for the bulk soil samples
361 and the <2 μm fractions and close to radioactive equilibrium for Fe-oxides (Fig 4b). Below 70 cm, the
362 ($^{230}\text{Th}/^{234}\text{U}$) ratios of the Fe-oxides are lower than 1 while the bulk soil samples exhibit ($^{230}\text{Th}/^{234}\text{U}$)
363 ratios close to radioactive equilibrium. As with the shallowest horizons, the <2 μm fractions exhibit
364 ($^{230}\text{Th}/^{234}\text{U}$) ratios higher than 1. Atmospheric dust is characterized by a ($^{230}\text{Th}/^{234}\text{U}$) ratio equal to
365 0.84-0.85.

366 The bulk soil samples show nearly constant ($^{238}\text{U}/^{232}\text{Th}$) activity ratios except in the deepest 150-170
367 cm layer, where this ratio increases (Fig. 4f). The < 2 μm fractions exhibit ($^{238}\text{U}/^{232}\text{Th}$) activity ratios
368 lower than those of the bulk soil samples through the entire soil profile, hinting at this fraction as a
369 main Th carrier. In contrast, the Fe-oxide fractions show ($^{238}\text{U}/^{232}\text{Th}$) activity ratios lower than that of
370 the bulk soil in the upper part of the profile, similar to that of the bulk soil in the middle part, and
371 higher than that of the bulk soil in the deep 150-170 cm layer.

372

373 *3.3.4 Activity ratios involving short-lived nuclides: ($^{226}\text{Ra}/^{230}\text{Th}$), ($^{228}\text{Ra}/^{232}\text{Th}$) and* 374 *($^{210}\text{Pb}/^{226}\text{Ra}$)*

375 The bulk soil samples show ($^{226}\text{Ra}/^{230}\text{Th}$) activity ratios close to radioactive equilibrium throughout
376 the entire soil profile (Fig. 4c). In contrast, ($^{228}\text{Ra}/^{232}\text{Th}$) activity ratios are lower than 1 (Fig. 4d). The
377 largest disequilibrium is observed in the 50-110 cm layer.

378 The Fe-oxide fractions exhibit both ($^{226}\text{Ra}/^{230}\text{Th}$) and ($^{228}\text{Ra}/^{232}\text{Th}$) ratios lower than 1, within a narrow
379 range of values from 0.65 to 0.76 and from 0.62 to 0.78, respectively. The low Fe-oxides content in
380 the 150-170 cm layer precluded analysis of short-lived nuclides by gamma spectrometry in this
381 fraction. In contrast, the ($^{226}\text{Ra}/^{230}\text{Th}$) and ($^{228}\text{Ra}/^{232}\text{Th}$) ratios are higher than radioactive equilibrium
382 in the <2 μm fractions, and both range from 1.1 to 1.5.

383 The ($^{210}\text{Pb}/^{226}\text{Ra}$) ratios in the shallowest, i.e., the 0-10 cm layer, of the bulk soil samples, in the Fe-
384 oxide and <2 μm fractions are higher than 1 due to atmospheric fallout of ^{210}Pb while this ratio
385 remains close to radioactive equilibrium in the bulk soil samples below (Fig 4e). In contrast, the Fe-
386 oxides exhibit ($^{210}\text{Pb}/^{226}\text{Ra}$) ratios lower than 1. The low amount of available sample yielded large
387 uncertainties for the measurement of the (^{210}Pb) activity in this fraction, but the ($^{210}\text{Pb}/^{226}\text{Ra}$) ratio is
388 nevertheless significantly lower than 1 in the 20 - 30 cm layer, with a value as low as 0.63.

389

390 3.4. Estimation of the deficit or excess of ²³⁴U and Ra isotopes in the separated fractions

391 U- and Th- series activity ratios show significant disequilibria in separated fractions, whereas the
392 ratios for bulk soil samples remain relatively close to radioactive equilibrium. This suggests that some
393 redistribution at the mineral scale between soil mineral fractions could have happened within this
394 soil profile. However, consideration of the activity ratios is inadequate to quantify the extent of such
395 mobility. For instance, a fraction can be characterized by a large radioactive disequilibrium but this
396 can yet be insignificant for bulk scale redistribution if this fraction represents a small mass fraction.
397 To quantitatively estimate such redistribution, the activities of ²³⁴U, ²²⁶Ra and ²²⁸Ra per g of bulk soil
398 held in deficit or excess with respect to the activities of their parents (²³⁸U, ²³⁰Th and ²³²Th
399 respectively) or daughter (²³⁰Th) in each mineral fraction were calculated, via the following equation
400 (hereafter presented for ²²⁶Ra relative to ²³⁰Th):

$$401 \quad \Delta(^{226}\text{Ra})_j \text{ (mBq/g of bulk soil)} = \left[(^{226}\text{Ra})_j - (^{230}\text{Th})_j \right] \times X_j \quad [\text{Eq. 3}]$$

402 where (²²⁶Ra)_j and (²³⁰Th)_j are the activities in the *j*th mineral fraction (mBq/g of *j* fraction) and *X_j*
403 represents the mass fraction of the *j*th mineral fraction (g of *j* fraction/g of bulk soil). Uncertainties
404 were estimated using the classical propagation error law. For comparison, the nuclide deficits or
405 excesses were also calculated for the bulk soil using Eq. 3 with *X_j* = 1. The results are shown in Fig. 5.
406 Negative values correspond to a deficit of nuclides (relative to its parent or daughter), while positive
407 values correspond to an excess.

408 Consistent with the (²³⁴U/²³⁸U) activity ratios close to 1, Δ(²³⁴U) with respect to ²³⁸U in the bulk soil
409 samples is close to zero and ranges from -0.5 to 0.3 mBq/g; one exception occurred in the 150 – 170
410 cm layer, where Δ(²³⁴U) reaches - 1.4 mBq/g. The deficit of ²³⁴U with respect to ²³⁸U in the < 2 μm and
411 the residual fractions ranges from – 0.3 to – 1.3 mBq/g and from – 0.2 to – 1.1 mBq/g, respectively.
412 In contrast, the Fe-oxide fractions above 130 cm exhibit positive Δ(²³⁴U) with respect to ²³⁸U, ranging
413 from +1.1 to +1.4 mBq/g, while in the deepest layer (150-170 cm) the Fe-oxide fraction does not
414 exhibit significant ²³⁴U excess on the bulk scale (Δ(²³⁴U) ≈ 0), despite a (²³⁴U/²³⁸U) ratio higher than 1.

415 The Δ(²³⁴U) with respect to ²³⁰Th in the bulk soil and the <2 μm fractions are analogous, ranging from
416 –1.1 to – 4.2 mBq/g. The ²³⁴U-²³⁰Th disequilibrium recorded in the bulk soil is therefore entirely held
417 by the < 2 μm fractions. Consequently, Δ(²³⁴U) with respect to ²³⁰Th in the Fe-oxides and the residual
418 fractions are, within the uncertainties, equal to zero throughout the entire soil profile.

419 The bulk soil samples exhibit Δ(²²⁶Ra) with respect to ²³⁰Th equal to zero whereas the Δ(²²⁸Ra) with
420 respect to ²³²Th ranges from – 2.1 to – 6.0 mBq/g. The Δ(²²⁶Ra) and the Δ(²²⁸Ra) in the < 2 μm
421 fractions are positive, ranging from +2.9 to +6.0 mBq/g and from +3.9 to +10.6 mBq/g, respectively.

422 The Fe-oxides display negative $\Delta(^{226}\text{Ra})$ and $\Delta(^{228}\text{Ra})$, ranging from -0.1 to -4.7 mBq/g and -10.4 to
 423 -3.3 mBq/g, respectively. Consequently, $\Delta(^{226}\text{Ra})$ and $\Delta(^{228}\text{Ra})$ in the residual fractions range from 0
 424 to -3.0 mBq/g and from -4.0 to -9.3 mBq/g, respectively.

425

426 4. Discussion

427 4.1. Meaning of bulk soil data: inheritance, weathering and redistribution

428 U-series disequilibria induced by water-rock interactions in soils and weathering profiles were
 429 previously used to calculate the time elapsed since the bedrock weathering was initiated (Chabaux et
 430 al., 2003a, 2013; Dequincey et al., 2002; Dosseto et al., 2006, 2008, 2012, 2019; Ma et al., 2010,
 431 2013; Rihs et al., 2011; Suresh et al., 2013; Keech et al., 2013, Gontier et al., 2015; Ackerer et al.,
 432 2016). The model used to describe the evolution of the U-series disequilibria in soils involves a
 433 continuous leaching and gain of nuclides in addition to radioactive decay. This model relies on the
 434 assumption that the successive soil layers represent the evolution through time of the same initial
 435 parent material. In addition it is assumed that the leaching and gain remain constant with time. The
 436 evolution of each nuclide activity (^{238}U , ^{234}U , ^{230}Th and ^{226}Ra) in the soil through time can be therefore
 437 modeled by the differential equations modified from Dequincey *et al.* (2002) and Dosseto *et*
 438 *al.*(2008):

$$439 \frac{d^{238}\text{U}}{dt} = -(\lambda_{238} + k_{238}) \times ^{238}\text{U} + f_{238} \times ^{238}\text{U}_0$$

$$440$$

$$441 \frac{d^n N}{dt} = \lambda_{n-1} \times ^{n-1}N - (\lambda_n + k_n) \times ^nN + f_n \cdot ^nN_0$$

$$442$$

} [Eqs. 4.]

443 where nN stands for the number of ^{234}U , ^{230}Th or ^{226}Ra atoms, nN_0 is the corresponding initial
 444 abundance at $t = 0$ and f_n , k_n and λ_n (y^{-1}) are the gain, leaching and decay constants of the nuclide nN ,
 445 respectively.

446 An unsuccessful attempt to solve Eqs. 4 was performed using the differential equation solver (ode45)
 447 proposed by the Matlab® commercial software with a Monte Carlo random trial of the unknown gain
 448 and leaching constants to try to reproduce bulk soil U-series disequilibria. 10^7 sets of k_n and f_n values
 449 were tested over 1.5 Ma to representatively cover a wide range of possible values. Based on the
 450 previously reported k_{238} values (Dosseto et al., 2008, Rihs et al., 2011; Suresh et al., 2013; Gontier et
 451 al., 2015), random k_{238} , k_{230} and k_{226} values ranging from 10^{-4} to 10^{-8} y^{-1} were tested. The k_{234} values

452 were chosen within the range of 1 to 2 x k_{238} . The input rate of ^{238}U (f_{238}) was taken over the same
453 range of values as k_{238} , while the other f values (f_{234} , f_{230} , f_{226}) were restricted to the range of 0.5 to 2
454 x f_{238} . No solution emerged. This model failed to reproduce the uneven evolution of U-series
455 disequilibria toward the surface. A separate modeling of two independent soil sections, i.e.: below
456 and above 80 cm, was similarly unsuccessful. Such failure can be explained by a variability of the
457 parent material or a variability of the gain and leaching constants through time or through the
458 different soil layers (Keech et al., 2013).

459 The possible heterogeneity of the parent Valanginian detrital sediments that result from successive
460 depositions and cross-stratifications was previously reported (Calvaruso *et al.*, 2017). This
461 heterogeneity can also be investigated throughout the variation of major elements, as well as in the
462 $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio. The major elements and U concentrations normalized to Ti are shown in Fig.
463 2. An enrichment of Na toward the surface is observed. Atmospheric input via wet deposition might
464 be inferred to explain this enrichment, but the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of atmospheric particles rule
465 out enrichment via dust deposition (Fig. 3). Contrastingly, no monotonic evolution with depth could
466 be highlighted for Si, Al or Fe contents in the bulk soil profile but some depleted or enriched horizons
467 seem to arise. For instance, the higher Fe/Ti, Al/Ti and U/Ti ratios in the 110-130 cm layer relative to
468 the overlying horizons could suggest downward transfer of Fe, Al and U leached from the shallowest
469 layers and immobilized in the 110-130 cm layer. However, several evidences argue against such an
470 interpretation and suggest that the observed geochemical variations most likely result from initial
471 mineralogical variations of the parent material. Indeed, the increase of U/Ti (or Al/Ti) ratio in the
472 110-130 cm layer corresponds to a decrease of Ti concentration relative to all the other soil layers.
473 Contrastingly the U concentration in the 110-130 cm layer remains in the range of over and
474 underlying layers. In addition the U-series activity ratios equal to 1 measured in this layer at the bulk
475 soil scale (Fig. 4) imply a closed-system behavior at least relative to these nuclides. These features
476 preclude a significant external U input in the 110-130 cm layer. The high U/Ti ratio observed in this
477 layer is therefore interpreted as inherited from the initial parent sediments. The heterogeneity of the
478 parent material is also revealed by $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio. This ratio is notably higher in the deepest
479 soil layer (150-170 cm) than the mean value in bulk soil (Fig. 3) highlighting a different origin. Above
480 150 cm, the ratio changes within a much narrower range, but is strongly correlated to the bulk soil
481 Fe_2O_3 contents ($R^2 = 0.90$, Fig. 6a). This correlation hints at a mixing between two endmembers. The
482 variable mixing proportions in the soil layers can be explained either by a preferential dissolution of
483 one of the two endmembers, as weathering progresses, or by inherited initial proportion. In the
484 weathering case, a relationship with depth is expected (weathering progresses toward the surface)
485 and other soluble elements such as Na should also display a correlation with Sr isotopic ratio. None

486 of these features are observed, even in the deepest layers exempted from atmospheric deposition
487 (Fig. 6a,b). As for U, the variation in Fe content through the profile is hence most likely explained by a
488 heterogeneous initial Fe-oxide fraction rather than by dissolution and downward transfer processes.
489 Since the highly different soil fractions, i.e.: Fe-oxides, clay minerals and residue, are expected to
490 display variable U, Th or Ra leaching constants, a variable proportion of these fractions in the
491 different soil layers result in variable leaching constants at bulk scale that can explain the failure of
492 the U-series model described above. In the frame of the proposed scenario, the relationship
493 observed between the ($^{234}\text{U}/^{238}\text{U}$) activity ratios and the bulk soil Fe_2O_3 contents (Fig 6c) suggests
494 that bulk U-series signatures are strongly influenced by the mineralogical heterogeneity of the parent
495 material, i.e.: a mixing of variable amounts of inherited Fe-oxides and clay minerals, in addition to
496 weathering processes.

497 To further investigate the potential influence of the different mineral fractions on the U- and Th-
498 series signal, we looked at the bulk soil as a mixture of three different fractions, namely the Fe-
499 oxides, the $< 2 \mu\text{m}$ and the estimated residue fractions, containing all other minerals such as quartz,
500 feldspars (in the shallowest layers) and organic matter. The contribution of each fraction to the U, Th,
501 and Ra budget was assessed using mass fraction (Fig. 7a) and the U, Th, ^{226}Ra and ^{228}Ra
502 concentrations measured in each mineral fraction. The resulting ^{238}U , ^{232}Th and Ra budgets are
503 mainly controlled by Fe-oxides and $< 2 \mu\text{m}$ fractions that hold more than 56% of the nuclides in all
504 soil layers (Table 2 and Fig. 7).

505 A shared distribution of U between the three separate fractions was highlighted (Fig. 7b). In the 110
506 – 130 cm layer the predominant location of U in the Fe-oxide fraction (51 %) is only due to the
507 abundance of Fe-oxides in this layer. The ^{232}Th budget is more clearly dominated by the $< 2 \mu\text{m}$ and
508 Fe-oxide fractions. The residue fractions host the lowest fraction of Th (up to only 25%) relative to
509 the other fractions, and also relative to the other nuclides; i.e., this fraction holds less Th than U or
510 Ra. These results, already highlighted by the low ($^{238}\text{U}/^{232}\text{Th}$) activity ratios observed in the $< 2 \mu\text{m}$
511 and Fe-oxide fractions (Fig. 4f), are consistent with the strong sorption of Th onto iron oxides
512 (Langmuir and Herman, 1980; Porcelli *et al.*, 2001; Bosia *et al.*, 2016) and clay minerals (Syed, 1999).
513 These minerals, however, also usually show a strong affinity for U (Ames *et al.*, 1983a; Ames *et al.*,
514 1983b; Allard *et al.*, 1999; Syed, 1999; Bachmaf and Merkel, 2011). However, in neutral or alkaline
515 waters the formation of uranyl-carbonate complexes can inhibit the sorption of U onto mineral
516 surfaces (Hsi and Langmuir, 1985; Waite *et al.*, 1994; Duff and Amrhein, 1996; Bargar *et al.*, 2000;
517 Payne *et al.*, 2004; Gustafsson *et al.*, 2009), probably explaining the weaker association of U with the
518 $< 2 \mu\text{m}$ fractions and the Fe-oxides, at least in the shallowest horizons of the soil profile.

519 Ra isotopes show a clear affinity for the < 2 μm fraction, with the proportion held in this fraction
520 increasing with depth from 46% to 67% for ^{226}Ra and from 62 to 88% for ^{228}Ra (Fig. 7d,e). The more
521 equilibrated distribution of ^{238}U or ^{232}Th between the soil fractions shows that the Ra association with
522 the < 2 μm fraction is due to a specific redistribution of Ra itself, rather than to parent-nuclide
523 mobility. This confirms the hypothesis that the < 2 μm soil fractions are strongly involved in the
524 retention of Ra, as proposed by Pourcelot *et al.* (2017) from study on nearby soil profiles. Several
525 authors also reported such strong Ra affinity with clay minerals (Wang *et al.*, 1993; Boscov *et al.*,
526 2001; Tachi *et al.*, 2001; Hidaka *et al.*, 2007; Reinoso-Maset and Ly, 2016; Robin *et al.*, 2017, Bosia *et*
527 *al.*, 2018).

528 For most of these soil samples, affinities of the four nuclides with Fe-oxide fractions (mainly
529 composed of goethite) therefore decreased in the order $\text{Th} > \text{U} > \text{Ra}$ whereas affinities with < 2 μm
530 fractions (mainly composed of kaolinite) decreased in the order $\text{Ra} > \text{Th} > \text{U}$.

531

532 **4.2. Uranium isotope redistribution**

533 Bulk soil samples show activity ratios ($^{234}\text{U}/^{238}\text{U}$) < 1 and ($^{230}\text{Th}/^{234}\text{U}$) as well as ($^{230}\text{Th}/^{238}\text{U}$) > 1 (Fig.
534 4a,b), which might be explained by a preferential loss of ^{234}U relative to ^{238}U and of both U isotopes
535 relative to ^{230}Th . The alpha recoil process and differential leaching of nuclides are classically invoked
536 to explain such ^{234}U - ^{238}U - ^{230}Th fractionation during chemical weathering (Bourdon *et al.*, 2003; Maher
537 *et al.*, 2006; Chabaux *et al.*, 2008; Neymark, 2011; DePaolo *et al.*, 2012). Alternatively, the excess of
538 ^{230}Th relative to ^{234}U and ^{238}U could also be explained by an external input of ^{230}Th , such as that from
539 atmospheric deposits. However, the analyzed atmospheric particles show activity ratios ($^{234}\text{U}/^{238}\text{U}$) >
540 1 (1.012 – 1.040) and ($^{230}\text{Th}/^{234}\text{U}$) < 1 (0.84 – 0.85, Table 2), consistent with previously reported ratios
541 of ($^{234}\text{U}/^{238}\text{U}$) > 1 and ($^{230}\text{Th}/^{234}\text{U}$) < 1 for Saharan dusts (Rydell and Prospero, 1972; Pelt *et al.*, 2013)
542 as well as ($^{234}\text{U}/^{238}\text{U}$) > 1 in Monaco dusts (Pham *et al.*, 2017). Consistent with the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope
543 data mentioned above, these values preclude a significant impact of solid atmospheric deposition on
544 the observed ($^{234}\text{U}/^{238}\text{U}$) < 1 and ($^{230}\text{Th}/^{234}\text{U}$) > 1 ratios of bulk soil. The observed ^{238}U - ^{234}U - ^{230}Th
545 disequilibria in bulk soil therefore seem to highlight leaching of both U isotopes from these samples.
546 In contrast, within separated soil fractions, ($^{234}\text{U}/^{238}\text{U}$) activity ratios significantly higher or lower than
547 1 in the Fe-oxides and the < 2 μm fractions, respectively (Fig. 4a), could, at first glance, suggest a
548 simple transfer of ^{234}U from one fraction to another. However, mass balance calculations emphasized
549 the amount of ^{234}U relative to ^{238}U (Fig.5a) or the amount of ^{234}U relative to ^{230}Th (Fig.5b) that was
550 gained or lost by each fraction. These calculations clearly demonstrated that the excess of ^{234}U in Fe-
551 oxides is higher than the deficit in the < 2 μm fraction, implying that Fe-oxides had collected more

552 ^{234}U than the $< 2 \mu\text{m}$ fraction had lost. A more careful examination of U isotope redistribution
 553 between the different soil fractions, including time considerations, must therefore be made.

554

555 4.2.1. Origin and timescale of the ^{234}U input to Fe-oxide fractions

556 The activity ratio ($^{234}\text{U}/^{238}\text{U}$) > 1 observed in Fe-oxides throughout the entire soil profile suggest that
 557 U, or at least ^{234}U , is adsorbed on or coprecipitated with goethite, which is the main constituent in
 558 this fraction. Innocent *et al.* (2019) also reported ($^{234}\text{U}/^{238}\text{U}$) ratios ranging from 1.04 and 1.18 in
 559 some ferruginous nodules in soils from Poitou (France) that had developed over detrital formations
 560 similar to those considered herein. Since the bulk soil samples exhibit ($^{234}\text{U}/^{238}\text{U}$) activity ratios close
 561 to – or slightly lower than - 1, a transfer of ^{234}U from another soil fraction to Fe-oxides, rather than an
 562 external ^{234}U -rich input can be inferred. However, such ^{234}U mobility is inconsistent with the
 563 ($^{230}\text{Th}/^{234}\text{U}$) ratio equal to 1 observed in the Fe-oxide fractions of the shallowest layers ($< 70 \text{ cm}$).
 564 Indeed, a "recent" gain of ^{234}U by Fe-oxide fractions would induce fractionation between ^{230}Th and
 565 ^{234}U , with a subsequent ratio ($^{230}\text{Th}/^{234}\text{U}$) < 1 . A removal of ^{238}U without ^{234}U and ^{230}Th loss could
 566 theoretically induce such ($^{234}\text{U}/^{238}\text{U}$) > 1 and ($^{230}\text{Th}/^{234}\text{U}$) = 1 ratios. A ^{238}U loss alone, however, is
 567 unlikely to happen without mobilization of ^{234}U . Consequently three hypotheses remain to explain
 568 the observed disequilibria in the shallowest layers (above 70 cm):

- 569 i) ^{234}U (and possibly ^{238}U) was incorporated into Fe-oxides a long time ago, and a closed-
 570 system evolution allowed the return to $^{234}\text{U} - ^{230}\text{Th}$ equilibrium while the ^{238}U - ^{234}U
 571 equilibrium has not yet been reached.
- 572 ii) ^{234}U was incorporated continuously into Fe-oxides for a long time and, as in the previous
 573 scenario, the time elapsed allowed return to the $^{234}\text{U} - ^{230}\text{Th}$ equilibrium.
- 574 iii) ^{230}Th was incorporated into Fe-oxides in addition to U isotopes.

575

576 The closed-system evolution considered in the first hypothesis allows to calculate the age of
 577 potential U uptake using the ^{238}U - ^{234}U - ^{230}Th theoretical evolution:

578

$$\begin{aligned}
 579 \quad & (^{238}\text{U})_t = (^{238}\text{U})_0 \times e^{-\lambda_{238} \times t} \\
 580 \quad & (^{234}\text{U})_t = (^{238}\text{U})_t \times [1 - e^{-\lambda_{234} \times t}] + (^{234}\text{U})_0 \times e^{-\lambda_{234} \times t} \\
 581 \quad & (^{230}\text{Th})_t = (^{238}\text{U})_t * \left[1 + \frac{\lambda_{230}}{\lambda_{234} - \lambda_{230}} e^{-\lambda_{234} \times t} + \frac{\lambda_{234}}{\lambda_{230} - \lambda_{234}} e^{-\lambda_{230} \times t} \right] + (^{234}\text{U})_0 \times \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \times
 \end{aligned}
 \quad \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} \begin{array}{l} \text{[Eqs. 5.]} \\ \\ 20 \end{array}$$

582
$$\left[e^{-\lambda_{234} \times t} - e^{-\lambda_{230} \times t} \right] + \left({}^{230}\text{Th} \right)_0 \times e^{-\lambda_{230} \times t}$$

583

584 where $({}^n\text{N})_t$, $({}^n\text{N})_0$ and λ_n represent for the present-day activity, the initial activity at the time of
 585 uptake and the decay constant of the nuclide ${}^n\text{N}$, respectively.

586 The minimum age is given by assuming no ${}^{238}\text{U}$ uptake, i.e., $({}^{230}\text{Th}/{}^{238}\text{U})_0 = 1$. In this case, Eqs. 5 allows
 587 to calculate that the mean measured $({}^{234}\text{U}/{}^{238}\text{U})$ and $({}^{230}\text{Th}/{}^{234}\text{U})$ activity ratios (1.14 and 1
 588 respectively, mean values from the three shallowest samples) imply an evolution during 190 ky from
 589 an initial $({}^{234}\text{U}/{}^{238}\text{U})_0 = 1.24$. In the case of ${}^{238}\text{U}$ uptake, the time required to return to radioactive
 590 equilibrium increases. Similar long term behavior of U-Th closed-systems in terrestrial ferruginous
 591 nodules was previously assessed (Short et al., 1989; Allard et al., 2018). However, the samples in
 592 these previous studies also exhibited quantitative retention of helium (Allard et al., 2018), while our
 593 samples show evidence of ${}^{222}\text{Rn}$ escape (see section 4.3. below). In addition, the obvious ${}^{230}\text{Th}$ - ${}^{226}\text{Ra}$
 594 and ${}^{232}\text{Th}$ - ${}^{228}\text{Ra}$ open-system characteristics of our samples, i.e., $(\text{Ra}/\text{Th}) \neq 1$, argue strongly against a
 595 possible closed-system evolution over 190 or more ky.

596 The two following hypotheses, ii) and iii), imply an open-system evolution in which radioactive decay,
 597 as well as a continuous gain of nuclides control the evolution in the abundance of each nuclide (${}^{238}\text{U}$,
 598 ${}^{234}\text{U}$, ${}^{230}\text{Th}$) over time. Such a system can be described with Eqs. 4 without leaching parameters (k_n
 599 values = 0)

600 Hypothesis ii) ascribes ${}^{238}\text{U}$ - ${}^{234}\text{U}$ - ${}^{230}\text{Th}$ disequilibria in Fe-oxide fractions to a continuous input of ${}^{234}\text{U}$.
 601 Without any *a priori* assumption about a possible input of ${}^{238}\text{U}$, the set of model equations 4 was
 602 solved using the differential equation solver (ode45) contained in the MATLAB® commercial
 603 software. We tested 5×10^5 sets of random f_{234} and f_{238} values ranging from 10^{-8} to 10^{-5} y^{-1} and solved
 604 the differential equations over 1.5 Ma. The model assumed no input of ${}^{230}\text{Th}$ ($f_{230} = 0$), and
 605 radioactive equilibrium was assumed for initial $({}^{234}\text{U}/{}^{238}\text{U})$ and $({}^{230}\text{Th}/{}^{234}\text{U})$ activity ratios. The
 606 required range of the ${}^{234}\text{U}$ input constant and the minimum time required to allow the $({}^{234}\text{U}/{}^{238}\text{U})$
 607 ratio to reach 1.14 (mean value above 70 cm) and the $({}^{230}\text{Th}/{}^{234}\text{U})$ ratio to return to equilibrium are
 608 $f_{234} = 4 - 5 \times 10^{-7} \text{ y}^{-1}$ and 700 ky (Fig 8, black curve). This f_{234} range corresponds to minimum f values
 609 because no ${}^{230}\text{Th}$ input was considered. If a small input of ${}^{230}\text{Th}$ is assumed, f_{234} would increase and
 610 the time required to reach the measured ratios would decrease simultaneously. For instance only
 611 500 ky would be required if it is assumed that $f_{234} = 5.5 \times 10^{-7} \text{ y}^{-1}$ and $f_{230} = 1.5 \times 10^{-7} \text{ y}^{-1}$ (Fig. 8, red
 612 curve). With the considered conditions (no ${}^{230}\text{Th}$ input), all suitable sets of solutions are characterized

613 by f_{238}/f_{234} ratios below 0.18 (Fig. 9a), meaning that, without ^{230}Th input, the observed activity ratios
614 imply no significant ^{238}U input.

615 Such ^{234}U input without ^{238}U could correspond to a direct α -recoil of ^{234}Th from the surrounding
616 minerals (Kigoshi, 1971). However, to be significant at the grain-size scale, this process implies a large
617 surface area. Surface area was not measured in our samples. However, SEM images of similar
618 nodules from French or Sicilian soils (Latrille *et al.*, 2001; Palumbo *et al.*, 2001) highlighted the large
619 porosities generally observed with this material. In addition, the needle-like morphology of goethite,
620 the main mineral identified in our samples, yielded a specific surface area as large as $100\text{ m}^2/\text{g}$
621 (Hiemstra *et al.*, 1989; Hiemstra and Van Riemsdijk, 1996; Weng *et al.*, 2008). This specific surface
622 area would be sufficient to drive significant α -recoil gain. Similar postdepositional redistribution of U
623 isotopes via α -recoil gain of ^{234}U was previously proposed in corals, marine carbonates and soil
624 calcretes (Henderson *et al.*, 2001; Thompson *et al.*, 2003; Villemant and Feuillet, 2003; Neymark,
625 2011). It should be noted that the mathematical formalism proposed in the studies mentioned above
626 is an approximation and not strictly capable of describing the case of a ^{234}U gain (see Thompson *et al.*,
627 2003 for further details) that is different from the one proposed in the present study. It predicts,
628 however, an evolution of the activity ratios that is identical to the one predicted by our model
629 (evolution labelled Neymark, 2011 in Fig. 8).

630 An alternative to the gain of recoiled ^{234}U over a long time period involves the sorption of U from
631 seepage waters. In this case, gains in both U isotopes are expected. The model tested above,
632 however, demonstrates that the observed activity ratios cannot be reproduced if gains of ^{238}U and
633 ^{234}U occur without ^{230}Th input. A gain of ^{238}U therefore implies an additional input of ^{230}Th
634 (hypothesis iii). The resolution of model equations 4 with $f_{230} \neq 0$ and $f_{234}/f_{238} < 3.5$ (representative of
635 most natural ($^{234}\text{U}/^{238}\text{U}$) activity ratios in surface waters, as reviewed for instance in Chabaux *et al.*,
636 2008), testing 10^5 sets of random f values over the range 10^{-8} - 10^{-5} y^{-1} resulted in an unresolved
637 system, i.e., an infinite number of solutions were found over the entire range of investigated values.
638 This demonstrated, however, that an f_{230}/f_{238} ratio > 0.7 was required for all solutions (Fig. 9b),
639 implying that a similar or even higher input flux of ^{230}Th relative to that of ^{238}U is mandatory. The
640 origin of such a ^{230}Th flux therefore requires explanation. External ^{230}Th input by atmospheric wet
641 deposition is precluded and today atmospheric dusts show, a depletion of ^{230}Th ($(^{230}\text{Th}/^{238}\text{U}) = 0.85$ -
642 0.88 , Table 3). Transfer from one or more other soil fractions would then be required. However, such
643 transfer would necessitate similar or even higher mobilization from the source-fraction of ^{230}Th
644 relative to ^{238}U , and a subsequent similar U and Th uptake by the Fe-oxides in different soil layers
645 down to at least -70 cm . Despite recent reports of enhanced Th mobility in soils resulting from
646 organic complexation (e.g.: Dosseto *et al.*, 2008; Rezzoug *et al.*, 2009; Rihs *et al.*, 2011; Keech *et al.*,

647 2013; Gontier *et al.*, 2015), a similar organic mobilization of ^{230}Th and ^{238}U followed by similar
648 adsorption onto the Fe-oxide nodules in surface (0-5 cm) as well as in deeper (50-70 cm) soil layers
649 seems highly unlikely.

650

651 The various models tested therefore suggest that a continuous and slow uptake of ^{234}U from
652 surrounding fractions produced by α -recoil most likely explains the activity ratios measured in the
653 Fe-oxide fractions. Since α -recoil ejection is significant only from solids with large specific surface
654 areas, the fine soil fraction could therefore be the source of the recoiled ^{234}U . Indeed, the $<2\ \mu\text{m}$
655 fractions showed a deficit of ^{234}U ($(^{234}\text{U}/^{238}\text{U}) < 1$). However, if this fraction was the source of ^{234}U , its
656 ($^{230}\text{Th}/^{234}\text{U}$) activity ratios and those of Fe-oxides would be returned to radioactive equilibrium, owing
657 to the required slow input rate of ^{234}U in Fe-oxides. Without an additional process, the time required
658 to return to ^{230}Th - ^{234}U equilibrium in the sink would induce a return to equilibrium in the source as
659 well. Actually, the $< 2\ \mu\text{m}$ fractions exhibited ($^{230}\text{Th}/^{234}\text{U}$) > 1 . In contrast, and despite the relatively
660 large uncertainties of our estimations, the residue fraction showed a ($^{230}\text{Th}/^{234}\text{U}$) activity ratio at or
661 close to radioactive equilibrium (Table 3), pointing out this fraction as the source of the recoiled ^{234}U .
662 For Fe oxides, this hypothesis implies a large specific surface area of this residue fraction.

663

664 4.2.2. U loss from the $< 2\ \mu\text{m}$ fractions

665 The $< 2\ \mu\text{m}$ fractions exhibit activity ratios ($^{234}\text{U}/^{238}\text{U}$) < 1 , ($^{230}\text{Th}/^{234}\text{U}$) > 1 and ($^{230}\text{Th}/^{238}\text{U}$) > 1 , which
666 imply a depletion of ^{234}U relative to ^{238}U and of both U isotopes relative to ^{230}Th . As mentioned
667 above, a simple transfer from the $< 2\ \mu\text{m}$ fraction to Fe oxide fraction does not seem to occur. In
668 contrast, the $< 2\ \mu\text{m}$ fractions and the bulk soil samples show the same deficit $\Delta(^{234}\text{U})$ with respect to
669 ^{230}Th , while Fe-oxides and residue fractions display $\Delta(^{234}\text{U})$ close to zero (Fig. 5b), meaning that the $<$
670 $2\ \mu\text{m}$ fraction is the fraction that hold the ($^{230}\text{Th}/^{234}\text{U}$) disequilibria recorded in the bulk soil samples.
671 The ^{234}U loss observed in the bulk soil samples seems, therefore to be due to ^{234}U mobilization from
672 the $< 2\ \mu\text{m}$ fractions. Unfortunately, the heterogeneity of the parent material (highlighted by the
673 $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio, section 4.1) precludes the use of the observed ($^{230}\text{Th}/^{234}\text{U}$) activity ratio
674 evolution from depth to the surface as a chronometer.

675

676 4.2.3. U mobility in the deepest layers (below 70 cm)

677 The 110 – 130 cm layer displays the highest Fe-oxide fractions (32 %, Fig. 7a). In contrast to the rest
678 of the profile, the bulk soil in this layer displays both ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{234}\text{U}$) activity ratios at

679 equilibrium, and the Fe-oxide fraction shows a ($^{230}\text{Th}/^{234}\text{U}$) ratio below 1. Such activity ratios in Fe-
680 oxides can be reproduced by the model involving ^{234}U input by α -recoil, as proposed above for the
681 rest of the profile (hypothesis ii in section 4.3.1); however this would imply a shorter duration for the
682 process. In this case a minimum ^{234}U input rate f_{234} equal to $2.5 \times 10^{-6} \text{ y}^{-1}$ over $\sim 40 \text{ ky}$ (this value
683 would decrease if f_{234} increases) is required to successfully describe the observed activity ratios
684 ($(^{234}\text{U}/^{238}\text{U}) = 1.09$ and $(^{230}\text{Th}/^{234}\text{U}) = 0.92$, Fig. 10). An input constant in this range would be almost an
685 order of magnitude higher than those of shallow samples ($f_{234} = 4 - 5 \times 10^{-7} \text{ y}^{-1}$ without ^{230}Th input),
686 which might reflect either a different source of ^{234}U , or a more efficient uptake of ^{234}U by the Fe-
687 oxides. In contrast to the case for the shallowest layer, a joint input of ^{234}U and ^{238}U could explain the
688 activity ratios measured for the deepest layers. Therefore an additional or a different mechanism of
689 U uptake occurred in this layer, which is also highlighted by the relationship between the bulk sample
690 and the $< 2 \mu\text{m}$ fraction. Indeed, the $< 2 \mu\text{m}$ fraction of this layer exhibits ^{234}U depletion while the
691 bulk soil, in contrast to those of the shallowest layers, does not ($(^{234}\text{U}/^{238}\text{U}) = (^{230}\text{Th}/^{234}\text{U}) = 1$). This
692 implies that ^{234}U is mobilized from the $< 2 \mu\text{m}$ fraction without loss of neither ^{234}U nor ^{238}U , at the
693 bulk scale. Consequently, the U lost from the $< 2 \mu\text{m}$ fraction must be trapped by another mineral
694 fraction of this layer, most likely Fe-oxides. The sorption of the U lost from the $< 2 \mu\text{m}$ fraction to Fe-
695 oxides can therefore be inferred for the Fe-rich 110-130 cm layer. Such sorption does not occur in
696 the shallowest layers. A decrease in the amount of CO_3^{2-} anions dissolved in soil solutions at greater
697 depths could explain such U sorption due to the decrease of uranyl-carbonate complex species (Hsi
698 and Langmuir, 1985; Waite *et al.*, 1994; Bargar *et al.*, 2000).

699 The low amount of Fe oxides present in the deepest 150-170 cm soil layer makes it difficult to
700 reliably identify a similar process occurring in this layer. For instance, the small loss of U from the
701 bulk soil, as determined from slight ^{238}U - ^{234}U - ^{230}Th disequilibria, could be due to reduced sorption of
702 dissolved U (as in the shallowest layers) as well as to a deficit of available reactive sites resulting from
703 the low concentrations of Fe-oxides. However, the high concentration of U in the Fe oxides of this
704 layer ($6.2 \mu\text{g/g}$ versus $3.5 \mu\text{g/g}$ in the shallowest layers, Table 3) hints at enhanced U sorption on the
705 Fe-oxide surface, as in the 110-130 cm layer. The low number of available reactive sites would
706 further explain the deficit in retention of U at the bulk soil scale.

707

708 The ^{238}U - ^{234}U - ^{230}Th disequilibria observed in the bulk soil and in separated fractions therefore suggest
709 that in the shallowest layers ($< 70 \text{ cm}$) a transfer of ^{234}U from the residue fraction to Fe-oxides
710 occurred; the $< 2 \mu\text{m}$ fraction released some U that was not retained, yielding a loss of both U
711 isotopes at the bulk soil scale (Fig. 11a). Consequently the ($^{230}\text{Th}/^{234}\text{U}$) disequilibria observed in the

712 bulk soil are almost exclusively due to the weathering intensity of the < 2 μm fraction. The ($^{234}\text{U}/^{238}\text{U}$)
713 activity ratio only slightly below 1 in the bulk soil while this ratio is significantly lower than 1 in the <
714 2 μm fraction reflects the U redistribution within the soil fractions. For instance, mixing a fraction
715 with ($^{234}\text{U}/^{238}\text{U}$) = 0.952 (value in the 20-30 cm < 2 μm fraction) and a fraction with ($^{234}\text{U}/^{238}\text{U}$) = 1
716 (hypothetically representing the mixture Fe-oxides-residue within which a transfer of U occurred
717 without output) yields a mean ($^{234}\text{U}/^{238}\text{U}$) ratio of 0.986 (value measured in the 20-30 cm bulk soil
718 layer) if 29 % of ^{238}U is located in the < 2 μm fraction. This calculation is based on the U isotopic ratio
719 and is entirely independent of the calculations of U distribution reported in Fig. 7.b, but is consistent
720 with the latter (37 ± 4 % of U in the 20-30 cm < 2 μm fraction). In contrast, in the deepest soil layers
721 (below 70 cm), the U released by the < 2 μm fraction seems to have been more efficiently scavenged
722 by surrounding Fe-oxides, yielding a reduced leaching of U at the bulk scale from this part of the soil
723 (Fig. 11b).

724

725 **4.3. Radium mobilization**

726 *4.3.1. Redistribution of ^{226}Ra between Fe-oxides and < 2 μm fractions.*

727 Previous studies carried out to evaluate Ra affinity for soil minerals, such as Fe-Mn-Al oxides, clays,
728 or organic matter, revealed the range of materials able to control Ra mobility in soils (Ames et al.,
729 1983c; Landa and Gray, 1995; Greeman *et al.*, 1999; Krupka *et al.*, 1999; Boscov *et al.*, 2001;
730 Komarneni *et al.*, 2001; Hidaka *et al.*, 2007; Thiry and Van Hees, 2008; Pourcelot *et al.*, 2017). Using
731 selective extractions, Landa *et al.* (1995) showed the strong association of Ra with alkaline-earth
732 sulfates and hydrous ferric oxides. Thiry and Van Hees (2008) demonstrated preferential adsorption
733 of Ra with Fe-Al oxy-hydroxides rather than organic matter. Alternatively, preferential Ra affinity for
734 organic matter and humic materials relative to clay minerals was also reported (Greeman *et al.*,
735 1999). However, several studies also reported the strong affinity of Ra for clay minerals (Ames et al.,
736 1983c; Komarneni *et al.*, 2001; Tachi *et al.*, 2001; Hidaka *et al.*, 2007; Pourcelot *et al.*, 2017; Robin *et*
737 *al.*, 2017; Chen and Kocar, 2018, Bosia et al., 2018). Hence, the mechanisms of transfer involved
738 during the mobilization and redistribution of Ra between the various soil fractions are still heavily
739 debated. In the present study, the observation of ($^{226}\text{Ra}/^{230}\text{Th}$) activity ratios close to radioactive
740 equilibrium in bulk soil samples throughout the entire soil profile strongly suggest that ^{226}Ra was not
741 mobile at the bulk scale. In contrast, the Fe-oxide fractions exhibit ($^{226}\text{Ra}/^{230}\text{Th}$) activity ratios < 1. The
742 scenario used above to explain U data implies no or slow (with respect to the decay rate of ^{226}Ra)
743 gain of ^{230}Th in Fe-oxide fractions. For instance, a ^{230}Th gain constant f_{230} as low as $1.5 \times 10^{-7} \text{ y}^{-1}$ (as
744 used in Fig. 8) would induce a gain rate too low to produce ^{226}Ra - ^{230}Th disequilibrium. Therefore, the
745 ($^{226}\text{Ra}/^{230}\text{Th}$) disequilibria observed in these fractions most likely reflects the occurrence of ^{226}Ra

746 leaching. Consequently, the ^{226}Ra mobilized from Fe-oxides must be sorbed onto another mineral
747 fraction within the bulk soil. Actually, a significant excess of ^{226}Ra with respect to ^{230}Th was observed
748 in the $< 2 \mu\text{m}$ fractions. However, estimation of the amount of ^{226}Ra in deficit or excess with respect
749 to ^{230}Th (Fig 5c) shows that the excess ^{226}Ra in the $< 2 \mu\text{m}$ fractions (2.9 ± 0.5 to 6.0 ± 0.8 mBq per
750 gram of bulk soil) is generally higher than the deficit of ^{226}Ra observed in Fe-oxides (-0.1 ± 0.3 to -4.7
751 ± 0.7 mBq per gram of bulk soil), implying an additional mode for the transfer of ^{226}Ra from the
752 residue fraction (including quartz, feldspar and organic matter) to the $< 2 \mu\text{m}$ fraction (-1.4 ± 1.3 to
753 -3.0 ± 1.2 mBq per g of bulk soil) (Fig. 11c).

754 The significant loss of ^{226}Ra from Fe oxides and residue fractions, which yielded some ($^{226}\text{Ra}/^{230}\text{Th}$)
755 activity ratios as low as 0.7, questions of the ^{226}Ra location within the solids. Short *et al.* (1989)
756 observed similar enhanced leaching of Ra, relative to U and Th, out of soil ferruginous nodules from
757 Australia and explained this mobility by considering the large difference between Fe and Ra ionic
758 radii (0.64 vs 1.43 Å, respectively). However, in addition to this chemical consideration, a significant
759 loss from Fe oxides raises the issue of the location of Ra within the solid, because Ra must either be
760 located close to the solid-water interface or be able to migrate quickly through the solid. The large
761 specific surface area for this fraction required to explain U data (α -recoil process) was already
762 assessed above (section 4.3.1.). In addition, some clues regarding the significant amount of ^{226}Ra
763 located close to the solid-water interface of the Fe oxides are also contained in the $^{210}\text{Pb}/^{226}\text{Ra}$ ratios.
764 Except in the 0-5 cm surface layer, where atmospheric input of ^{210}Pb occurs, this ratio is indeed
765 significantly lower than 1 (0.47 - 0.82) in Fe oxides (Fig. 4e). Considering the very low mobility of ^{210}Pb
766 generally observed in soils (Appleby and Oldfield, 1992, He and Walling, 1996), these ratios below 1
767 are most likely explained by ^{222}Rn escape. As a noble gas, this decay product of ^{226}Ra (prior to ^{210}Pb) is
768 not retained in the solids by chemical bonds. In the case of ^{226}Ra located at or close to the surface of
769 the mineral, the ^{222}Rn produced would therefore escape instead of being trapped within the mineral
770 lattice (Andrews and Wood, 1972; Ball *et al.*, 1991). The escape of ^{222}Rn would result in a deficit of
771 ^{210}Pb production in the mineral. The measured ($^{210}\text{Pb}/^{226}\text{Ra}$) ratios in Fe oxides thus suggest that up
772 to 50% of ^{226}Ra might be located close to the water-solid interface of the Fe oxides, making it
773 available for desorption processes.

774 The dominant association of Ra with the $< 2 \mu\text{m}$ fraction (Fig. 7d,e) is consistent with the strong
775 affinity of Ra with clay minerals previously reported (Wang *et al.*, 1993; Boscov *et al.*, 2001; Tachi *et*
776 *al.*, 2001; Reinoso-Maset *et al.*, 2016). A recent experimental and modeling study of Ra ion-exchange
777 on a swelling clay (i.e., beidellite) showed the significant affinity of Ra for smectite in complex
778 mixtures representative of natural matrixes, which include organic material and Fe(III)-
779 oxy/hydroxides (Robin *et al.*, 2017). The authors suggested that under low-pH conditions ($\text{pH} \leq 6$) the

780 contribution of smectite to the overall adsorption of ^{226}Ra is of the same order of magnitude or even
781 greater than that of organic material. Chen and Kocar (2018) also demonstrated that the level of
782 sorption of Ra on sodium montmorillonite was larger than that on Fe-(hydr)oxides (including
783 goethite, ferrihydrite and pyrite) at all tested pH values (i.e., from 3 to 9). On the other hand, several
784 studies also reported that under certain conditions, Ra mobility was mainly controlled by Fe-Mn-Al
785 oxides (Gonneea *et al.*, 2008; Thiry and Van Hees, 2008; Sajih *et al.*, 2014). However, no evidence for
786 irreversible incorporation within the goethite lattice was found during ferrihydrite-goethite
787 transformation (Sajih *et al.*, 2014). This latter study also showed that calcium competes strongly with
788 Ra for Fe-oxide surface sites and showed the large influence of pH on Ra sorption at the Fe-oxide
789 surface. This result clearly demonstrated almost negligible sorption at pH <5, consistent with the
790 results of Gonneea *et al.* (2008) for Fe-Mn-rich sediments. For comparison, although this was closely
791 dependent on the experimental conditions, the distribution coefficient K_d for Ra sorption on the
792 smectite surface ranged from 300 to 3000 ml.g^{-1} at pH = 5 (depending on the solution ionic strength,
793 Robin *et al.*, 2017) while K_d remained below 10 for Ra sorption on ferrihydrite and goethite (Sajih *et al.*
794 *et al.*, 2014). The pH values of the study soils ranged from 4.3 to 4.8 (Table 1), which probably explains
795 the desorption of Ra from Fe-oxide surfaces and the predominant sorption of ^{226}Ra onto clay
796 minerals (Fig. 11c). Considering the short half-life of Ra isotopes, this transfer from Fe-oxides in the <
797 2 μm fraction must occur over a timescale significantly shorter than that observed for U
798 redistribution. These results illustrate the decoupling mechanism and timescale that might affect U-
799 series nuclide mobility in soils.

800

801 4.3.2. Contrasted mobility of Ra isotopes

802 Unlike the ($^{226}\text{Ra}/^{230}\text{Th}$) activity ratios that are close to radioactive equilibrium in the bulk soil
803 samples, ($^{228}\text{Ra}/^{232}\text{Th}$) ratios are below unity through most of the soil profile (Fig. 4d), which infers a
804 net loss of ^{228}Ra . The short half-life of ^{228}Ra implies a fast and continuously active removal of the
805 nuclide. In separated fractions, the ($^{228}\text{Ra}/^{232}\text{Th}$) ratios show disequilibria similar to the ($^{226}\text{Ra}/^{230}\text{Th}$)
806 ratios, i.e., < 1 in the Fe-oxides and > 1 in the $< 2\ \mu\text{m}$ fractions. In the shallowest layers (above 70
807 cm), the excess of ^{228}Ra in the $< 2\ \mu\text{m}$ fractions (+ 8 to 10 mBq/g) is significantly higher than the
808 deficit of ^{228}Ra in Fe-oxides (– 3.3 to – 4.7 mBq/g; Fig. 5d). In contrast, this excess amount in the < 2
809 μm fractions is close to the deficit in the residue fraction (– 7.9 to – 9.3 mBq/g). From mass balance
810 estimates, the deficit in this latter fraction involves a remaining ^{228}Ra amount close to zero (Fig. 7e).
811 Even if a part of the ^{228}Ra location is due the location of ^{232}Th , i.e., the residue fraction is depleted in
812 ^{232}Th (Fig. 7c), this does not explain the apparently complete removal of ^{228}Ra from the residue
813 fraction. In turn, the deficit of ^{228}Ra in Fe-oxides closely corresponds to the ^{228}Ra net loss at the bulk
814 scale (Fig. 5d). A transfer of ^{228}Ra from the residue fraction to the $< 2\ \mu\text{m}$ fraction is therefore
815 expected, while the ^{228}Ra removed from Fe-oxides seems to be lost (Fig. 11c). In contrast, the ^{226}Ra
816 removed from Fe-oxides was retrieved in the $< 2\ \mu\text{m}$ fraction. In the deepest 110-130 cm layer,
817 however, the deficit of ^{228}Ra in Fe-oxides is balanced by the excess ^{228}Ra in the $< 2\ \mu\text{m}$ fractions. As
818 for U data, different processes seem to occur in shallow (above 70 cm) and deep soils.
819 These results highlight a mobilization of Ra from two soil fractions, i.e., Fe-oxides and residue
820 fractions, with a striking difference in mobility between Ra isotopes; this involves a much more
821 significant removal of ^{228}Ra relative to ^{226}Ra from the residue fraction which cannot solely be
822 explained by the Th depletion, relative to U, in this fraction, and a net loss of ^{228}Ra at the bulk scale
823 when ^{226}Ra is retained.

824 Few prior studies have assessed mobility differences for Ra isotopes. Marley *et al.* (1993) reported a
825 higher mobilization of ^{228}Ra relative to ^{226}Ra in a sandy aquifer after the injection of water with
826 dissolved organic matter. Gonnee *et al.* (2008) reported that the ($^{228}\text{Ra}/^{226}\text{Ra}$) activity ratios of
827 samples desorbed from sediment cores of a subterranean estuary changed with changes in salinity.
828 Rezzoug *et al.* (2009) also observed discrepancy between ($^{226}\text{Ra}/^{230}\text{Th}$) and ($^{228}\text{Ra}/^{232}\text{Th}$) in a soil
829 profile where ^{228}Ra was depleted with respect to ^{232}Th but ^{226}Ra was not depleted with respect to
830 ^{230}Th . The authors suggested an enhanced mobility of ^{230}Th relative to ^{232}Th to explain these apparent
831 differences. The difference of mobility between Th isotopes (i.e., ^{230}Th and ^{232}Th) was previously
832 attributed to distinct locations of the two isotopes in soil or sediment fractions (Dosseto *et al.*, 2008;
833 Ma *et al.*, 2010; Rihs *et al.*, 2011; Keech *et al.*, 2013; Gontier *et al.*, 2015). In the present study, the
834 enhanced removal of ^{228}Ra (relative to ^{226}Ra) from the residue fraction (comprising quartz, feldspar

835 and organic matter) could reflect a more accessible location of ^{232}Th (and then ^{228}Ra) to water,
836 relative to ^{230}Th (and then ^{226}Ra). This assumption is consistent with the low amount of Th still
837 present in the residue fraction (section 4.1 and Fig. 7c). Further identification of such specific ^{232}Th
838 location, however, remains challenging. The most significant ^{228}Ra mobilization from the residue
839 fraction occurred in the shallowest layers (Fig. 5d) where feldspars were specifically identified but no
840 hint of ^{232}Th -enrichment in feldspar arose. More likely, the shallowest layers hold a significant
841 content of organic matter (Kirchen *et al.*, 2017), and the strong complexation of ^{232}Th with such
842 matter (e.g.: Langmuir *et al.* 1980; Oliva *et al.* 1999) could result in the binding of ^{232}Th to this
843 fraction, which would yield highly removable ^{228}Ra . However, although the level was lower, some
844 ^{228}Ra removal from the residue fraction occurred even in the deepest 150-170 cm soil layer, where
845 the amount of organic matter is negligible (Kirchen *et al.*, 2017).

846 Alternatively, the loss of ^{228}Ra at the bulk soil scale could partially reflect a deficit of ^{228}Ra restitution
847 from vegetation rather than a real enhanced ^{228}Ra isotope mobility. Indeed, several studies
848 previously highlighted the importance of the transfer of Ra to plants (review in IAEA, 2014), the
849 possible influence of vegetation on Ra isotope levels in soils (Rihs *et al.*, 2016, Chabaux *et al.*, 2019),
850 and the long residence time of Ra, i.e., several years, deduced from $^{228}\text{Ra}/^{226}\text{Ra}$ in vegetation (Baeza
851 *et al.*, 1999; Lascar, 2019). Because of the short half-life of ^{228}Ra , such a long residence time produces
852 a significant decay of ^{228}Ra during the cycling of Ra through trees, while ^{226}Ra would not be affected.
853 The restitution to the soil of the Ra removed by the vegetation, through degradation of litter, would
854 therefore produce a ^{228}Ra -depleted restitution flux, while ^{226}Ra cycling would remain invisible in a
855 close-to steady-state system, i.e., one without wood export, for instance. To our knowledge, such
856 ^{228}Ra loss from a significantly large soil thickness has never been reported; generally, only thin and
857 localized soil horizons show ^{228}Ra depletion (e.g. Rezzoug *et al.*, 2009; Rihs *et al.*, 2011; Gontier *et al.*,
858 2015; Rihs *et al.*, 2016). These results therefore imply that at the study site, the Ra flux involved in
859 the biological cycle is high enough to impact the soil down to at least a 1 m depth. Further
860 investigations beyond the scope of this study would, however, be necessary to refine the scope of
861 this biogeochemical cycling.

862

863 **4.4. Implications for U-series dating method**

864 Recent publications have investigated the interest of mineral separations and sequential extractions
865 of primary and/or secondary minerals to probe weathering rates using U-series disequilibria (Suresh
866 *et al.*, 2014; Martin *et al.*, 2015; Menozzi, 2016; Menozzi *et al.*, 2016; Rihs *et al.*, 2016, Dosseto *et al.*,
867 2019, Rihs *et al.*, 2020). Redistribution processes among minerals within sediments, soil or regolith

868 profiles were studied because they can strongly interfere with the weathering signature recorded by
869 U- series. Pett-Ridge et al. (2007) demonstrated the control of U budget by Fe-oxides in soils. Martin
870 *et al.* (2015) successfully removed nondetrital matter and clay minerals using mild HF/HCl etching
871 procedures to improve accuracy for the comminution dating method. Menozzi *et al.* (2016)
872 recommended using pretreatment procedures for soils but not for saprolite samples to derive
873 regolith production rates using U-series nuclides. Dosseto et al. (2019) investigated quartz and biotite
874 grain separation in a regolith profile and showed that some adsorption of U and/or Th can occur at
875 the mineral surface. Additional treatment to remove these adsorbed nuclides was needed. Rihs *et al.*
876 (2016) separated primary minerals (biotite, muscovite and perthitic feldspar) and performed
877 selective extractions of Fe and Al oxides from several podzolic soil profiles. These extractions
878 revealed that a significant fraction of U and Th was primarily held by Fe-bearing silicates but that
879 further U and Th mobility was associated with Al dynamic rather than Fe dynamics in these soils.
880 These pedogenic processes led to unsuitable use of U-series data in the shallowest soil layers.
881 However, the soil production rate was accurately deduced for the deepest soil layers that were not
882 affected by such processes.

883 In the present study, our results clearly demonstrate that bulk U- and Th-series disequilibria fail to
884 probe weathering processes and duration in a soil developed on detrital sediment, but instead reflect
885 the mixing of different components with different histories. For instance, the bulk ($^{230}\text{Th}/^{234}\text{U}$)
886 disequilibrium measured in the study soil reflected mixing between a close-to-radioactive
887 equilibrium fraction (Fe-oxides and residue fractions) and a highly out-of-equilibrium fraction (the < 2
888 μm fractions). The bulk ($^{234}\text{U}/^{238}\text{U}$) ratio, which was close to equilibrium throughout the entire soil
889 profile, also led to an erroneous picture of U immobility. The meaning of the bulk data cannot, in this
890 case, be related to weathering processes, and the separation of the different soil fractions becomes
891 mandatory to obtain accurate information on the chemical mobility occurring in this soil. Providing
892 achievement of this separation, our results show that U-series data can record distinct histories of
893 the different soil fractions over different timescales. For instance, the ferruginous nodules acted as a
894 trap for U and immobilized a part of the ^{234}U released from the residue and < 2 μm fractions over
895 several hundred ky. This process, however, relates to ferruginous nodules history that could have
896 started within parent material before the soil formation process began and therefore cannot be
897 related to the rate of soil formation. In contrast, the < 2 μm fractions, composed primarily of
898 kaolinite minerals, showed a loss of U. In soils formed from homogeneous bedrock (unfortunately
899 not the case in the present study), the residence time of clay minerals in soils could then be assessed
900 with long-lived U-series nuclides. Minerals from the residue fractions could also possibly be suitable
901 for U-series dating, if careful identification and proper separation of each mineral were carried out

902 (Bosia et al., 2018, Dosseto et al., 2019, Rihs et al., 2020). In contrast, Ra isotopes seem to probe
903 more recent pedogenic processes, likely impacted by biogeochemical cycling, at least in the shallow
904 soil layers (Rihs et al., 2016, Chabaux et al., 2019).

905

906 **5. Conclusion**

907 U- and Th-series disequilibria were measured in bulk samples and in separated fractions of a forested
908 soil profile to evaluate the meaning of bulk soil data to probe weathering. This study assesses the
909 redistribution of U, Th and Ra nuclides between mineral fractions and thus identifies the mechanisms
910 and the timescales of the mobilization and/or retention of these nuclides. The study soil profile
911 evolved from acidic Valanginian heterogeneous sediments that were mainly composed of goethite,
912 clay minerals, quartz and minor amount of feldspar. Our results precise the respective roles of the
913 fine < 2 μm fraction and Fe-oxides in the U- and Th-series signature of the bulk soil. Hence, the
914 affinity of the nuclides for Fe-oxide decreases in the order Th > U > Ra, while the affinity for the < 2
915 μm fraction decreases as Ra > Th > U.

916 In contrast to their apparent moderate mobility at the bulk scale, the data highlighted an important
917 transfer of U and Ra between mineral fractions. For long-lived U-series nuclides, a transfer of ^{234}U
918 from the residue fraction (including quartz, feldspar and organic matter) to Fe-oxides (goethite) was
919 observed through the entire soil profile. ^{234}U may be mobilized from the residue fraction by α -recoil
920 process over several hundred ky. We also highlighted leaching of U from the < 2 μm fraction through
921 a different mechanism (removal of both isotopes instead of a ^{234}U α -recoil process). The overall
922 process leads the < 2 μm fraction to hold the $(^{230}\text{Th}/^{234}\text{U})$ disequilibria observed in the current bulk
923 soil. In the deepest soil layers, the migration of U is limited by Fe-oxides, leading to an apparent
924 “closed-system” at the bulk soil scale, i.e., $(^{234}\text{U}/^{238}\text{U}) = (^{230}\text{Th}/^{234}\text{U}) = 1$, despite the occurrence of
925 some important transfers between mineral fractions. These transfers, however, could have occurred
926 over shorter timescales than in shallowest soil layers (several tens, instead of hundreds, of ky). ^{226}Ra
927 also shows apparent immobility at the bulk scale. Nevertheless, poor retention of Ra by Fe-oxides
928 was underlined, most likely caused by the low pH of the soil (pH < 5). An important transfer of Ra
929 therefore occurs from Fe-oxides but also from the residue fraction to the < 2 μm fraction, which acts
930 as a barrier to the release of Ra from the profile. Some discrepancies between Ra isotopes appear,
931 since ^{228}Ra seems to be more efficiently removed from the residue fraction than ^{226}Ra and then lost,
932 in contrast the case of ^{226}Ra at the bulk soil scale. In the residue fraction a more accessible location of
933 ^{232}Th (and subsequently ^{228}Ra), relative to ^{230}Th (and subsequently ^{226}Ra) to water interaction as well
934 as a deficit of ^{228}Ra restitution from the vegetation are assumed to explain these differences. These

935 results therefore imply that at the study site, the Ra flux involved in the biological cycle, which was
936 invisible for ^{226}Ra but highlighted by ^{228}Ra , is high enough to impact the soil down to a depth of at
937 least 1 m.

938 This study demonstrates the relevance of U-series data to reveal some processes that would remain
939 imperceptible on elements concentration basis only, but also underlines the limit that may arise to
940 the use U-series disequilibria in soils developed on sediments to probe weathering rates. Conversely,
941 this study contributes to the recent efforts made to increase the accuracy of weathering production
942 rate determinations by applying the U-dating method to separated minerals. The $< 2 \mu\text{m}$ fraction is a
943 promising U-dating soil fraction if evidence of homogenous inherited clay minerals can be found in
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945

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953

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