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1 A methodology for detecting and characterising actinide-bearing micro-
2 particles in soils and sediment of the Fukushima Prefecture, Japan

3
4 Hugo Jaegler¹, Fabien Pointurier², Yuichi Onda³, Jaime F. Angulo⁴, Nina M. Griffiths⁴, Agnes
5 Moureau⁴, Anne-Laure Faure², Olivier Marie², Amélie Hubert² & Olivier Evrard^{1*}

6
7 ¹Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, Unité Mixte de
8 Recherche 8212 (CEA-CNRS-UVSQ), Université Paris-Saclay, F-91198 Gif-sur-Yvette, France

9 ²CEA, DAM, DIF, F-91297 Arpajon, France

10 ³Center for Research in Isotopes and Environmental Dynamics (CRIED), University of Tsukuba,
11 Tsukuba, Japan

12 ⁴Laboratoire de Radio Toxicologie, CEA, Université Paris-Saclay, 91297 Bruyères-le-Châtel,
13 France

14
15 (*) Corresponding author (email address: olivier.evrard@lsce.ipsl.fr).

16
17 **Abstract:**

18 The Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident released limited amounts of
19 actinides on soils of Japan. Characterisation of these particles is essential to determine the fate
20 of actinides in the environment. The method presented in this paper, based on α -tracks
21 detections, microscope observations and mass-spectrometry measurements, was designed to
22 identify and characterize actinide-bearing particles in soil samples. The method was tested on a

23 road dust sample collected in the main radioactive plume of the Fukushima region. Accordingly,
24 α -tracks detection was demonstrated to provide a powerful technique to localise these particles
25 and prepare their morphological, elemental and isotopic characterization.

26

27 **Keywords**

28 Fukushima Dai-ichi Nuclear Power Plant accident; actinide-bearing particles; Solid State Nuclear
29 Track Detector; microscope characterisation; mass spectrometry

30

31 **Introduction**

32 Most radionuclides released into the environment during the Fukushima Dai-ichi Nuclear Power
33 Plant (FDNPP) accident were activation or fission products, like radioiodine or radiocesium. In
34 contrast, the estimated releases of uranium and plutonium emitted in the atmosphere were
35 comparatively very low [1]. Therefore, only trace amounts of plutonium [2–4] and uranium [1,
36 5–8] isotopes from the nuclear fuel have been detected in environmental samples collected in
37 the vicinity of the power plant.

38

39 It has been shown that actinides released by nuclear events like atmospheric tests [9], nuclear
40 weapon accidents [10, 11] and more recently the Chernobyl accident [12] are at least in part
41 contained in microparticles. After the FDNPP accident, several authors investigated the
42 occurrence of radioactive microparticles, and successfully detected cesium-rich microparticles in
43 the environment [13–15]. These microparticles were identified from ^{137}Cs gamma emission
44 using gamma-imaging plates. However, when detected, uranium was a minor constituent of

45 these particles [16–18]. Actinide-bearing microparticles do not necessarily contain fission
46 products, because actinide and fission products are characterised by different levels of volatility
47 and melting points. Actinide-bearing particles therefore are not necessarily detectable with
48 gamma-radiography. Following the FDNPP accident release of plutonium particles was
49 suspected [19, 20] and the emission of uranium particles was confirmed [16, 21]. The post-
50 accidental fate of these actinides is strongly influenced by several factors including the size, the
51 geometry, the microstructure and the different elemental (i.e. in other chemical elements than
52 actinides) and molecular composition of these particles. These characteristics require
53 investigation as they will influence the dissolution, the mobilization, the transport or the
54 retention processes affecting the actinides [9].

55
56 Since uranium and plutonium were already present in the environment before the FDNPP
57 accident, as a result of the global fallout associated with atmospheric nuclear weapon tests, the
58 source of these actinides need to be carefully investigated [22]. Furthermore, compared with
59 the very low additional input of FDNPP-derived uranium, naturally-occurring uranium is found at
60 concentrations ranging around $1.9 \pm 1.2 \mu\text{g/g}$, 2σ in the Japanese soils ([23, 24]). These sources
61 of uranium are characterised by different isotopic compositions, mainly for ^{235}U and ^{238}U .
62 Moreover, the measurement of ^{236}U – a minor uranium isotope - may also provide a strong
63 indicator of the anthropogenic source of uranium [1, 25], as the $^{236}\text{U}/^{238}\text{U}$ isotope ratio provides
64 a very good discrimination between different sources of uranium [6]. Measurements of these
65 isotope ratios were mainly performed by “bulk” analyses [1, 5–8]. The characterisation of
66 FDNPP-derived uranium particles deserves isotopic analyses at the particle scale.

67
68 To the best of our knowledge, Imoto et al. [15] are the only authors who determined uranium
69 isotope ratios based on Secondary Ion Mass Spectrometry (SIMS) measurements in three
70 caesium-containing microparticles extracted from paddy soil and gravel located below
71 drainpipes from the Fukushima region. They identified the source of uranium in these particles
72 showing an isotopic ratio $^{235}\text{U}/^{238}\text{U}$ value close to 0.03 ± 0.003 (compared to 0.0072 in natural
73 uranium), which is characteristic of enriched nuclear fuel. They thereby demonstrated that
74 these particles were composed of uranium from FDNPP. However, these particles were
75 detected with gamma-imaging plates, which does not allow the detection of particles with
76 uranium as a major component. To do so, nuclear track radiography provides a more
77 appropriate screening method to identify selectively uranium particles, when analysing a soil
78 sample or another type of powder sample composed of large amounts of any type of particles.

79
80 Nuclear track radiography has been used in numerous studies [26, 27], mainly in those
81 investigations conducted after the Chernobyl accident [9, 28–30], to identify and extract “hot”
82 radioactive particles from soil samples. These experiments consist in positioning a contaminated
83 sample in close contact with a Solid State Nuclear Track Detector (SSNTD). When emitted by
84 radionuclides contained in the particles, α -particles generate damage on the SSNTD located just
85 above the particle, leaving characteristic tracks (the so-called α -tracks) with well-known star-
86 shapes whose centre is located just above the α -emitting particle.

87

88 The current research was conducted on a road dust sample, also referred to as “black
89 substance”, in order to maximize the probability to detect anthropogenic particles. Indeed, after
90 the FDNPP accident, several studies [1, 8] were performed on this type of material, which is
91 composed of aerosol and tyre particles, asphalt and environmental residues including soil and
92 lichen debris. “Black substances” are accumulated on the sides of the roads as a result of wind
93 and water erosion, and were shown to contain particularly high concentrations of radionuclides.
94 In previous studies [1, 8], this type of material was analysed using “bulk” analytical methods to
95 characterise uranium and plutonium isotope ratios, i.e. without focusing the investigations on
96 individual actinide-bearing micro particles.

97
98 To meet this goal a preliminary study was carried out in order to check the occurrence of μm -
99 sized actinide-bearing particles in a powder sample. Then, we developed a new methodology
100 for the detection and isolation of these particles. The elemental, morphological and isotopic
101 characterisation of these particles was finally performed together with the isotope analyses on
102 these μm -sized particles. The overall objective of this work was therefore to develop an
103 innovative method for the detection and characterisation of actinide-bearing micro-particles
104 found in environmental samples contaminated with the radioactive fallout associated with the
105 FDNPP accident.

106

107 **Methodology**

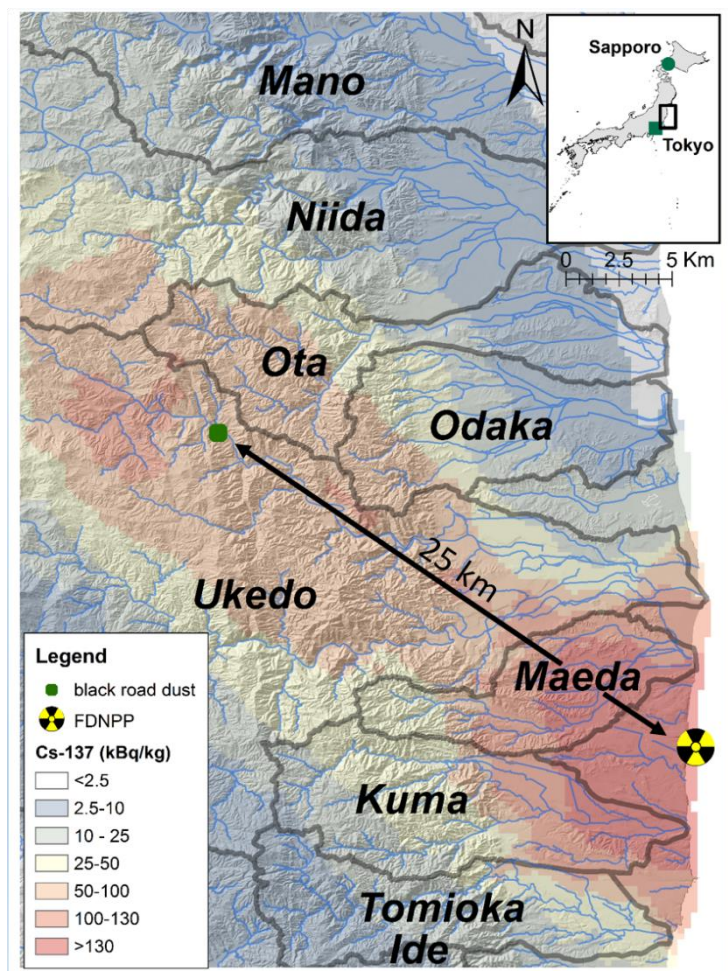
108

109 Sampling

110

111 The “black substance” sample was collected in November 2015 in the Ukedo River catchment
112 along a road located in the main radioactive plume, approximately 25 km to the northwest of
113 FDNPP (GPS coordinates: N 37.553371; E 140.834940, see Fig. 1) in the Namie Municipality. The
114 emitted radiation dose measured at the sampling location with a radiameter (LB123 D-H10,
115 Berthold Technologies) exceeded $100 \mu\text{Sv h}^{-1}$ at 1-cm distance from the soil surface.

116



117

118 **Fig. 1** Location of the sampling site of the road dust sample within the main radioactive pollution plume of
119 Fukushima, Japan

120
121 Preliminary study: sample screening by means of Scanning Electron Microscopy and Energy-
122 Dispersive X-ray spectrometry

123
124 The goal of this preliminary study was to check the presence of actinide particle in sub-samples,
125 so as to confirm that the collected sample was appropriate for the implementation of the
126 developed methodology. For this purpose, samples were directly analysed by Scanning Electron
127 Microscopy (SEM) and Energy-Dispersive X-ray spectrometry (EDX). Observations by SEM (FEI
128 Quanta 3D FEG, Eindhoven, The Netherlands) were conducted in the low vacuum mode (60 Pa)
129 to allow the analysis of non-conductive materials, with the use of backscattered electron
130 detectors on a wide field (approximately 500 μm by 500 μm). This allows the detection of the
131 particles with a density higher than an average atomic number of 20 with the chosen analytical
132 parameters (detection size limit is 0.55 μm for uranium particles), which likely corresponds to
133 radioactive particles. Among the detected particles, only those identified as “uranium particles”
134 (i.e. those for which uranium was the major constituent) were analysed individually by EDX
135 spectroscopy (EDAX Apollo SDD 10 mm²) for chemical characterisation. Due to the low
136 abundance of plutonium in nuclear fuel (both irradiated UO₂ and MOX) compared to that of
137 uranium, it is very unlikely to detect directly plutonium in particles. Accordingly, only those
138 particles in which uranium is a major constituent were initially targeted by these experiments.

139
140 In this preliminary experiment, two milligrams of the sample were randomly collected with
141 Sticky Carbon Tapes (SCT, n=14) dabbed onto walls of the vials containing the road dust sample.

142 SCTs consist of double sided carbon-based electrically conductive and non-porous adhesive
143 mounted on an aluminum holder, which is a suitable support for SEM and EDX analyses.
144 Accordingly, SCTs were directly analysed by SEM and EDX following a three-step process: i)
145 automated search for particles with high average atomic numbers, including particles for which
146 uranium is the major constituent, using the Gun Shot Residue (GSR) software. This software also
147 provides an EDX spectrum and indicates the major elemental constituents of the detected
148 particles; ii) more precise EDX spectrum for each particle identified as 'uranium-particle' with a
149 longer acquisition time (one minute instead of a few seconds) to confirm the presence of
150 uranium as a major constituent and to identify minor constituents (i.e. with concentrations
151 above ~1%); iii) high resolution imaging of the detected actinide particles with high
152 magnification.

153
154 In previous studies, uranium was shown to be associated with Zn-Fe oxide [15] or trapped in
155 spherical SiO₂ particles [14], so that the occurrence of particles of Fe and Zn or spherical
156 particles of Si were also investigated in order to verify the possible presence of uranium and Cs
157 as minor constituents in these particles.

158
159 **Nuclear track autoradiography to isolate actinide-bearing particles**

160
161 Following investigation of the occurrence of actinide-bearing particles in the sample, the
162 difficulty of micro-particle transfer from the SCTs to carbon plate to conduct isotopic
163 measurements led to the development of a second screening method. To this end, the

164 detection and the isolation of actinide-bearing particles were performed through alpha-
165 autoradiography using a Solid-State Nuclear Track Detector (SSNTD).

166
167 The SSNTD used in the current study was the Tastrak™ detector (TASL, Ltd, Bristol, UK) with a
168 density of 1.30 g/cm³, a thickness of 500 μm and a cut-off angle of 20° for alpha particles. A key
169 point for α-track autoradiography is the measurement of the yield of the experiments, as it
170 determines the capability of the SSNTD to record the activity of particles. We experimentally
171 estimated the yield through by the deposition of different concentrations of a ²⁴²Pu solution
172 (Plutonium-242 Radioactivity Standard, Standard Reference Material 4334I, National Institute of
173 Standards & Technology, CERCA-LEA, F 26701 PIERRELATE cedex; www.lea-cerca.com) on a
174 rough filter to simulate the particulate nature of the sample. The SSNTD was put in close contact
175 with the filter that was protected by mylar foil (3.5 μm thickness) during 6, 10 and 11 weeks.
176 The numbers of α-tracks on the SSNTD were counted by microscopy observation using a ccd
177 camera piloted by Archimed (version 7.0.10) and the number of tracks quantified using Histolab
178 (version 8.0.10) from Microvision instruments, (Lisses, France; <https://www.microvision.fr>). The
179 number of tracks allowed to calculate the activity and to compared it with the activity of the
180 standard reference solution. The experimental yield cannot exceed 50 %, as only half of the α-
181 particles are emitted upwards and will therefore impact the SSNTD. Moreover, alpha-particles
182 are subject to self-attenuation within the particle and in the bulk sample, which will significantly
183 reduce the yield factor. We estimated the yield of the α-track experiments to be 30 % of the
184 ²⁴²Pu certified solution. Accordingly, the yield correction factor (η) was set to 0.3 in the
185 calculations. This value is in good agreement with those found in the literature [26].

186
187 With regard to the road dust sample, a thin sample layer of dust was deposited on square
188 polycarbonate support plates (n = 90) with collodion to ensure a perfect immobilisation of the
189 sample during experiments. Sample support plates and SSNTD were welded and pierced
190 together in order to provide coordinates in order to locate of α -emitting particles for isolation.
191 Tastrak SSTND was positioned in close contact with the sample during 2, 4 and 6 months.
192 Twenty SSNTD plates were revealed and observed after 2 months, then twenty additional plates
193 after 4 months and, finally, fifty plates after 6 months. At the end of each experiment, SSNTD
194 was etched in a 6 M NaOH solution at 80°C during 1 h. Tracks were observed by optical
195 microscopy. After localisation of α -track clusters, SSNTD and plates were separated and α -
196 emitting particles were localised using the coordinates on both SSNTD and plates. The support
197 plates containing the α -emitting particles were then analysed by SEM and EDX, using the same
198 methodology as described for the preliminary experiments (see section 'Sample screening by
199 means of SEM/EDX').

200
201 The number of α -tracks per cluster was used to estimate the activity of the corresponding
202 particle. It was hypothesized that: 1) all α -emitters had the same yield, 2) the samples were
203 assumed to be composed of the following three proportions of actinides:

- 204
- 205 • Composition 1: natural uranium ore with 99.3 % of ^{238}U , 0.720 % of ^{235}U and 0.005 % of
206 ^{234}U , which contains also α -emitter daughter nuclides of ^{235}U and $^{238}\text{U} - ^{234}\text{U}$ decay chains
207 (devoid of plutonium);

- 208 • Composition 2: nuclear fuel composition at the moment of the accident in reactor 1 [31],
 209 with 97.5 % of ^{238}U , 1.66 % of ^{235}U , 3.10×10^{-4} % of ^{234}U , 0.455 % of ^{239}Pu and 0.157 % of
 210 ^{240}Pu ;
- 211 • Composition 3: MOX fuel with 2.5 % of plutonium (80 % of ^{239}Pu and 20 % of ^{240}Pu) and
 212 97.5 % of uranium (98 % of ^{238}U , 2 % of ^{235}U and 0.01 % of ^{234}U) (Reactor 3);
- 213 • Composition 4: natural uranium with 99.3 % of ^{238}U , 0.720 % of ^{235}U and 0.005 % of ^{234}U ,
 214 which contains also α -emitting daughter radionuclides from ^{235}U and $^{238}\text{U} - ^{234}\text{U}$ decay
 215 chains and global fallout plutonium (estimation of ^{239}Pu and ^{240}Pu abundances based on
 216 the ^{239}Pu concentrations measured in Japan [32])

217

218 Then, the number of atoms of actinide in the particle (n_{act}) was estimated based on the number
 219 of α -tracks recorded on the SSNTD ($n_{\alpha\text{-tracks}}$) divided by the yield η , the time t (in second), a_i the
 220 atomic abundances of the α -emitter isotope i (which is an isotope of uranium or plutonium),
 221 and the λ_i the decay constant of α -emitter i (which is an isotope of uranium or plutonium) as in
 222 Eq. (1).

$$n_{\text{act}} = \frac{n_{\alpha\text{-tracks}}}{\eta \times \Delta t \times \sum_i (a_i \times \lambda_i)} \quad (1)$$

223

224 The equivalent diameter ϕ of the particle (assumed to be spherical and made of UO_2) is
 225 therefore calculated as in Eq. (2) [33].

$$\phi = \sqrt[3]{\frac{6 \times n_{\alpha\text{-tracks}} \times M_{\text{UO}_2}}{\pi \times \rho \times \mathcal{A} \times \eta \times \Delta t \times \sum_i (a_i \times \lambda_i)}} \quad (2)$$

226

227 Where \mathcal{A} is the Avogadro Number, ρ the density of UO_2 (10.97 g/cm³), M_{UO_2} the molar mass of
228 UO_2 (270 g/mol).

229

230 Secondary Ion Mass Spectrometer measurements

231

232 SIMS measurements were performed to determine the isotopic composition of the particles.

233 Prior to SIMS analysis, a small part of the polycarbonate plate (square shape, 5 mm side) was

234 cut around the theoretical position of the uranium-bearing particle. These subsamples that

235 were assumed to include the particle were dissolved in ethanol overnight and deposited on a

236 carbon plate with PolyIsoButylen acting as a sticking agent. Samples were heated in a furnace at

237 400°C for 30 min to evaporate the liquid deposition and eliminate any organic residue.

238

239 Details on SIMS function have been described elsewhere [34]. In brief, the SIMS instrument is a

240 double focusing instrument (Cameca IMS 7f, Gennevilliers, France) equipped with a

241 duoplasmatron (O_2^+) source. This primary beam was accelerated to 15 keV, whereas the

242 secondary ion beam was accelerated to 5 keV. The mass resolving power was set to 450 in

243 order to obtain flat-top peak. An Automatic Particle Measurement (APM) software allows the

244 efficient detection of uranium particles, through the acquisition of ion images of $^{238}\text{U}^+$ in a series

245 of 500 $\mu\text{m} \times 500 \mu\text{m}$ fields over the entire carbon plate. Ion images at $m/z=233$ and 234 were

246 also recorded and used as indicators of isobaric interference levels in the sample. After APM

247 data acquisition, microbeam measurements were performed on the selected individual particle.

248 $^{234}\text{U}^+$, $^{235}\text{U}^+$, $^{236}\text{U}^+$ and $^{238}\text{U}^+$ isotopic intensities were measured to determine precisely the

249 uranium isotopic compositions. Mass bias of these measurements was corrected through the
250 measurement of certified particles, and the ^{236}U signal was corrected from ^{235}UH species. Ion
251 images of $^{235}\text{U}^+$ and $^{238}\text{U}^+$ were also acquired for visualizing the particle. In order to investigate
252 the potential presence of plutonium isotope in the particle, a mass scan was also performed
253 from ^{238}U to ^{242}Pu masses.

254

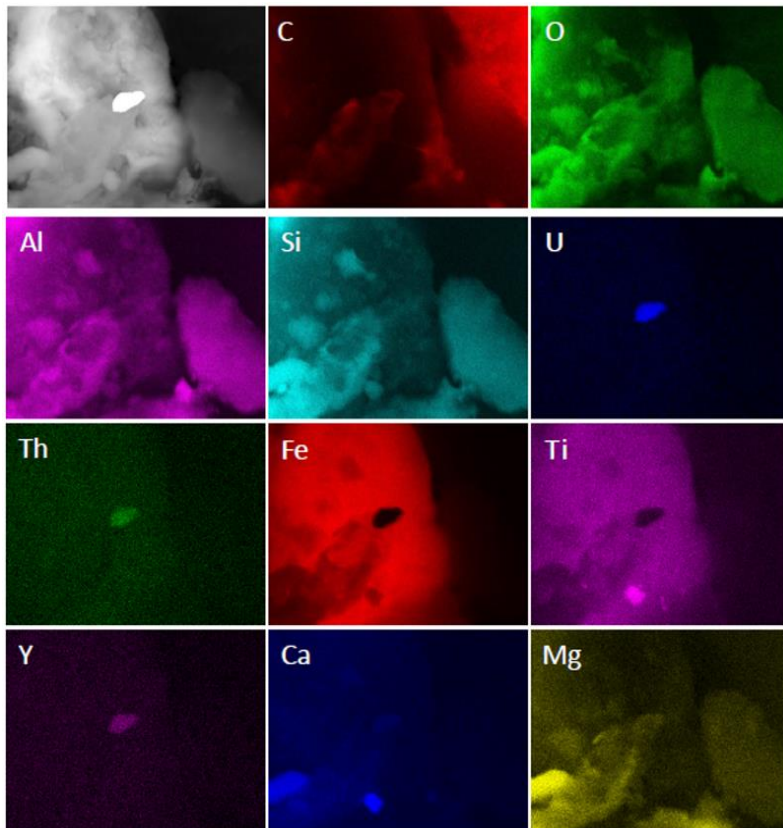
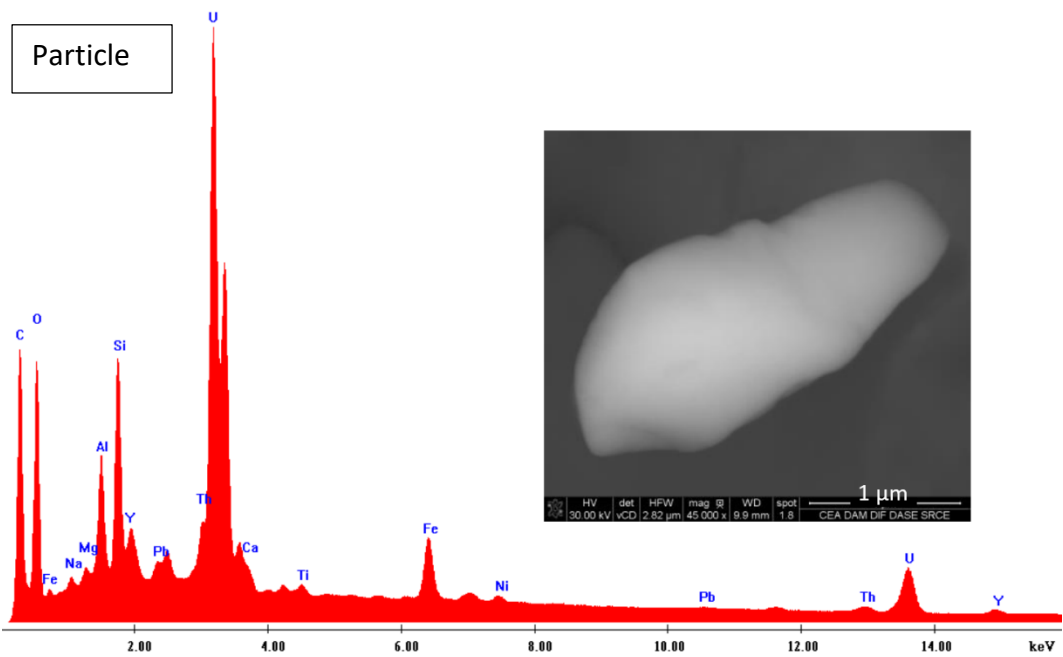
255 Results and discussion

256

257 Sample screening by means of SEM/EDX

258

259 Four uranium particles were detected by SEM from the 14 analysed SCTs used to collect sub-
260 samples of the road dust sample. Pictures of the particle 1 (photography, EDX spectra and
261 elemental mappings) are presented in Fig. 2; pictures of the 3 other particles are provided in
262 Supplementary Information (Fig. S1 – S3). The size of these particles ranged from 2 to 3 μm . In
263 addition to uranium, these particles mainly contained C, O, Al, Si, U and Fe. Traces of Na, Mg, Y,
264 Pb, Th, Ca, Ti, Co and Ni were also detected by EDX. However, no trace of Cs, Zn or Pu was
265 detected, with detection limits of $\sim 1\%$.



268 **Fig. 2** Electronic image, EDX spectrum and elemental mapping of the particle #1 identified as an U-bearing particle.

269 The mapping shows qualitatively that some elements (C, O, Al, Si, Fe, Ti) detected in the EDX spectrum may come

270 from surrounding particles, whereas Y, Th, Ca and Mg are obviously present in the particle. This is an indication that
271 this U-bearing particule may be of natural origin

272

273 This preliminary study confirms the presence of uranium particles in the samples collected in
274 the vicinity of the FDNPP. Caesium and plutonium, if present are in very low amounts that
275 are below the EDX detection limits (approximately 1%). However, EDX analyses do not allow the
276 determination of the source of these uranium particles (FDNPP or naturally-occurring). Further
277 analyses, including isotopic measurements, were required to confirm the sources of these
278 particles. Unfortunately, the direct isotope analysis by SIMS on SCTs is not possible (because of
279 the melting of the conductive glue under the primary ion beam). Moreover, the micro-sampling
280 of particles, which would be required to deposit them on a support material suitable for SIMS
281 analysis (i.e. perfectly plane and conductive), is not possible on SCTs. Also, the automatic search
282 of particles by means of GSR software is very time-consuming and ineffective for analysis of
283 relatively large amounts of sample (at least a few mg). Accordingly, nuclear track
284 autoradiography experiments were performed to increase the quantity of analysed material and
285 to conduct both morphological and elemental analyses by SEM/EDX, and isotope analysis by
286 SIMS on the detected α -emitting particles.

287

288 Lastly, 9 FeZn particles were also analysed. Their sizes ranged from 3.5 μm to 20 μm . Their
289 shape was also heterogeneous: some particles were sharp and rough, while others were
290 completely spherical (see examples provided on Fig. S4). They were mainly composed of C, O,

291 Al, Si, Fe and Zn. Trace amounts of Na, Mg, P, S, K, Ca, Ti, Mn and Cu were also detected.
292 However, no trace of Cs, Pu and U could be detected in these particles.

293
294 It should be noted that many spherical Si particles were observed. Twenty of these were
295 analysed (one example is provided on Fig. S5). The size of these particles ranged from 4 to
296 10 μm , and they were mainly composed of C, O, Al and Si. Traces of C, O, Na, Mg, Al, Si, S, K, Ca,
297 Ti and Mn were also detected. Again, no trace of U, Pu and Cs could be detected in these
298 spherical Si particles.

299
300 α -track autoradiography experiments or Solid-State Nuclear track Detector experiments

301
302 Of the 90 prepared SSNTD plates, 20 were revealed after 2 months of exposure, 20 were
303 revealed after a 4-month exposure and the last 50 after a 6-month exposure. The total numbers
304 of detected particles for each exposure are given in Table 1.

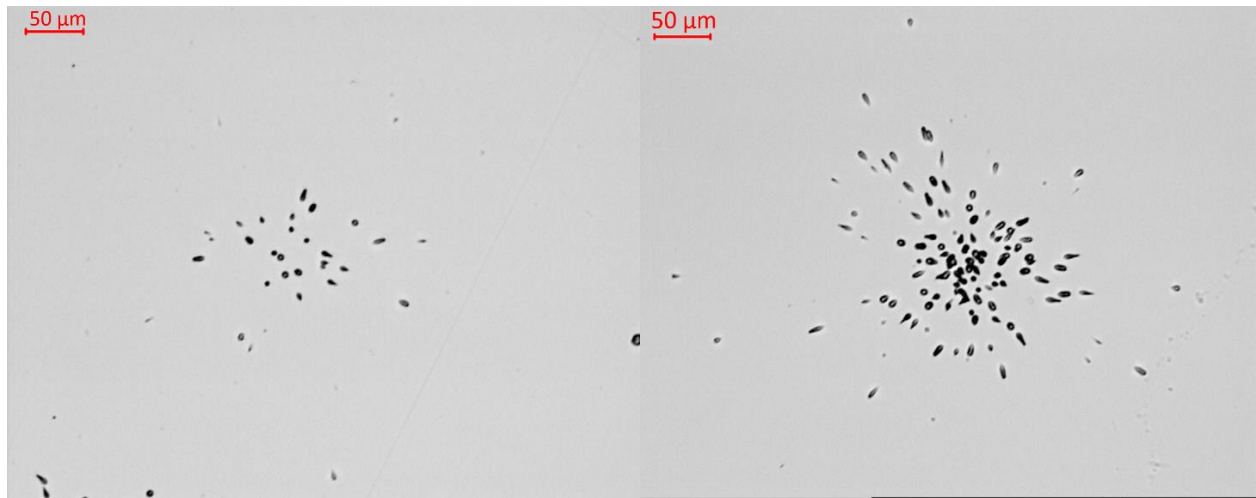
305
306 **Table 1** Summary of particle detection and analysis after α -track radiography.

Time of exposure	Number of revealed SSNTD plates	Number of detected particles	Number of particles analysed by SEM and EDX
2 months	20	27	3
4 months	20	30	9
6 months	50	40	16
TOTAL	90	97	28

307
308 However, most of these clusters have less than 20 α -tracks (Fig. 3, left). For example, the
309 number of detected particles after the 2-month exposure revealed that only 3 clusters were

310 composed of more than 100 α -tracks (Fig. 3, right), with 104 (particle A), 118 (particle B) and
311 162 (particle C) α -tracks recorded on the SSNTD, respectively.

312



313
314 **Fig. 3** Optical images of α -tracks clusters after 2 months of exposure. Left: example of a small cluster, with less than
315 20 α -tracks. Right: example of large cluster, with more than 100 α -tracks

316

317 The size of these particles can be roughly estimated (Table 2), through the comparison of
318 potential scenarios on the composition of the particles (see the Methodology section). These
319 theoretical calculations demonstrated that, for a given activity, particles are smaller by almost
320 one order of magnitude when they contain FDNPP-derived plutonium.

321

322

323

324

325

326 **Table 2** Theoretical particle sizes, based on the following hypotheses made on the composition of the particles: 1:
 327 natural uranium; 2: FDNPP uranium fuel; 3: FDNPP MOX fuel ; 4 : natural uranium and global fallout plutonium (see
 328 Methodology section). Particles A, B and C correspond to the three large clusters detected on the SSNTD after a
 329 two-month exposure and analysed by SEM and EDX (see Table 1).

Particle	Composition 1			Composition 2			Composition 3			Composition 4		
	A	B	C	A	B	C	A	B	C	A	B	C
Number of α -tracks recorded	104	118	162	104	118	162	104	118	162	104	118	162
Theoretical equivalent diameter (μm)	3.9	4.1	4.5	0.82	0.85	0.95	0.53	0.55	0.61	3.9	4.1	4.6

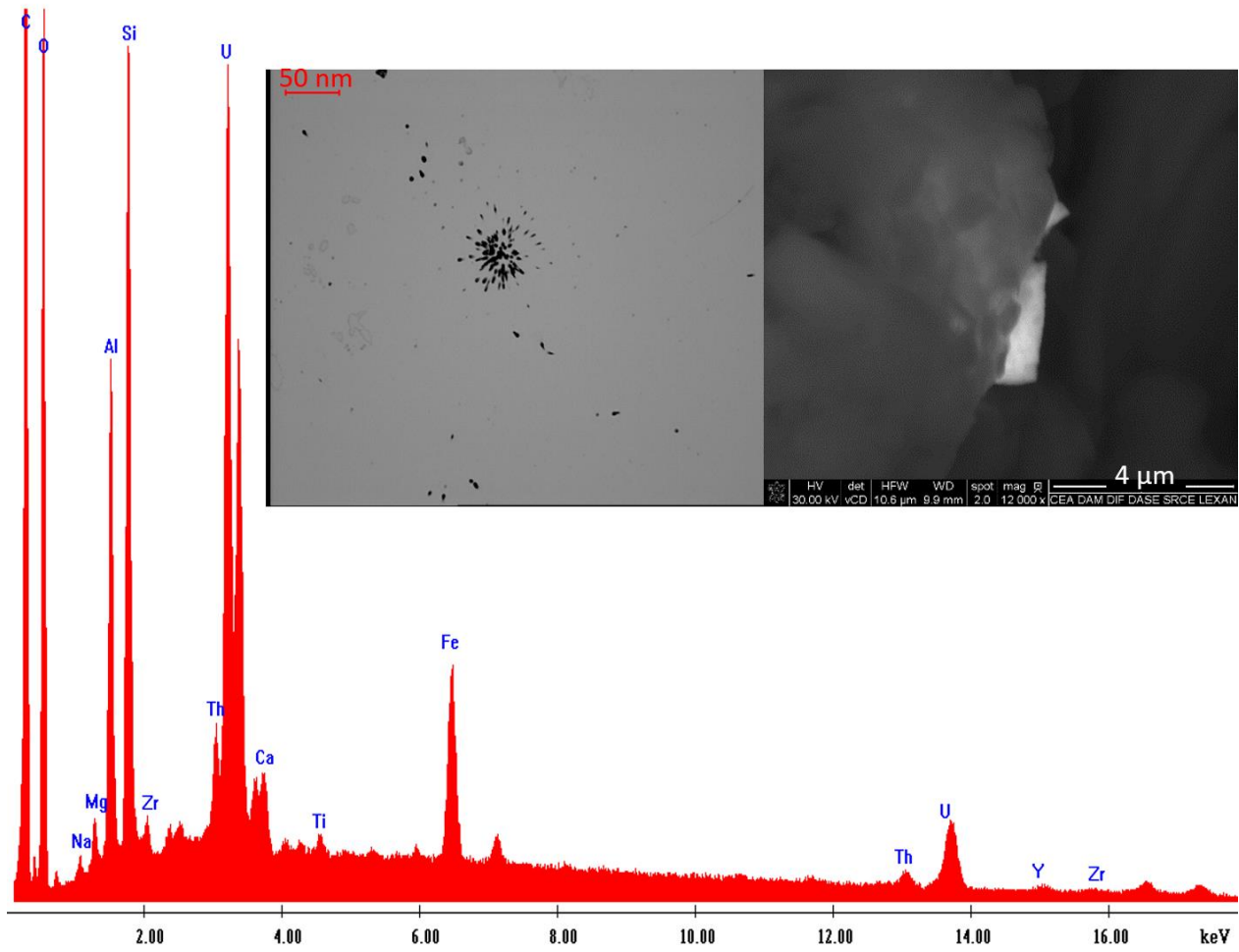
330
 331
 332 After 4 months of exposure, 20 other SSNTD plates were revealed and observed. 30 α -tracks
 333 clusters were observed, among which 9 were particularly dense in terms of number of α -tracks
 334 recorded on the SSNTD. Finally, after 6 months of exposure, the last 50 SSNTD were revealed
 335 and observed: 40 α -track clusters were detected, among which 16 were particularly dense. 28
 336 particles corresponding to the more α -emitting clusters identified after the 2, 4 and 6-month
 337 exposure times were then observed and analysed by SEM.

338
 339 SEM observation of particles

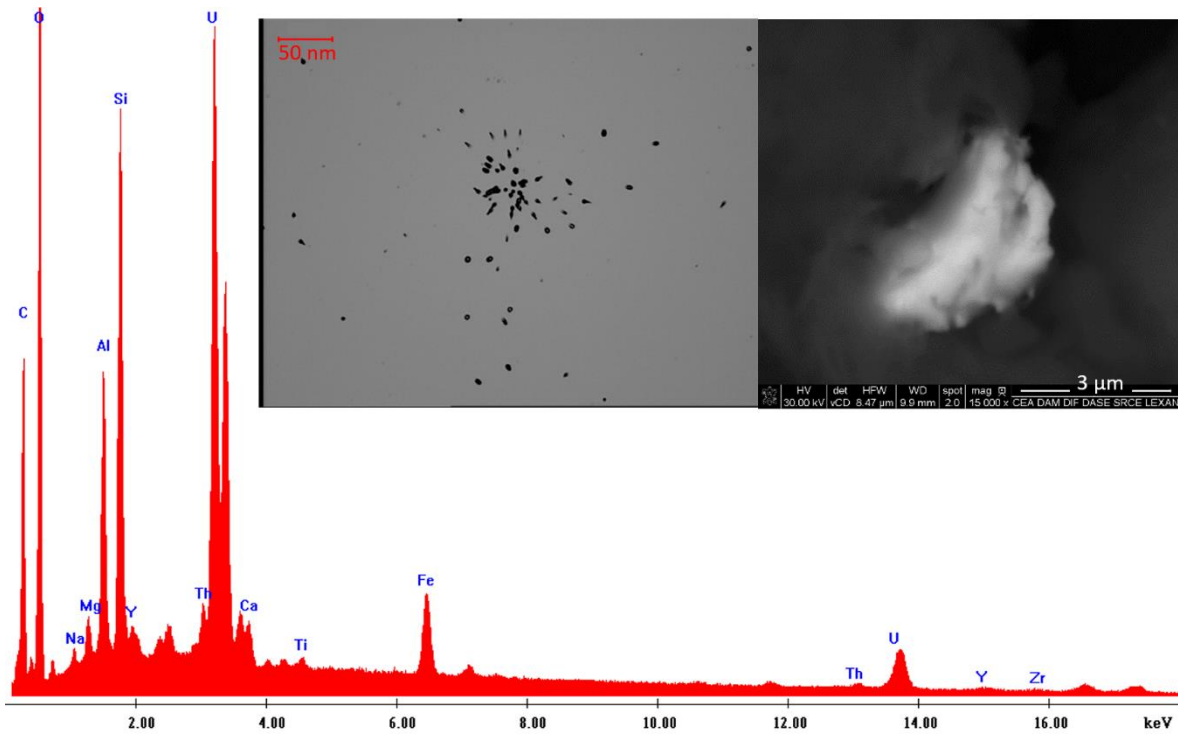
340
 341 Four types of particles were observed by SEM: 1) 10 zircon particles (ZrSiO_4) with sizes (apparent
 342 mean diameter) ranging from 30 to 100 μm . It should be noted that α -tracks are produced by U
 343 and Th isotopes that are substituted to Zr in zircon. 2) 7 particles of thorite, composed by

344 ThSiO₄, (mainly ²³²Th, T_{1/2} = 1.4×10¹⁰ y) of approximately 20 μm. 3) 7 Monazite particles
345 composed by (Ce, La, Nd, Pr)PO₄ with size ranging from 30 to 100 μm. Th is also present as a
346 minor constituent and detected by EDX in these particles. 4) 4 uranium particles were detected.
347 The size of these particles was estimated to approximately 4 μm for particle 1 (Fig. 4), 4 μm for
348 particle 2 (Fig. 5), 6 μm for particle 3 (Fig. 6) and 8 μm for particle 4 (Fig. 7). Th, Si, O, Fe, Al and
349 Y were also detected as minor constituents in the uranium particles. It should be noted that
350 presence of other chemical elements than uranium (Si, Fe, Al, etc.) may be due to intrinsic
351 impurities, and/or to the influence of neighbouring mineral particles which are partly included
352 in the analysed volume. In the first case, particles could be made of naturally-occurring uranium
353 or uranium from FDNPP mixed with concrete or other metals. However the presence of Th as a
354 minor constituent was detected in all four particles which provides a strong indicator for a
355 natural origin since Th is absent in the nuclear fuel but abundant in many uranium ores [35].

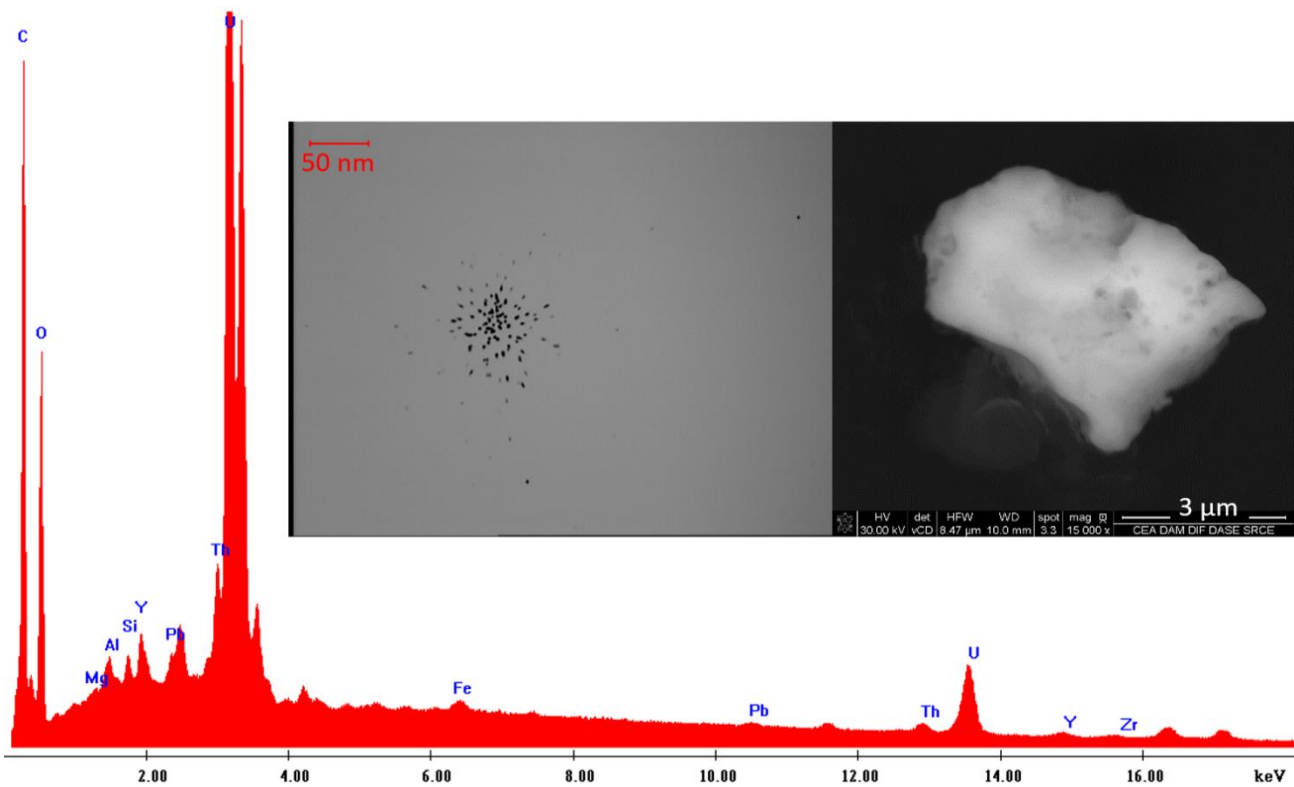
356



357
 358 **Fig. 4** Optical image of α -tracks recorded on the SSNTD after a 4 month-exposure time, SEM image and associated
 359 EDX spectrum for particle #1

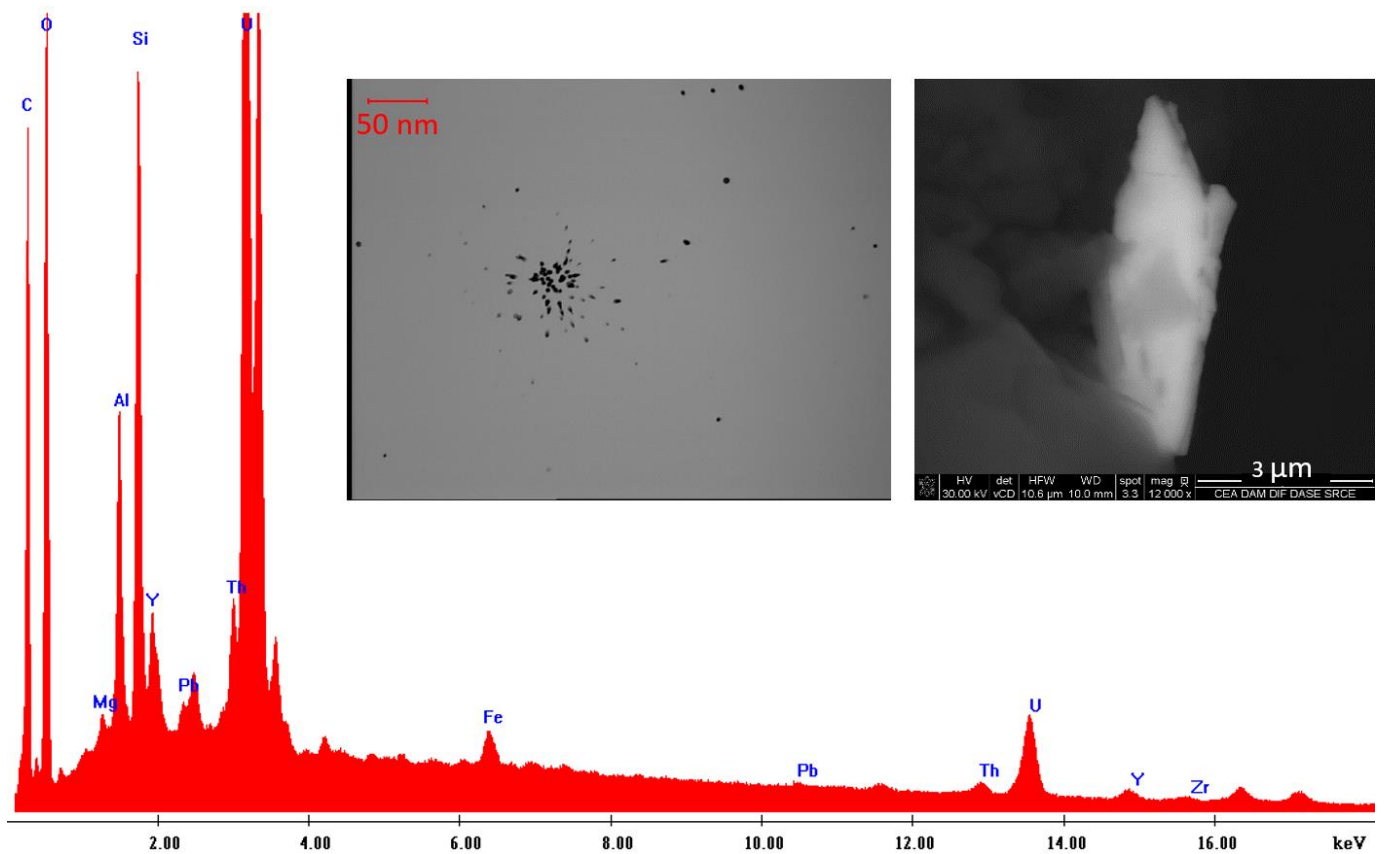


360 Fig. 5 Optical image of α -tracks recorded on the SSNTD after a 4 month-exposure time, SEM image and associated



361 EDX spectrum for particle #2

362 **Fig. 6** Optical image of α -tracks recorded on the SSNTD after a 6 month-exposure time, SEM image and associated
363 EDX spectrum for particle #3



364
365 **Fig. 7** Optical image of α -tracks recorded on the SSNTD after a 6 month-exposure time, SEM image and associated
366 EDX spectrum for particle #4

367
368 **Composition and origin of uranium particles**
369
370 With the activities calculated according to the α -tracks recorded on the SSNTD and based on the
371 yield previously determined (about 30%), the size (equivalent diameter) of the uranium
372 particles can be estimated. The number of α -tracks recorded on the SSNTD and the calculated

373 equivalent diameters deduced according to the four hypothetical compositions considered in
 374 this study are compiled in Table 3.

375
 376 **Table 3** Theoretical particle sizes (equivalent diameters assuming UO₂ density) of the uranium particles localized by
 377 means of α-track autoradiography and characterised by SEM/EDX according to the four hypothetical compositions
 378 considered in this study.

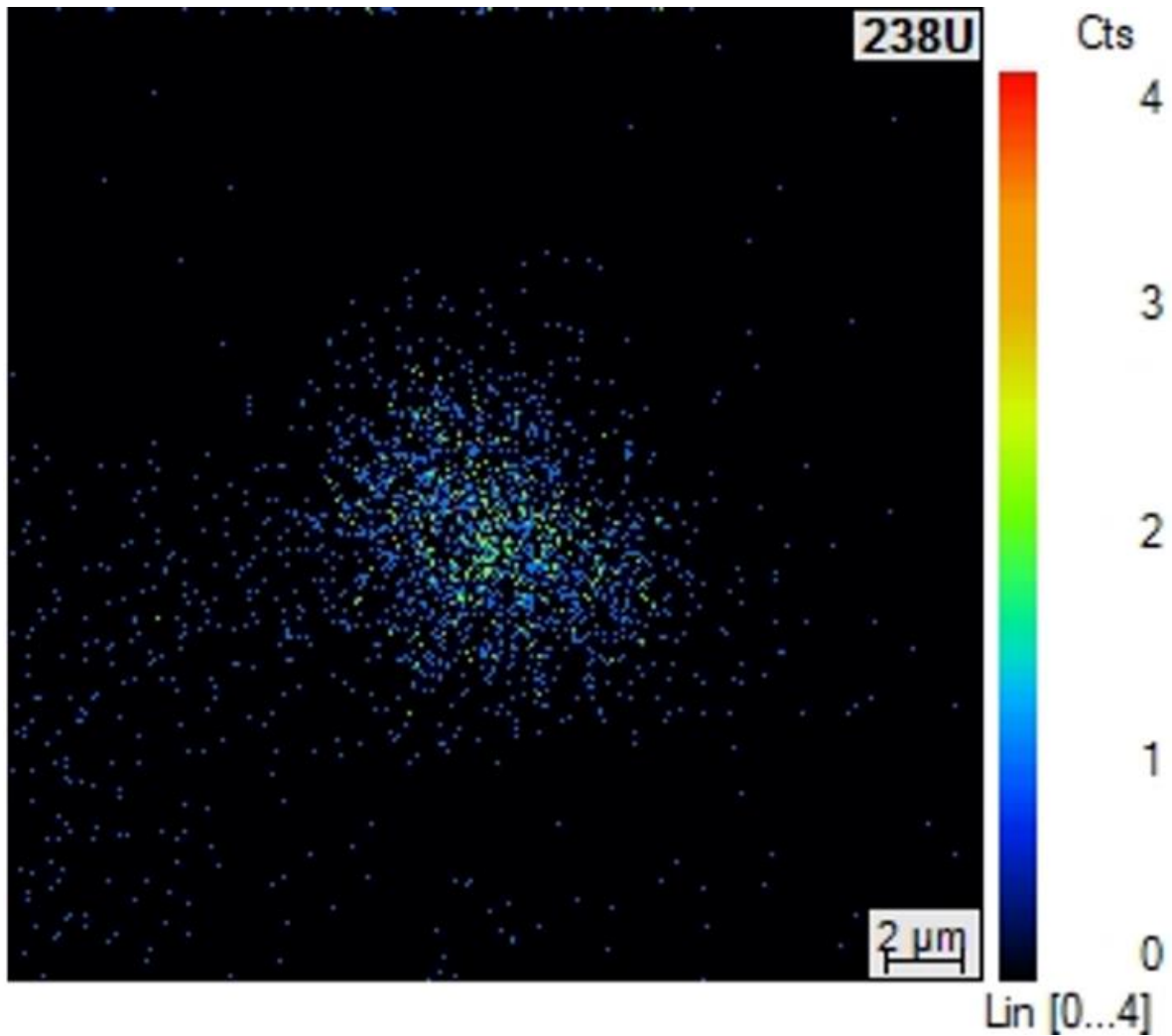
Particle number		1	2	3	4
Exposure time (months)		4	4	6	6
Number of α-tracks recorded		98	53	117	76
Calculated equivalent diameter (μm)	composition 1	3.0	2.5	2.8	2.4
	Composition 2	0.64	0.52	0.59	0.51
	Composition 3	0.41	0.33	0.38	0.33
	Composition 4	3.0	2.5	2.8	2.4

379
 380 Compared with the sizes estimated based on the SEM observations (4, 4, 6 and 8 μm,
 381 respectively), the results suggest that these particles did not contain FDNPP-derived plutonium,
 382 as their activities would be higher or the particles would be smaller. Accordingly, this first
 383 estimation suggests that the U is of natural origin.

384
 385 To investigate further this issue, SIMS measurements were performed on particle 1. Other
 386 particles could not be recovered after collodion dissolution and sample deposition onto graphite
 387 disks. After detection by APM, an ion image was acquired (Fig. 8). The isotopic composition was
 388 determined to $^{235}\text{U}/^{238}\text{U} = 0.00736 \pm 0.00017$ and $^{234}\text{U}/^{238}\text{U} = (5.37 \pm 0.83) \times 10^{-5}$, after mass bias
 389 correction. These results demonstrated unambiguously that this particle contained only natural
 390 uranium. Nevertheless, plutonium isotopes were investigated through the scanning of the
 391 particle from 239 to 242 atomic mass units. As expected, no plutonium isotope was detected in

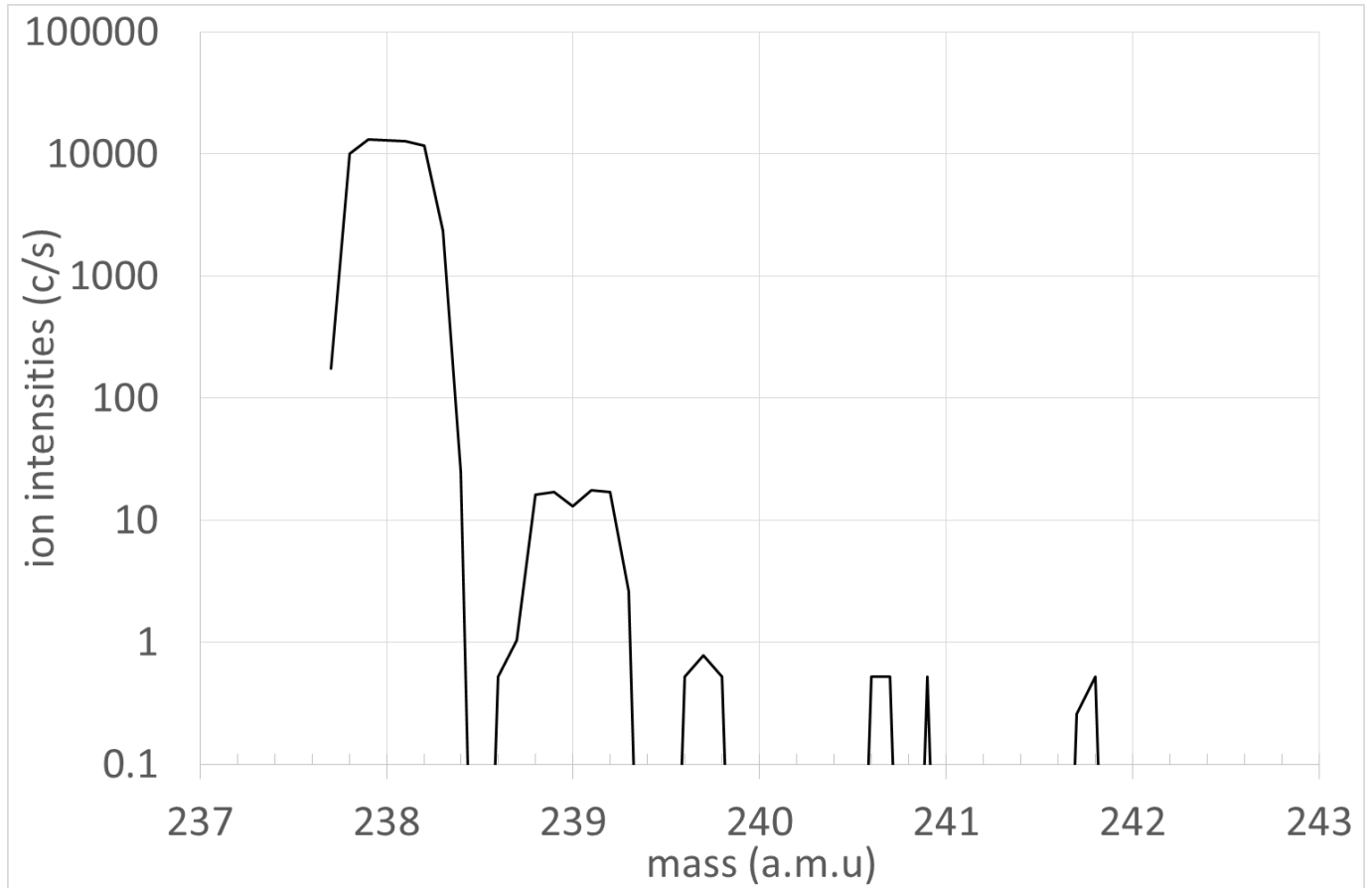
392 the particle (Fig. 9). Unfortunately, the very high uranium hydride formation rate ($^{238}\text{UH}^+ / ^{238}\text{U}^+ =$
393 3.10×10^{-3}) did not allow the determination of $^{236}\text{U} / ^{238}\text{U}$ for values lower than 2×10^{-5} , and the
394 ^{236}U concentration was below the limit of detection which is compatible with naturally-
395 occurring uranium with $^{236}\text{U} / ^{238}\text{U}$ isotope ratios ranged from 10^{-15} to 10^{-10} [36, 37]. To measure
396 the ^{236}U at such low levels, other analytical techniques should be performed, such as laser-
397 ablation ICP-MS [12, 38] or Thermal Ionisation Mass Spectrometry (TIMS) [39].

398



399
400 **Fig. 8** ion images at ^{238}U mass obtained with an O_2^+ primary ion current of 250 pA and a raster size of
401 $25 \mu\text{m} \times 25 \mu\text{m}$

402



403

404 **Fig. 9** Mass spectrum on the uranium particle at the plutonium isotope masses, obtained with an O_2^+ primary ion
405 current of 250 pA and a raster size of $25 \mu m \times 25 \mu m$. Intensities at 239 atomic mass units is likely due to $^{238}UH^+$
406 species

407

408 Conclusions

409

410 We have developed an analytical methodology to localize and characterize the morphological,
411 elemental and isotopic compositions of α -emitting actinide bearing micro-particles. These
412 analyses were performed on road dust sample collected at 25 km from the FDNPP. Particles

413 containing α -emitting elements were deposited along with numerous mineral matrix particles
414 on polycarbonate plates, embedded in a collodion layer and covered with an SSNTD. Alpha track
415 autoradiography allowed localisation of the active particles. The presence of uranium was
416 confirmed by SEM. Thereafter they were transferred finally to a graphite disk for measurement
417 of isotope composition by SIMS analysis..

418
419 The correlation between the numbers of α -tracks and the mean observed diameters of the
420 corresponding particles measured by SEM led to the rejection of the hypothesis of actinide-
421 bearing particles released during the FDNPP accident. Twenty-eight particles chosen as the
422 strongest α -emitting ones were examined by SEM/EDX, but only four of them were pure
423 uranium particles. Only one of these particles was analysed by SIMS and showed the typical
424 isotopic composition of natural uranium.

425
426 To increase the probability for detection of FDNPP-derived actinide particles, experiments
427 should be performed using larger quantities of samples. In addition, the method for transferring
428 particles from polycarbonate plates to graphite disks for SIMS measurements should be
429 improved. This study however showed that uranium particles can be isolated efficiently from
430 environmental samples and individually analysed by SEM, EDX detector and SIMS. For future
431 analyses, direct isotope analyses could be tested on the polycarbonate plates using laser
432 ablation coupled to ICP-MS. This would avoid the need to dissolve the collodion, as well as the
433 transfer of particles onto another support material. Further measurements will be required on

434 other α -emitting particles detected in soil or road dust samples in order to detect uranium, and
435 possibly the plutonium released by the FDNPP.

436

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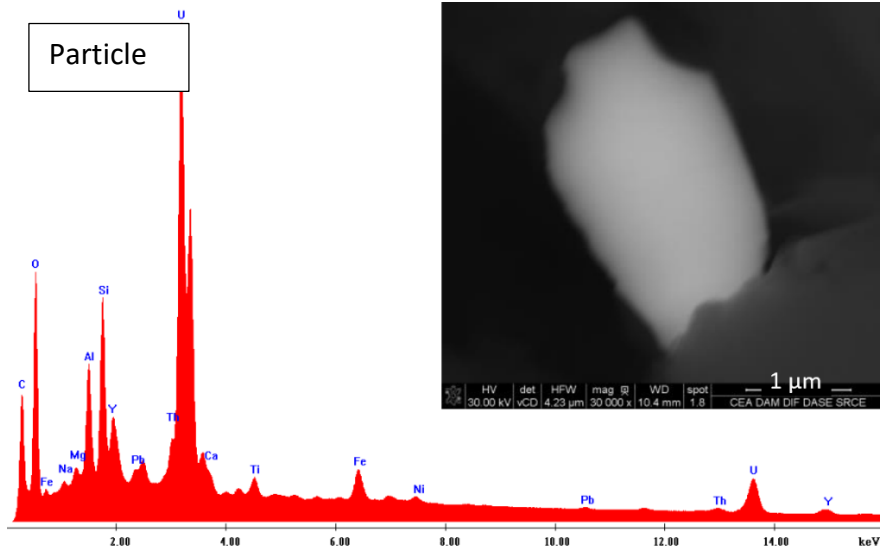
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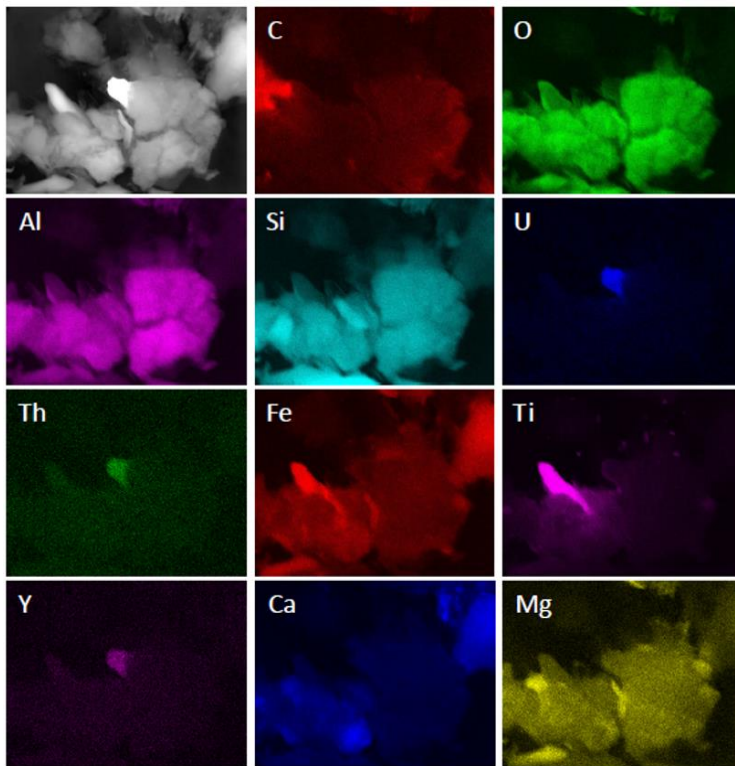
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574 Supplementary information

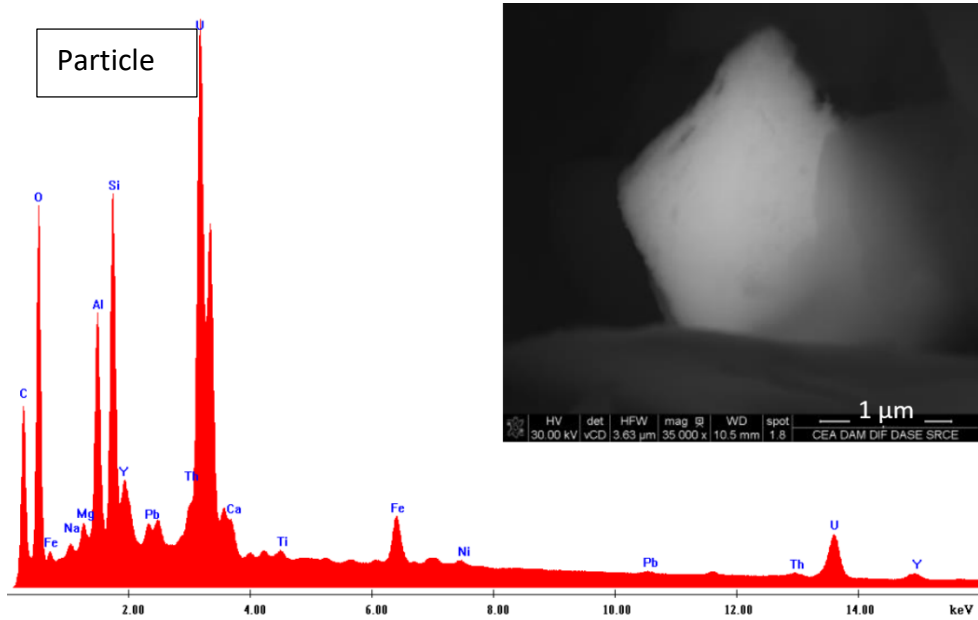


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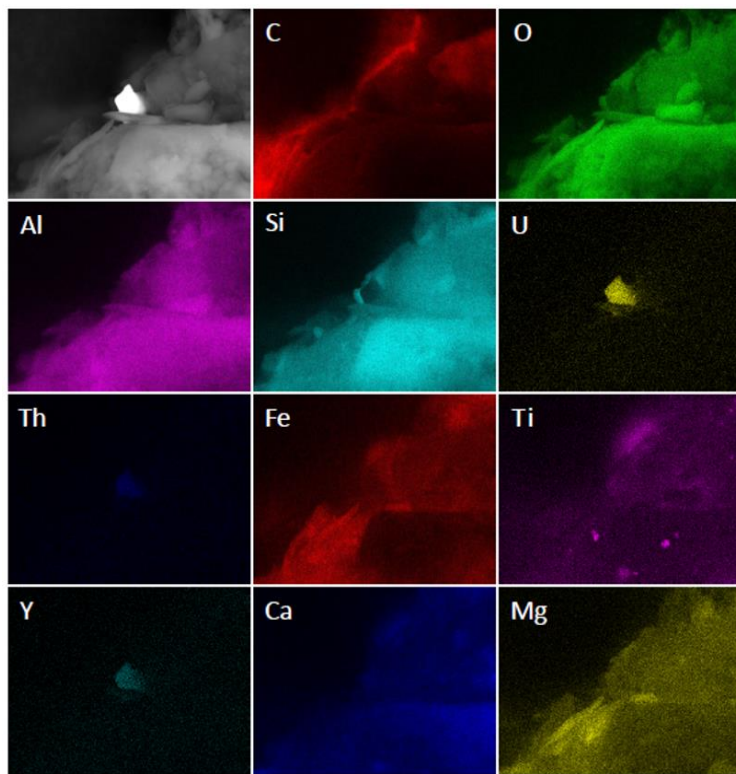


576

577 **Fig. S1** Electronic image, EDX spectrum and elemental mapping of the particle #2 identified as an U-bearing
578 particle. The mapping shows qualitatively that some elements (C, O, Al, Si, Fe, Ti, Ca, Mg) detected in the EDX
579 spectrum may come from surrounding particles, whereas Y and Th are obviously present in the particle. This is an
580 indication that this U-bearing particle may be of natural origin

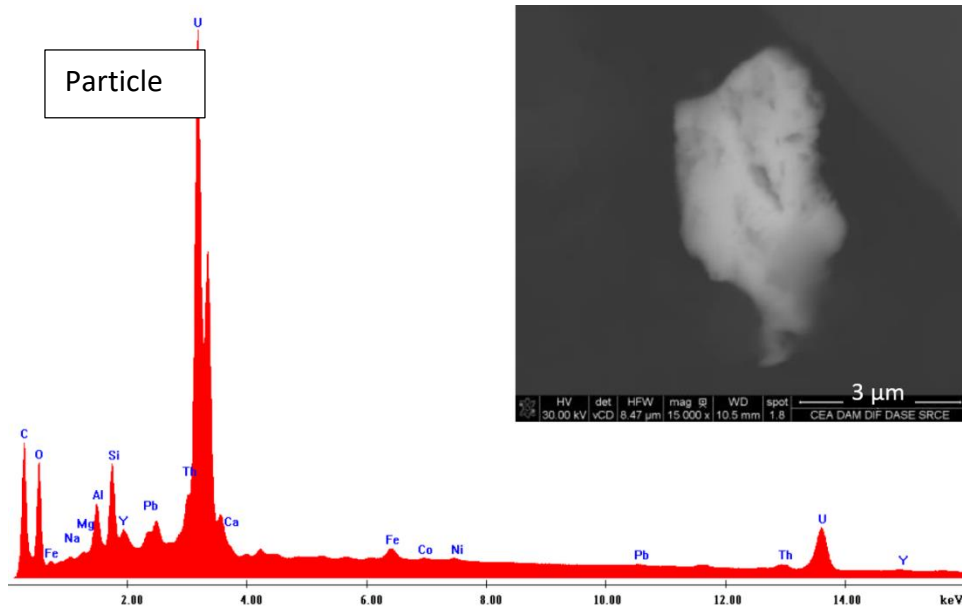


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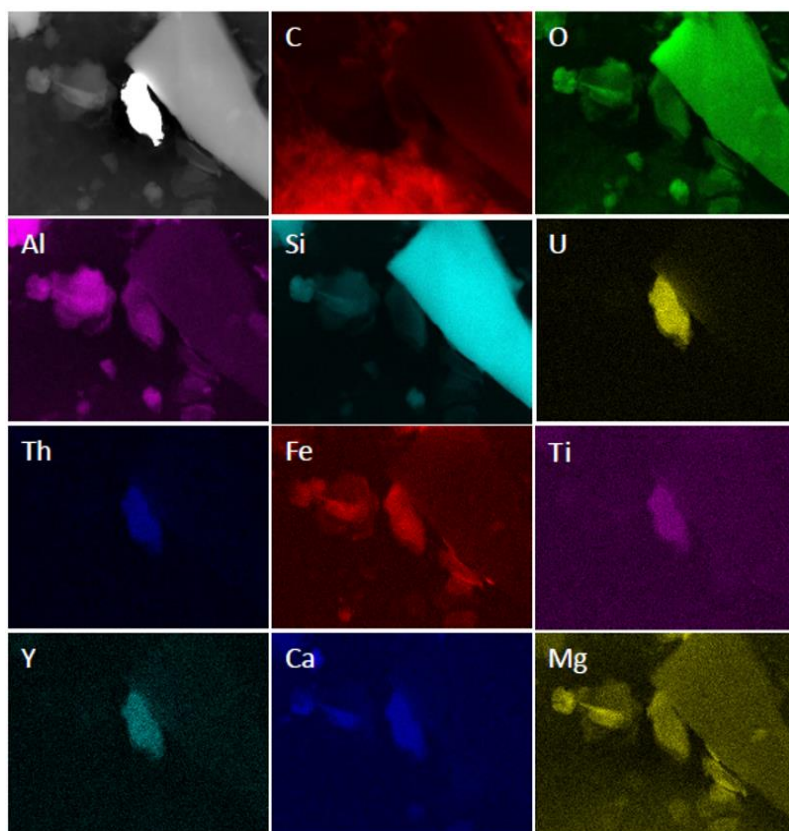


582

583 **Fig. S2** Electronic image, EDX spectrum and elemental mapping of the particle #3 identified as an U-bearing
 584 particle. The mapping shows qualitatively that some elements (C, O, Al, Si, Fe, Ti, Ca, Mg) detected in the EDX
 585 spectrum may come from surrounding particles, whereas Y and Th are obviously present in the particle. This is an
 586 indication that this U-bearing particle may be of natural origin

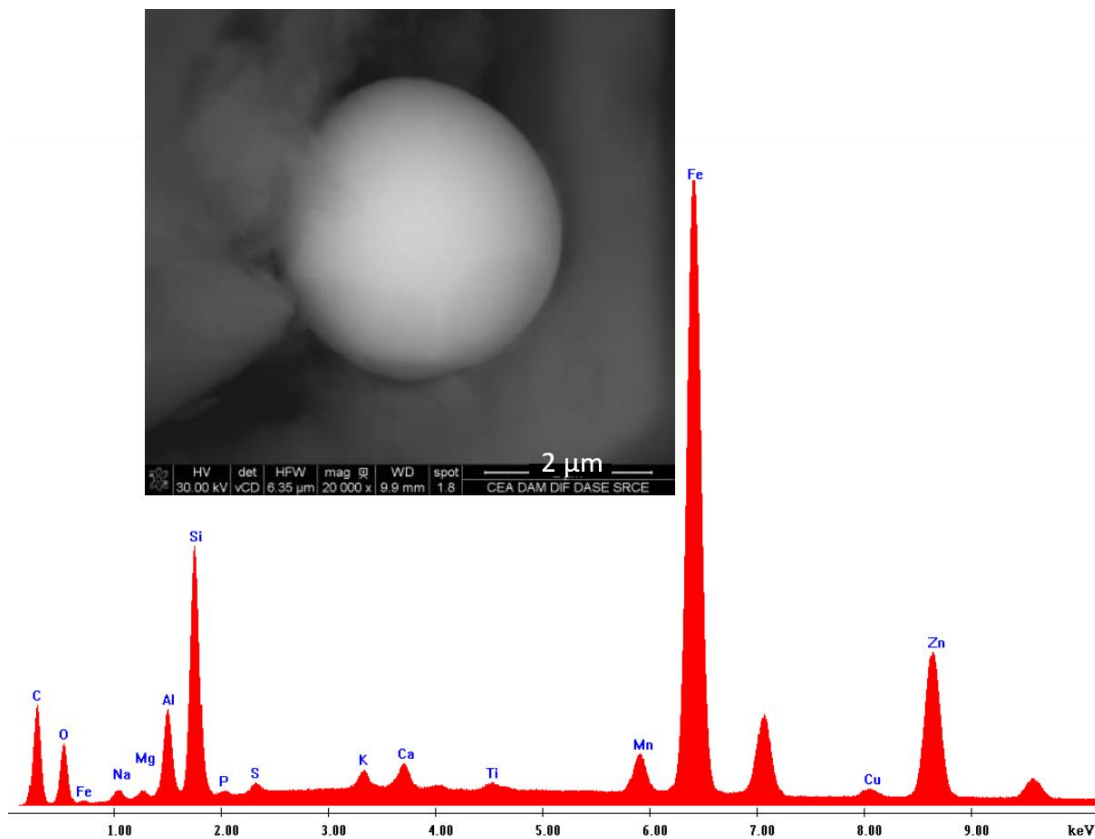


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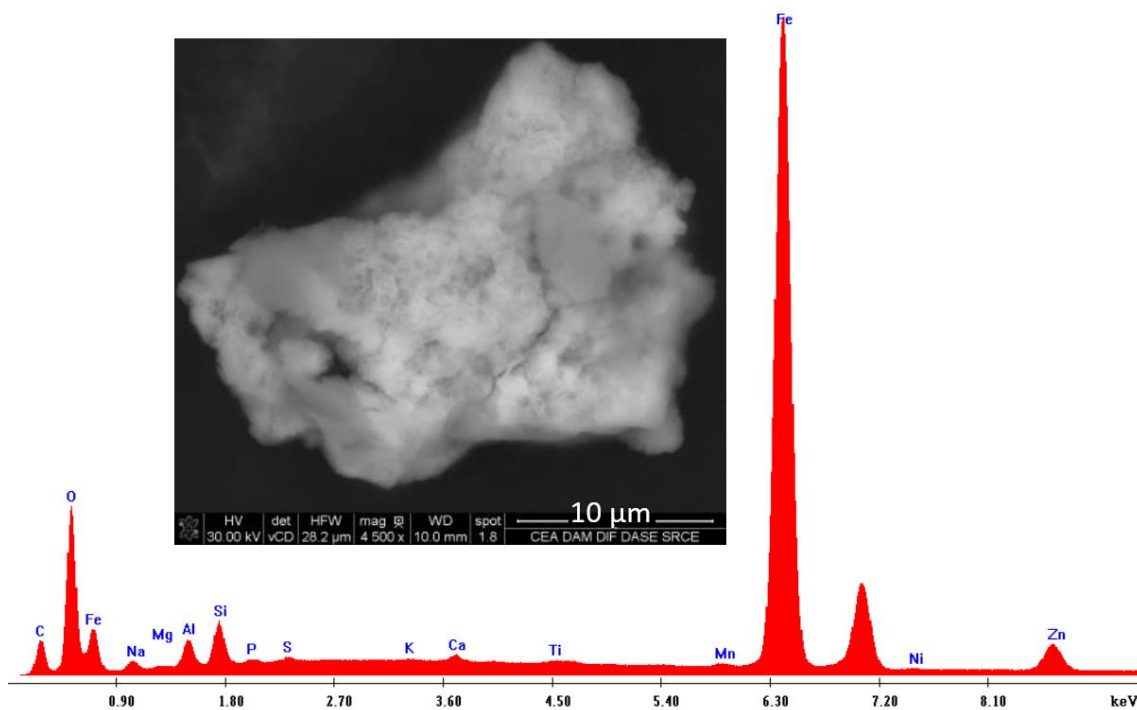


588

589 **Fig. S3** Electronic image, EDX spectrum and elemental mapping of the particle #3 identified as an U-bearing
 590 particle. The mapping shows qualitatively that all the detected elements detected in the EDX spectrum are
 591 obviously present in the particle. This is a strong indication that this U-bearing particule may be of natural origin

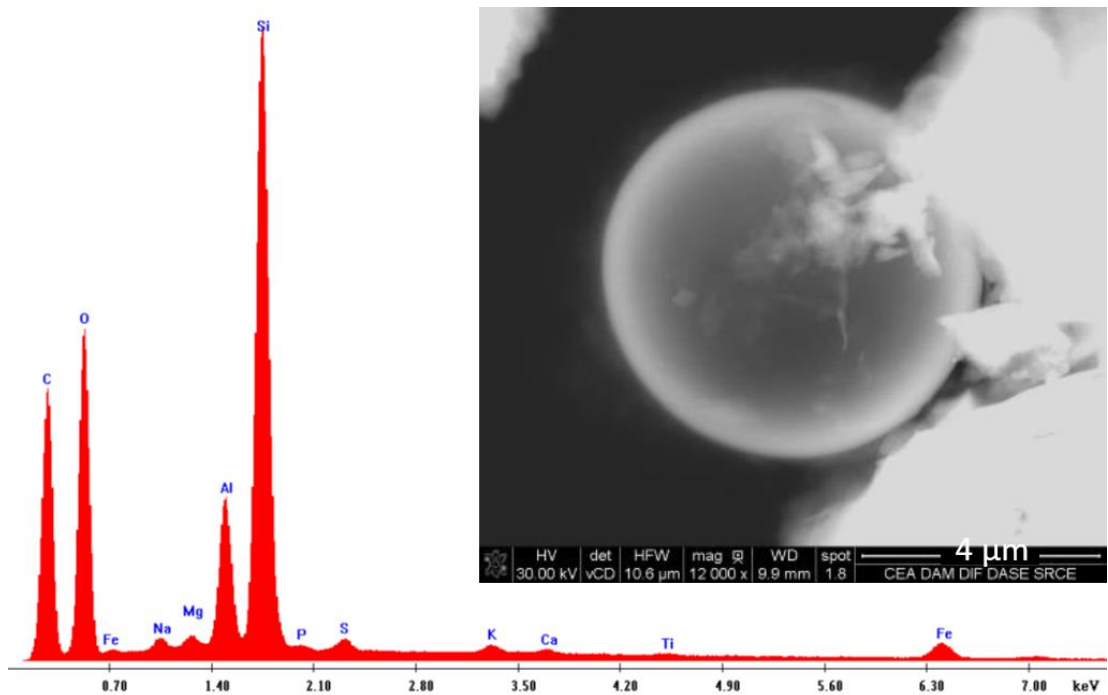


592



593

594 **Fig. S4** Examples of electronic images of FeZn particles and associated EDX spectra



595

596 **Fig. S5** Example of an electronic image of a spherical Si particle and associated EDX spectrum.