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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

S. RIHS^{1,*}, E. LASCAR¹, L. POURCELOT², P. CALMON², P.O. REDON³, C. GALY³, M.P. TURPAULT⁴, E.

PELT¹, F. CHABAUX¹

¹ Institut Terre Environnement Strasbourg, EOST, Université de Strasbourg and CNRS, 5 rue Descartes, 67000 Strasbourg, France.

²Institut de Radioprotection et de Sûreté Nucléaire, IRSN Cadarache BP3, 13115 Saint-Paullez-Durance, France

³Agence Nationale pour le Gestion des Déchets Radioactifs, Centre de Meuse/Haute-Marne, Route départementale 960, BP 9, 55290 Bure, France

⁴Laboratoire de Biogéochimie des Ecosystèmes Forestiers, INRAE, Champenoux, France

*corresponding author: rihs@unistra.fr

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-Andra experimental beech-forested site of Montiers (Meuse, France), which was developed on acidic 10 11 detrital sediments inherited from tropical paleosoils erosion. U- and Th-series activity nuclides were measured in bulk soil samples and in separated Fe nodules and clay-size (<2 µm) fractions. 12 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, Th and Ra within soil fractions. Fe-oxide nodules controlled the overall mobility of U on the bulk soil 17 scale, while the fine < 2 μ m fraction controlled the mobility of Ra. A capture of ²³⁴U by Fe-oxide 18 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 μ m 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 μ m 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 scale, despite the large release of this nuclide from Fe-oxides. The measured (²¹⁰Pb/²²⁶Ra) activity 25 ratios suggested that up to 50% of 226 Ra in Fe-oxides is available for desorption. However, the < 2 μ m 26 27 fraction strongly readsorbed the released Ra and prevented the loss of this nuclide at the bulk soil scale. Considering the short half-life of 226 Ra, such transfer from Fe-oxides to the < 2 μ m fraction 28 29 occurred over a significantly shorter timescale than U mobilization. In addition, the analysis of the short-lived ²²⁸Ra isotope emphasized the flux involved in the biological cycle and the potential impact 30 31 of vegetation on the soil radionuclide redistribution over a short timescale.

36	Key words: U-series, Th- series, soil weathering, ferruginous nodule, clay, radionuclide mobility.
35	
34	homogenous inherited clays.
33	clay minerals in soils by the U-series dating method, if the soil profile can be assumed to consist of
32	Our results suggest that the fine < 2 μ m fractions might be suitable for probing the residence time of

39 **1. Introduction**

Uranium, thorium and radium belong to the Naturally Occurring Radioactive Materials (NORMs). 40 41 Their behavior in soils is of substantial concern in risk assessment since their mobility or retention may lead to concentration in foodstuffs or waters, which has increased risks for humans (e.g.: 42 Miekeley et al., 1992; Hakam et al., 2001; Isam Salih et al., 2002; Vera Tome et al., 2003; 43 44 Asaduzzaman et al., 2014). In addition to naturally occurring production from rocks weathering, many industrial activities including milling and mining of uranium ores, production of coal, oil and gas 45 46 or phosphate industry produce residues containing U, Th and their decay products (IAEA, 2014). In addition to its high mobility in a number of common environmental conditions, the tendency of Ra 47 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 between U and Th is mainly explained by different oxidation states. Tetravalent U and Th ions have 52 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 hexavalent oxidation state to form soluble uranyl UO₂²⁺ ions (Langmuir, 1978). The alkaline earth Ra 55 56 is generally more mobile than U or Th, although it can adsorb onto negatively charged clays, mineral coatings, and/or particulate organic matter (Langmuir and Riese, 1985; Ames et al., 1983c). The 57 interaction of these three nuclides with inorganic ligands (such as carbonate, phosphate and sulfate) 58 59 or organic matter can significantly modify their mobility (Benes et al., 1982; LaFlamme and Murray, 1987; Lin et al., 1996; Langmuir and Herman, 1980). Several approaches have been used to specify 60 61 the mobility of these nuclides in underground and surface environments, including studies of former mining sites or contaminated areas (Blanco et al., 2002; Allard et al., 2007; Thiry and Van Hees, 2008; 62 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 fields (Greenman et al., 1999; Vandenhoven et al., 2009; review in IAEA, 2014), of 65 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., 2009; Sajih et al., 2014; Robin et al., 2017). The observation of radioactive disequilibria in U- and Th-68 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).

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

79 ²³⁸U (T= 4.47×10⁹y) →²³⁴U (T= 2.45×10⁵y) →²³⁰Th (T= 7.57×10⁴y) →²²⁶Ra (T= 1600y) →...

80 232 Th (T= 1.41×10¹⁰y) \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 the activity ratios among all members equal 1. During weathering, chemical and physical 84 85 fractionation occurring between a parent nuclide and its daughter beaks 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 ²²⁶Ra and ²²⁸Ra - 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.

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103

2. Material and methods

104 2.1. Site and sampling

at the Montiers-sur-Saulx ecosystem 105 The study was carried out research site 106 (https://www6.nancy.inrae.fr/bef/Moyens-analytiques/Montiers), located in northeastern France in the Meuse Department (48° 31' 54" N, 5° 16' 08" E) (Fig. 1). This beech-forested experimental site 107 108 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.

The lithology of the site consists of Tithonian limestone overlain by heterogeneous marine 112 Valanginian detrital sediments inherited from lower-Cretaceous weathering episodes of lateritic 113 114 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 at an elevation ranging from 340 to 386 m above sea level, with an overall mean slope of 4.25%. The 117 118 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 December 2015. The pit was dug by a compact excavator and samples weighing between 1 and 2 kg 124 125 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 high-volume sampler at an average flow rate of 335 m³ h⁻¹. This sampler belongs to the OPERA-air 127 128 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 level) (Fig. 1.). Air was sampled at 1.8 m above ground level. Air filtration was performed using 4-132 133 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 can thus be considered very efficient for the size spectrum of ambient aerosols. Two samples (AD-1 135 and AD-2) were collected from the 7th to 13th and from the 14th to 20th of March, 2016, respectively. 136

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 μ m using an agate ball mill.

151

152 2.2.2 Mineral fractions separation

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

Approximately 100 to 150 g of bulk soil samples milled at < 250 μ m were sieved at 50 μ m without 157 158 further grinding. The < 2 μ m fraction was then extracted from the sieved < 50 μ m 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 μ m 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 $(NaPO_3)_6$ at 110 g/l. In 163 addition, a specific extraction of the < 2 μ m 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 isodynamic magnetic separator was used to separate Fe nodules from the nonmagnetic fraction of 166 167 the bulk soil. Repeated separations were performed to obtain a purified Fe nodule fraction, which was checked first by binocular microscopy and then by XRD analysis. Non-magnetic fractions 168 169 comprised more than 98 % quartz and feldspars. No clay minerals were detected in either fraction.

Before elemental and isotopic analyses, the Fe-oxides and nonmagnetic fractions were crushed following the procedure described above (section 2.2.1); however the Fe-oxide fraction extracted from the 150 – 170 cm soil sample was not treated in this way, owing to the very low amount 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 μ m 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 performed for chemical blank determination. 186

187

188 2.3. Mineralogical, elemental and isotopic analyses

189 2.3.1 Mineralogical analyses

190 The mineral composition of powders milled at < 250 μ m of the bulk soil samples, the Fe nodule 191 fractions, the residual nonmagnetic fractions as well as the < 2 μ m fractions were determined using 192 X-ray diffraction (XRD) spectroscopy (Brücker D5000) with Cu-K α radiation (40kV/30mA) and 3s 193 counting time per 0.02°/ 2 θ interval for the < 2 μ m samples or 10s counting time per 0.04°/ 2 θ 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

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

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

Due to the low amount of available sample, the major elements concentrations of the 150 – 170 cm
 Fe-oxide fraction as well as of atmospheric dusts were analyzed from an aliquot of the acid digestion
 procedure used for U-series analysis. SiO₂ content was therefore not measured in these samples.

209

210 2.3.3. U- and Th-series and ⁸⁷Sr/⁸⁶Sr isotopic ratio analyses

Measurements of U, Th and ²²⁶Ra concentrations and U, Th and Sr isotopic compositions were 211 212 performed from an aliquot of \approx 100 mg of the < 50 μ m 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 spiked with a ²³³U-²²⁹Th tracer and a ²²⁸Ra tracer purified from ²³²Th salt. The concentration of the 215 ²³³U-²²⁹Th tracer was calibrated using the gravimetric standard solutions NIST SRM 3164 and 3159 216 and the ²²⁸Ra concentration with the AThO rock standard, using the ²²⁶Ra concentration from Peate 217 218 et al. (2001).

219 The sample-spike mixture was then dissolved using a three-step digestion procedure with HNO₃-HF 220 acids, HClO₄ and HCl-H₃BO₃ 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.

U and Th concentrations as well as ²³⁴U/²³⁸U, ²³⁰Th/²³²Th and ⁸⁷Sr/⁸⁶Sr isotopic ratios were measured with a MC-ICP-MS Thermo-Scientific Neptune. ²²⁶Ra concentration was measured by Thermal lonization Mass Spectrometry (TIMS) using a Thermo-Scientific Triton mass spectrometer. Uranium and thorium concentrations were calculated from the measured ²³⁵U/²³³U and ²³²Th/²²⁹Th ratios, respectively. A standard-sample-standard bracketing method was applied to correct raw data for instrumental mass bias using the IRMM-184 standard solution for U measurements and a mixture of
IRMM-035 standard solution and ²²⁹Th spike for Th measurements (see Pelt et al., 2008 or Jeambrun
et al., 2012 for details). The ²³²Th/²³⁰Th isotopic ratio proposed by Sims et al. (2008) for the IRMM035 standard was used (87873 ± 738 2SD) rather than the original certified value. The ²³²Th tailing
over the ²³⁰Th was corrected by an exponential law fitted on the signals measured in 229.6 and 230.6
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 period of data acquisition (2016-2017), average (²³⁴U/²³⁸U) activity ratios and ²³²Th/²³⁰Th isotopic 243 244 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 (Cheng et al., 2000; Delanghe et al., 2002) and IRMM-036 (Sims et al., 2008; Bosia et al., 2018). The 246 change in the Ra spike isotopic ratio observed over time due to ²²⁸Ra decay was found to be 247 248 consistent with the theoretical decay within 0.7 % (2SD, N=12). The reproducibility and accuracy of the U, Th and ²²⁶Ra concentrations were checked by replicating analyses of the BE-N and BCR-2 basalt 249 250 standard (Govindaraju, 1994; Sims et al., 2008). Overall analytical uncertainties (2SD) are estimated to be 1 % for U and Th, 1.5 % for ²²⁶Ra concentrations, 0.5 % for (²³⁴U/²³⁸U), 1 % for (²³⁰Th/²³²Th), 1.5 251 % for (²³⁰Th/²³⁴U) and 2 % for (²²⁶Ra/²³⁰Th) (Rihs et al., 2020). For few samples holding a really low 252 amount of ²²⁶Ra, the internal error of the (²²⁸Ra/²²⁶Ra) activity ratio measurement exceeded the usual 253 254 internal error of rock samples measurements, i.e. < 0.5%. In this case, the uncertainty was estimated by summing internal and external errors (at 2SD level). The average measured ⁸⁷Sr/⁸⁶Sr ratio of the 255 256 SRM 987 standard was equal to 0.710249 ± 0.000003 (2SD, N= 25) over the study period.

257 The (²²⁸Ra) and (²¹⁰Pb) 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 μ m fractions were sealed in polyethylene tubes. The (²²⁸Ra) activity was determined by means of the ²²⁸Ac emission at 338.3 and 911.1 keV and the 260 (²¹⁰Pb) activity by the ²¹⁰Pb emission at 46.5 keV. Uncertainties of the measured activities were 261 262 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 soils for each photopeak of interest, yielding a counting statistics better than 6 % (2 SD) for (²²⁸Ra) 265 266 activity in bulk soil sample and in most of the separated fractions. Counting statistics for (²¹⁰Pb) 267 activity was better than 10 % (2 SD) in bulk soil samples, but can rise up to 30 % in separated fractions due to the low amount of available material. Self-absorption of γ -rays inside the sample matrix was corrected using the model proposed by Appleby *et al.* (1992) for each photopeak. The measured (²²⁸Ra) 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 μ 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 cm) (Fig. A1 in the electronic annex). Fe nodule fractions are composed of more than 75 % of goethite, with the remaining 25% containing quartz impurities (Fig. 284 A2 in the electronic annex). This fraction will therefore hereafter be called the Fe-oxide fraction. The 285 286 < 2 µm fractions comprise mostly kaolinite, in addition to vermiculite, illite/mica and some 287 lepidocrocite, in the deepest horizons (>70 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 μ m fractions in the bulk samples were estimated 290 by the following set of equations:

$$291 \quad \begin{cases} [Fe_2O_3]_{Bulk} = \mathbf{X}_{Fe-oxides} [Fe_2O_3]_{Fe-oxides} + \mathbf{X}_{<2\ \mu m} [Fe_2O_3]_{<2\ \mu m} + (1 - \mathbf{X}_{Fe-oxides} - \mathbf{X}_{<2\ \mu m}) [Fe_2O_3]_{non\ magn.} \\ [Al_2O_3]_{Bulk} = \mathbf{X}_{Fe-oxides} [Al_2O_3]_{Fe-oxides} + \mathbf{X}_{<2\ \mu m} [Al_2O_3]_{<2\ \mu m} + (1 - \mathbf{X}_{Fe-oxides} - \mathbf{X}_{<2\ \mu m}) [Al_2O_3]_{non\ magn.} \end{cases}$$
[Eqs. 1]

where $[Fe_2O_3]_i$ and $[Al_2O_3]_i$ are the measured concentrations in the bulk, the Fe-oxides, the < 2 µm and the nonmagnetic fractions (Table 1) and X_1 is the relative mass proportion of the Fe-oxides and <2 µm fractions. The measured Fe₂O₃ and Al₂O₃ concentrations of the nonmagnetic and Fe-oxides extracted from the > 50 µm fractions are assumed to be representative of the Fe₂O₃ and Al₂O₃ concentrations in the whole > 2 µm fraction. The resulting estimates are reported in Table 2 and are consistent with the mass of Fe-oxides retrieved during separation processes (correlation factor R² = 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 mass budget allows us to estimate this content (i.e., 100 - sum of all the others including LOI) as 304 305 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

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

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

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

The U and Th concentrations of the Fe-oxides are higher than those in the bulk soil samples (Table 3). The ²²⁶Ra concentrations in the Fe-oxides are lower than those in the bulk soil samples in the shallowest horizons (< 70 cm) but increase with depth. Conversely, ²²⁶Ra concentrations in the < 2 μ m fractions are higher than those in bulk soil samples and decrease with depth. U and Th concentrations in the < 2 μ m fractions are also higher than those in bulk soil. The ²²⁸Ra concentrations of the Fe-oxides are higher than the bulk soil concentrations in the shallowest horizons (< 70 cm) and are approximately equal to those in the deepest horizons. These 330 concentrations are significantly higher in the < 2 μ m fractions than in the bulk soil samples and 331 exhibit weak variations with depth.

U, Th and ²²⁶Ra concentrations in the AD-1 and AD-2 atmospheric particles are equal to 0.16 - 0.25 μ g per g of bulk particles, 0.35 - 0.53 μ g/g and 60 - 84 fg/g, respectively. When expressed per g of inorganic matter, i.e., the refractory mass after calcination instead of bulk masses of particles, these values reach 1.4 - 2 μ g/g, 2.9 - 4.4 μ g/g and 466 - 750 fg/g, respectively, similar to the concentrations 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

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

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

343 where X_j represents the mass fraction of the given separated jth 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.

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

351

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

The activity ratios of the bulk soil samples, the separated fractions and the atmospheric particles are reported in Table 3. The ($^{234}U/^{238}U$) activity ratios in the bulk soil samples decrease with depth, from radioactive equilibrium at the surface to 0.954 in the deepest layer, except in two layers (50–70 cm and 110–130 cm), where the ($^{234}U/^{238}U$) ratio remains close to radioactive equilibrium (Fig 4a). The ($^{234}U/^{238}U$) ratio in the <2 µm-fraction also decreases with depth from 0.966 to 0.927 while this ratio varies from 1.136 to 1.089 in Fe-oxides. Atmospheric particles exhibit a ($^{234}U/^{238}U$) ratio slightly higher than 1 (1.012 - 1.040). 360 In the shallowest horizons (< 70 cm) the (230 Th/ 234 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 Th/ 234 U) ratios of the Fe-oxides are lower than 1 while the bulk soil samples exhibit (230 Th/ 234 U) 363 ratios close to radioactive equilibrium. As with the shallowest horizons, the <2 µm fractions exhibit 364 (230 Th/ 234 U) ratios higher than 1. Atmospheric dust is characterized by a (230 Th/ 234 U) ratio equal to 365 0.84-0.85.

The bulk soil samples show nearly constant ($^{238}U/^{232}Th$) activity ratios except in the deepest 150-170 cm layer, where this ratio increases (Fig. 4f). The < 2 µm fractions exhibit ($^{238}U/^{232}Th$) activity ratios lower than those of the bulk soil samples through the entire soil profile, hinting at this fraction as a main Th carrier. In contrast, the Fe-oxide fractions show ($^{238}U/^{232}Th$) activity ratios lower than that of the bulk soil in the upper part of the profile, similar to that of the bulk soil in the middle part, and 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: (²²⁶Ra/²³⁰Th), (²²⁸Ra/²³²Th) and
 374 (²¹⁰Pb/²²⁶Ra)

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

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

The (²¹⁰Pb/²²⁶Ra) ratios in the shallowest, i.e., the 0-10 cm layer, of the bulk soil samples, in the Feoxide and <2 μm fractions are higher than 1 due to atmospheric fallout of ²¹⁰Pb while this ratio remains close to radioactive equilibrium in the bulk soil samples below (Fig 4e). In contrast, the Feoxides exhibit (²¹⁰Pb/²²⁶Ra) ratios lower than 1. The low amount of available sample yielded large uncertainties for the measurement of the (²¹⁰Pb) activity in this fraction, but the (²¹⁰Pb/²²⁶Ra) ratio is 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. To quantitatively estimate such redistribution, the activities of ²³⁴U, ²²⁶Ra and ²²⁸Ra per g of bulk soil 397 held in deficit or excess with respect to the activities of their parents (238U, 230Th and 232Th 398 399 respectively) or daughter (²³⁰Th) in each mineral fraction were calculated, via the following equation (hereafter presented for ²²⁶Ra relative to ²³⁰Th): 400

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

402 where $(^{226}Ra)_j$ and $(^{230}Th)_j$ 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.

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

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

The bulk soil samples exhibit Δ (²²⁶Ra) with respect to ²³⁰Th equal to zero whereas the Δ (²²⁸Ra) with respect to ²³²Th ranges from – 2.1 to – 6.0 mBq/g. The Δ (²²⁶Ra) and the Δ (²²⁸Ra) in the < 2 µm 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 Δ (²²⁶Ra) and Δ (²²⁸Ra), ranging from 0.1 to 4.7 mBq/g and 10.4 to 423 – 3.3 mBq/g, respectively. Consequently, Δ (²²⁶Ra) and Δ (²²⁸Ra) 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

U-series disequilibria induced by water-rock interactions in soils and weathering profiles were 428 429 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, 2013; Rihs et al., 2011; Suresh et al., 2013; Keech et al., 2013, Gontier et al., 2015; Ackerer et al., 431 432 2016). The model used to describe the evolution of the U-series disequilibria in soils involves a continuous leaching and gain of nuclides in addition to radioactive decay. This model relies on the 433 434 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 evolution of each nuclide activity (²³⁸U, ²³⁴U, ²³⁰Th and ²²⁶Ra) in the soil through time can be therefore 436 437 modeled by the differential equations modified from Dequincey et al. (2002) and Dosseto et al.(2008): 438

439
$$\frac{d^{238}U}{dt} = -(\lambda_{238} + k_{238}) \times {}^{238}U + f_{238} \times {}^{238}U_0$$
440
441
$$\frac{d^{n}N}{dt} = \lambda_{n-1} \times {}^{n-1}N - (\lambda_n + k_n) \times {}^{n}N + f_n \cdot {}^{n}N_0$$
442

443 where "N stands for the number of ²³⁴U, ²³⁰Th or ²²⁶Ra atoms, "N₀ 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 "N, 445 respectively.

An unsuccessful attempt to solve Eqs. 4 was performed using the differential equation solver (ode45) proposed by the Matlab[®] commercial software with a Monte Carlo random trial of the unknown gain and leaching constants to try to reproduce bulk soil U-series disequilibria. 10^7 sets of k_n and f_n values were tested over 1.5 Ma to representatively cover a wide range of possible values. Based on the previously reported k₂₃₈ values (Dosseto et al., 2008, Rihs et al., 2011; Suresh et al., 2013; Gontier et al., 2015), random k₂₃₈, k₂₃₀ and k₂₂₆ values ranging from 10^{-4} to 10^{-8} y⁻¹ were tested. The k₂₃₄ 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 depositions and cross-stratifications was previously reported (Calvaruso et al., 2017). This 460 461 heterogeneity can also be investigated throughout the variation of major elements, as well as in the 462 ⁸⁷Sr/⁸⁶Sr 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 be inferred to explain this enrichment, but the ⁸⁷Sr/⁸⁶Sr isotopic ratios of atmospheric particles rule 464 out enrichment via dust deposition (Fig. 3). Contrastingly, no monotonic evolution with depth could 465 466 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 layers and immobilized in the 110-130 cm layer. However, several evidences argue against such an 469 470 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 ⁸⁷Sr/⁸⁶Sr 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 observed between the $(^{234}U/^{238}U)$ activity ratios and the bulk soil Fe₂O₃ contents (Fig 6c) suggests 493 494 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 μ 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, and Ra budget was assessed using mass fraction (Fig. 7a) and the U, Th, ²²⁶Ra and ²²⁸Ra 501 concentrations measured in each mineral fraction. The resulting ²³⁸U, ²³²Th and Ra budgets are 502 503 mainly controlled by Fe-oxides and < 2 μ 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 abundance of Fe-oxides in this layer. The 232 Th budget is more clearly dominated by the < 2 μ m and 507 508 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 Ra. These results, already highlighted by the low ($^{238}U/^{232}Th$) activity ratios observed in the < 2 μ m 510 511 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 surfaces (Hsi and Langmuir, 1985; Waite et al., 1994; Duff and Amrhein, 1996; Bargar et al., 2000; 516 517 Payne et al., 2004; Gustafsson et al., 2009), probably explaining the weaker association of U with the 518 < 2 µm 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 μ m fraction, with the proportion held in this fraction increasing with depth from 46% to 67% for ²²⁶Ra and from 62 to 88% for ²²⁸Ra (Fig. 7d,e). The more 520 equilibrated distribution of ²³⁸U or ²³²Th between the soil fractions shows that the Ra association with 521 the < 2 μ m fraction is due to a specific redistribution of Ra itself, rather than to parent-nuclide 522 523 mobility. This confirms the hypothesis that the < 2 μ m soil fractions are strongly involved in the retention of Ra, as proposed by Pourcelot et al. (2017) from study on nearby soil profiles. Several 524 525 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 Th > U > Ra whereas affinities with < 2 μ m 530 fractions (mainly composed of kaolinite) decreased in the order Ra > Th > U.

531

532 4.2. Uranium isotope redistribution

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

²³⁴U than the < 2 μ m fraction had lost. A more careful examination of U isotope redistribution between the different soil fractions, including time considerations, must therefore be made.

554

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

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

- i) ²³⁴U (and possibly ²³⁸U) was incorporated into Fe-oxides a long time ago, and a closed system evolution allowed the return to ²³⁴U ²³⁰Th equilibrium while the ²³⁸U-²³⁴U
 equilibrium has not yet been reached.
- 572 ii) ²³⁴U was incorporated continuously into Fe-oxides for a long time and, as in the previous
 573 scenario, the time elapsed allowed return to the ²³⁴U ²³⁰Th equilibrium.
- 574 iii) ²³⁰Th 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 ²³⁸U-²³⁴U-²³⁰Th theoretical evolution:

578

579
$$\left(^{238}U\right)_t = \left(^{238}U\right)_0 \times e^{-\lambda_{238} \times t}$$

580
$${\binom{234}{U}}_t = {\binom{238}{U}}_t \times [1 - e^{-\lambda_{234} \times t}] + {\binom{234}{U}}_0 \times e^{-\lambda_{234} \times t}$$

581
$$({}^{230}Th)_t = ({}^{238}U)_t * \left[1 + \frac{\lambda_{230}}{\lambda_{234} - \lambda_{230}}e^{-\lambda_{234} \times t} + \frac{\lambda_{234}}{\lambda_{230} - \lambda_{234}}e^{-\lambda_{230} \times t}\right] + ({}^{234}U)_0 \times \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \times C_{12}$$

20

[Eqs. 5.]

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

583

where $({}^{n}N)_{t}$, $({}^{n}N)_{0}$ and λ_{n} represent for the present-day activity, the initial activity at the time of uptake and the decay constant of the nuclide ${}^{n}N$, respectively.

The minimum age is given by assuming no 238 U uptake, i.e., $(^{230}$ Th/ 238 U)₀ = 1. In this case, Eqs. 5 allows 586 to calculate that the mean measured (²³⁴U/²³⁸U) and (²³⁰Th/²³⁴U) activity ratios (1.14 and 1 587 588 respectively, mean values from the three shallowest samples) imply an evolution during 190 ky from an initial $(^{234}U/^{238}U)_0 = 1.24$. In the case of ^{238}U uptake, the time required to return to radioactive 589 equilibrium increases. Similar long term behavior of U-Th closed-systems in terrestrial ferruginous 590 nodules was previously assessed (Short et al., 1989; Allard et al., 2018). However, the samples in 591 592 these previous studies also exhibited quantitative retention of helium (Allard et al., 2018), while our samples show evidence of ²²²Rn escape (see section 4.3. below). In addition, the obvious ²³⁰Th-²²⁶Ra 593 and 232 Th- 228 Ra open-system characteristics of our samples, i.e., (Ra/Th) \neq 1, argue strongly against a 594 595 possible closed-system evolution over 190 or more ky.

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

Hypothesis ii) ascribes ²³⁸U-²³⁴U-²³⁰Th disequilibria in Fe-oxide fractions to a continuous input of ²³⁴U. 600 Without any *a priori* assumption about a possible input of ²³⁸U, the set of model equations 4 was 601 602 solved using the differential equation solver (ode45) contained in the MATLAB® commercial 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 603 604 the differential equations over 1.5 Ma. The model assumed no input of 230 Th (f₂₃₀ = 0), and radioactive equilibrium was assumed for initial (234U/238U) and (230Th/234U) activity ratios. The 605 required range of the ²³⁴U input constant and the minimum time required to allow the (²³⁴U/²³⁸U) 606 ratio to reach 1.14 (mean value above 70 cm) and the (²³⁰Th/²³⁴U) ratio to return to equilibrium are 607 f_{234} = 4 - 5 × 10⁻⁷ y⁻¹ and 700 ky (Fig 8, black curve). This f_{234} range corresponds to minimum f values 608 because no ²³⁰Th input was considered. If a small input of ²³⁰Th is assumed, f₂₃₄ would increase and 609 the time required to reach the measured ratios would decrease simultaneously. For instance only 610 500 ky would be required if it is assumed that $f_{234} = 5.5 \times 10^{-7}$ y⁻¹ and $f_{230} = 1.5 \times 10^{-7}$ y⁻¹ (Fig. 8, red 611 curve). With the considered conditions (no ²³⁰Th input), all suitable sets of solutions are characterized 612

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

Such 234 U input without 238 U could correspond to a direct α -recoil of 234 Th from the surrounding 615 616 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 m²/g 621 (Hiemstra et al., 1989; Hiemstra and Van Riemsdijk, 1996; Weng et al., 2008). This specific surface area would be sufficient to drive significant α -recoil gain. Similar postdepositional redistribution of U 622 623 isotopes via α -recoil gain of ²³⁴U 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 is an approximation and not strictly capable of describing the case of a ²³⁴U gain (see Thompson et 626 627 al., 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).

An alternative to the gain of recoiled ²³⁴U over a long time period involves the sorption of U from 630 631 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 ²³⁸U and ²³⁴U occur without ²³⁰Th input. A gain of ²³⁸U therefore implies an additional input of ²³⁰Th 633 634 (hypothesis iii). The resolution of model equations 4 with $f_{230} \neq 0$ and $f_{234}/f_{238} < 3.5$ (representative of most natural (²³⁴U/²³⁸U) activity ratios in surface waters, as reviewed for instance in Chabaux et al., 635 636 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. This demonstrated, however, that an f_{230}/f_{238} ratio > 0.7 was required for all solutions (Fig. 9b), 638 639 implying that a similar or even higher input flux of ²³⁰Th relative to that of ²³⁸U is mandatory. The origin of such a ²³⁰Th flux therefore requires explanation. External ²³⁰Th input by atmospheric wet 640 deposition is precluded and today atmospheric dusts show, a depletion of 230 Th ((230 Th/ 238 U) = 0.85-641 642 0.88, Table 3). Transfer from one or more other soil fractions would then be required. However, such transfer would necessitate similar or even higher mobilization from the source-fraction of ²³⁰Th 643 644 relative to ²³⁸U, 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 ²³⁰Th and ²³⁸U 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

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

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664 4.2.2. U loss from the < 2 μ m fractions

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

675

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

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

equilibrium, and the Fe-oxide fraction shows a (²³⁰Th/²³⁴U) ratio below 1. Such activity ratios in Fe-679 oxides can be reproduced by the model involving 234 U input by α -recoil, as proposed above for the 680 rest of the profile (hypothesis ii in section 4.3.1); however this would imply a shorter duration for the 681 process. In this case a minimum 234 U input rate f_{234} equal to 2.5×10^{-6} y⁻¹ over ~ 40 ky (this value 682 would decrease if f₂₃₄ increases) is required to successfully describe the observed activity ratios 683 $((^{234}U/^{238}U) = 1.09 \text{ and } (^{230}Th/^{234}U) = 0.92$, Fig. 10). An input constant in this range would be almost an 684 order of magnitude higher than those of shallow samples ($f_{234} = 4 - 5 \times 10^{-7}$ y⁻¹ without ²³⁰Th input), 685 which might reflect either a different source of ²³⁴U, or a more efficient uptake of ²³⁴U by the Fe-686 oxides. In contrast to the case for the shallowest layer, a joint input of ²³⁴U and ²³⁸U could explain the 687 activity ratios measured for the deepest layers. Therefore an additional or a different mechanism of 688 689 U uptake occurred in this layer, which is also highlighted by the relationship between the bulk sample 690 and the < 2 μ m fraction. Indeed, the < 2 μ m fraction of this layer exhibits ²³⁴U depletion while the bulk soil, in contrast to those of the shallowest layers, does not $((^{234}U/^{238}U) = (^{230}Th/^{234}U) = 1)$. This 691 implies that 234 U is mobilized from the < 2 μ m fraction without loss of neither 234 U nor 238 U, at the 692 693 bulk scale. Consequently, the U lost from the < 2 μ 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 μ m fraction to Feoxides can therefore be inferred for the Fe-rich 110-130 cm layer. Such sorption does not occur in 695 the shallowest layers. A decrease in the amount of CO_3^{2-} anions dissolved in soil solutions at greater 696 697 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 bulk soil, as determined from slight ²³⁸U-²³⁴U-²³⁰Th disequilibria, could be due to reduced sorption of 701 702 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 µg/g versus 3.5 µg/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.

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

bulk soil are almost exclusively due to the weathering intensity of the < 2 μ m fraction. The (²³⁴U/²³⁸U) 712 713 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 with $(^{234}U/^{238}U) = 0.952$ (value in the 20-30 cm < 2 μ m fraction) and a fraction with $(^{234}U/^{238}U) = 1$ 715 (hypothetically representing the mixture Fe-oxides-residue within which a transfer of U occurred 716 without output) yields a mean (²³⁴U/²³⁸U) ratio of 0.986 (value measured in the 20-30 cm bulk soil 717 718 layer) if 29 % of 238 U is located in the < 2 μ m 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 μ m fraction). In contrast, in the deepest soil layers 721 (below 70 cm), the U released by the < 2 μ m 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).

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725 4.3. Radium mobilization

4.3.1. Redistribution of ²²⁶Ra between Fe-oxides and < 2 μ m fractions.

727 Previous studies carried out to evaluate Ra affinity for soil minerals, such as Fe-Mn-Al oxides, clays, or organic matter, revealed the range of materials able to control Ra mobility in soils (Ames et al., 728 729 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., 1983c; Komarneni et al., 2001; Tachi et al., 2001; Hidaka et al., 2007; Pourcelot et al., 2017; Robin et 736 737 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 debated. In the present study, the observation of (²²⁶Ra/²³⁰Th) activity ratios close to radioactive 739 equilibrium in bulk soil samples throughout the entire soil profile strongly suggest that ²²⁶Ra was not 740 mobile at the bulk scale. In contrast, the Fe-oxide fractions exhibit (²²⁶Ra/²³⁰Th) activity ratios < 1. The 741 742 scenario used above to explain U data implies no or slow (with respect to the decay rate of ²²⁶Ra) gain of ²³⁰Th in Fe-oxide fractions. For instance, a ²³⁰Th gain constant f₂₃₀ as low as 1.5×10⁻⁷ y⁻¹ (as 743 used in Fig. 8) would induce a gain rate too low to produce ²²⁶Ra-²³⁰Th disequilibrium. Therefore, the 744 (²²⁶Ra/²³⁰Th) disequilibria observed in these fractions most likely reflects the occurrence of ²²⁶Ra 745

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

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

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

contribution of smectite to the overall adsorption of ²²⁶Ra is of the same order of magnitude or even 780 greater than that of organic material. Chen and Kocar (2018) also demonstrated that the level of 781 782 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 studies also reported that under certain conditions, Ra mobility was mainly controlled by Fe-Mn-Al 784 785 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 results of Gonneea et al. (2008) for Fe-Mn-rich sediments. For comparison, although this was closely 790 791 dependent on the experimental conditions, the distribution coefficient K_d for Ra sorption on the smectite surface ranged from 300 to 3000 ml.g⁻¹ at pH = 5 (depending on the solution ionic strength, 792 Robin et al., 2017) while K_d remained below 10 for Ra sorption on ferrihydrite and goethite (Sajih et 793 794 al., 2014). The pH values of the study soils ranged from 4.3 to 4.8 (Table 1), which probably explains the desorption of Ra from Fe-oxide surfaces and the predominant sorption of ²²⁶Ra onto clay 795 796 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.

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801 4.3.2. Contrasted mobility of Ra isotopes

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

These results highlight a mobilization of Ra from two soil fractions, i.e., Fe-oxides and residue fractions, with a striking difference in mobility between Ra isotopes; this involves a much more significant removal of ²²⁸Ra relative to ²²⁶Ra from the residue fraction which cannot solely be explained by the Th depletion, relative to U, in this fraction, and a net loss of ²²⁸Ra at the bulk scale when ²²⁶Ra is retained.

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

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

Alternatively, the loss of ²²⁸Ra at the bulk soil scale could partially reflect a deficit of ²²⁸Ra restitution 846 from vegetation rather than a real enhanced ²²⁸Ra isotope mobility. Indeed, several studies 847 previously highlighted the importance of the transfer of Ra to plants (review in IAEA, 2014), the 848 849 possible influence of vegetation on Ra isotope levels in soils (Rihs et al., 2016, Chabaux et al., 2019), and the long residence time of Ra, i.e., several years, deduced from ²²⁸Ra/²²⁶Ra in vegetation (Baeza 850 et al., 1999; Lascar, 2019). Because of the short half-life of ²²⁸Ra, such a long residence time produces 851 a significant decay of ²²⁸Ra during the cycling of Ra through trees, while ²²⁶Ra would not be affected. 852 853 The restitution to the soil of the Ra removed by the vegetation, through degradation of litter, would 854 therefore produce a ²²⁸Ra-depleted restitution flux, while ²²⁶Ra 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 ²²⁸Ra loss from a significantly large soil thickness has never been reported; generally, only thin and localized soil horizons show ²²⁸Ra depletion (e.g. Rezzoug et al., 2009; Rihs et al., 2011; Gontier et al., 857 858 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.

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863 4.4. Implications for U-series dating method

Recent publications have investigated the interest of mineral separations and sequential extractions
of primary and/or secondary minerals to probe weathering rates using U-series disequilibria (Suresh
et al., 2014; Martin *et al.*, 2015; Menozzi, 2016; Menozzi *et al.*, 2016; Rihs *et al.*, 2016, Dosseto et al.,
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 the mixing of different components with different histories. For instance, the bulk (²³⁰Th/²³⁴U) 885 disequilibrium measured in the study soil reflected mixing between a close-to-radioactive 886 887 equilibrium fraction (Fe-oxides and residue fractions) and a highly out-of-equilibrium fraction (the < 2 888 μ m fractions). The bulk (²³⁴U/²³⁸U) 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 trap for U and immobilized a part of the 234 U released from the residue and < 2 μ m fractions over 894 895 several hundred ky. This process, however, relates to ferruginous nodules history that could have started within parent material before the soil formation process began and therefore cannot be 896 897 related to the rate of soil formation. In contrast, the < 2 μ m 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 μ m 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 μ m fraction decreases as Ra > Th > U. 915

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 ²³⁴U 918 from the residue fraction (including quartz, feldspar and organic matter) to Fe-oxides (goethite) was observed through the entire soil profile. ²³⁴U may be mobilized from the residue fraction by α -recoil 919 process over several hundred ky. We also highlighted leaching of U from the < 2 μ m fraction through 920 921 a different mechanism (removal of both isotopes instead of a 234 U α -recoil process). The overall process leads the < 2 μ m fraction to hold the (²³⁰Th/²³⁴U) disequilibria observed in the current bulk 922 923 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., $\binom{234}{238}U = \binom{230}{h}\binom{234}{234}U = 1$, 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). ²²⁶Ra 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 μ m fraction, which acts 930 as a barrier to the release of Ra from the profile. Some discrepancies between Ra isotopes appear, 931 since ²²⁸Ra seems to be more efficiently removed from the residue fraction than ²²⁶Ra and then lost, 932 in contrast the case of ²²⁶Ra at the bulk soil scale. In the residue fraction a more accessible location of 933 ²³²Th (and subsequently ²²⁸Ra), relative to ²³⁰Th (and subsequently ²²⁶Ra) to water interaction as well 934 as a deficit of ²²⁸Ra restitution from the vegetation are assumed to explain these differences. These

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

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

945

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