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Marine Ballini, Camille Chautard, Jérémy Nos, Vannapha Phrommavanh, Catherine Beaucaire, et al.. A multi-scalar study of the long-term reactivity of uranium mill tailings from Bellezane site (France). Journal of Environmental Radioactivity, 2020, 218, pp.106223. 10.1016/j.jenvrad.2020.106223 . hal-02735745

HAL Id: hal-02735745

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1 A MULTI-SCALAR STUDY OF THE LONG-TERM REACTIVITY OF URANIUM
2 MILL TAILINGS FROM BELLEZANE SITE (FRANCE)

3
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33 **Abstract**

34 The mill tailings from uranium mines constitute very low-level, long-lived, radioactive process waste. Their long-
35 term management therefore requires a good understanding of the geochemical mechanisms regulating the mobility
36 of residual U and ^{226}Ra . This article presents the results of the detailed characterization of the tailings resulting from
37 the dynamic leaching processes used on the ore of the La Crouzille mining division and stored at the Bellezane site
38 (Haute-Vienne, France) for over 25 years. A multi-scalar and multidisciplinary approach was developed based on a
39 study of the site's history, on the chemical, radiological and mineralogical characterizations of the solid fraction of
40 the tailings, and on porewater analyses. These were supplemented by thermodynamic equilibrium models to predict
41 the long-term mobility of U and ^{226}Ra . Weakly acidic (pH = 6.35) and oxidizing (Eh = 138 mV/SHE) porewaters had
42 a sulfated-magnesian facies ($[\text{SO}_4]_{\text{tot}} = 43 \text{ mmol/L}$; $[\text{Mg}]_{\text{tot}} = 33 \text{ mmol/L}$) with an accessory calcium bicarbonate
43 component (TIC = 25 mmol/L ; $[\text{Ca}]_{\text{tot}} = 13 \text{ mmol/L}$) and dissolved concentrations of uranium and ^{226}Ra of 12×10^{-6}
44 mol/L and 0.58 Bq/L respectively. Ultra-filtration at 10 kDa indicated the absence of colloidal phases. The
45 characterization of the tailings confirmed their homogeneity from a radiological, chemical and mineralogical point
46 of view. The residual U and ^{226}Ra concentrations measured in the solid were 160 ppm and 25 Bq/g respectively, in
47 accordance with the initial ore grades and mill yields, or more than 99% of the total stock. In terms of chemical and
48 mineralogical composition, the tailings were mainly composed of minerals from the granitic ore (quartz, potassium
49 feldspar, plagioclases and micas) in association with their weathering products (smectite and ferric oxyhydroxides)
50 and with neo-formed minerals following rapid diagenesis after neutralization of the tailings before their emplacement
51 (gypsum and barite). All these minerals are effective traps for the retention of U and ^{226}Ra . The uranium is distributed
52 partly in micrometer scale uraninite and coffinite refractory phases embedded in grains of quartz, and partly sorbed
53 to smectite and ferric oxyhydroxides. The ^{226}Ra on the other hand is trapped mainly within the barite. The aqueous
54 concentrations of U and ^{226}Ra could be described using a thermodynamic approach so that their long-term mobility
55 can subsequently be assessed by modeling. The paragenesis of the tailings could be seen to be stable over time with
56 the exception of neo-formed gypsum and calcite, which will gradually dissolve. The presence of retention traps
57 offering surplus capacity, *i.e.* smectite, ferric oxyhydroxides and barite, will maintain the U and the ^{226}Ra at very low
58 aqueous concentrations, even under oxidizing conditions. Moreover, the low permeability of the mill tailings leads,
59 in the case of ^{226}Ra , to behavior dictated only by the radioactive decay.

60

61 **Highlights (no more than 85 characters, including spaces)**

- 62
- U mill tailings from Bellezane (France) were studied 25y after their deposition (81 characters)
- 63
- U and ²²⁶Ra are immobile through retention process (50 characters)
- 64
- U mobility is constrained by sorption onto smectite and ferrihydrite (70 characters)
- 65
- ²²⁶Ra mobility is governed by coprecipitation into barite and radioactive decay (81 characters)
- 66

67 **Keywords (maximum of 6 keywords)**

68 Uranium, mill tailings, ²²⁶Ra, geochemical modeling, reactivity, retention

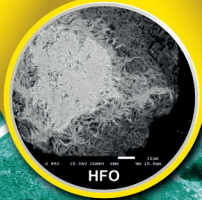
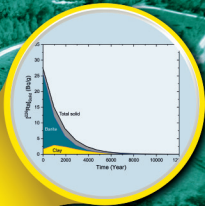
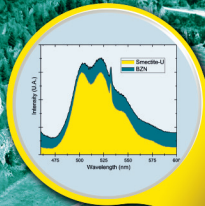
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71 **Graphical abstract**

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73



**Long term retention
of ^{226}Ra and U**

74 1 Introduction

75 Uranium mining took place in France throughout the second half of the twentieth century (1948-2001) with some
76 250 mining sites of varying sizes being operated. This yielded aggregate production of 76,000 tU at the national
77 level, roughly the equivalent of a year's worldwide output today (WNA, 2019). At the same time, this activity
78 generated nearly 160 Mt of mine waste rock and 52 Mt of mill tailings (AREVA, 2004).

79 During this period, the uranium mines were operated by conventional techniques, either as open-pit mines or
80 underground mine workings. The ore was then milled either by heap leaching at the mining sites, or by dynamic
81 leaching in eight processing plants or mills. The milling processes used were generally the same from case to case,
82 consisting, after crushing the ore, in an acid extraction process in a sulfuric and oxidizing medium, involving a series
83 of physico-chemical processes (mainly dissolution, oxidation, filtration, extraction, and concentration), leading to
84 the formation of "yellowcake" on the one hand, and to the production of mill tailings on the other. The latter therefore
85 corresponded to the fraction of the rock rejected after extracting most of the uranium through chemical processes.
86 These mill tailings were then stored near the ore processing plants, as is the case for mines operating today overseas
87 (see for instance Déjeant et al. (2016) for Niger and Robertson et al. (2019) for Canada).

88 Today, 17 storage facilities for mill tailings (referred to as Tailings Management Facilities or TMFs) are spread over
89 16 sites in France, generally located close to former production sites. Remediated in accordance with regulations on
90 ICPE-classified environmentally regulated sites (ICPE - Installations Classées pour la Protection de
91 l'Environnement), these TMFs are subject to environmental monitoring. Each TMF has a surface area of between
92 one and a few dozen hectares. Depending on the mining method used, these sites may hold between a few thousand
93 and several million tons of dynamic, static or combined process tailings (AREVA, 2004). This contrasts with current
94 uranium extraction methods, as nearly 50% of the world's uranium production is now produced by *In Situ Recovery*,
95 without production of mill tailings (WNA, 2019). The configuration chosen for these TMFs was determined
96 according to the topography of each mining site. For example, the tailings could be stored "in-pit" by filling in the
97 open pits of mined-out surface deposits, with or without a tailings dyke, or else in a thalweg dammed with a dyke.
98 They are capped with a vegetated solid cover or water layer (see for example Chautard et al. (2017) for France and
99 Robertson et al. (2019) for Canada). Finally, where tailings from dynamic leaching processes were cycloned, the
100 coarser fraction was used to backfill old underground workings or to create dams, while the finer fraction was stored
101 in tailings piles.

102 From a mineralogical and geochemical point of view, process tailings can be considered as milled ore that has
103 undergone oxidative dissolution through a sulfuric medium and has a low residual uranium content. Chemical
104 composition can sometimes be more complex because it depends on the nature of the ore undergoing the mill process,
105 the mining process used, and the operating history of the TMF. The vast majority of the stored materials therefore
106 consist of ore tailings, but may also contain a marginal proportion of slurry from water treatment stations. Indeed,
107 there are three main elements of concern (or EOCs) - both from a chemical and radiological standpoint - generally
108 associated with tailings: residual U, radon (^{222}Rn) and radium (^{226}Ra). Despite the high extraction yields achieved by
109 the mills, the residual U is generally present in the tailings on average at concentrations in the order of 5 to 25% of
110 that of the ore processed, i.e. in the order of 100 ppm, and may therefore present chemical toxicity in aqueous form.
111 In addition, the mill tailings also contain the other non-extracted radionuclides belonging to the two families of natural

112 uranium (^{238}U and ^{235}U) including radon (^{222}Rn) and radium (^{226}Ra). The installation of a solid cover or a water layer
113 limits the migration of radon in gaseous form. With its half-life (~ 1600 years) and high specific activity (3.66×10^{10}
114 Bq.g^{-1}), radium 226 is one of the main EOCs in the tailings solids. The tailings thus constitute very low-level, long-
115 lived, radioactive process waste.

116 Numerous studies have been conducted on the reactivity of U mill tailings (Fernandes et al., 1996; Abdelouas et al.,
117 1998; Donahue et al., 2000; Martin et al., 2003; Moldovan et al., 2003; Landa, 2004; Scheinost et al., 2006; Essilfie-
118 Dughan et al., 2010; Déjeant et al., 2014; Yan and Luo, 2015; Chautard et al., 2017; Liu et al., 2017). However, these
119 studies are mostly specific to the sites considered and to the associated ores and processes. Indeed, apart from the
120 uranium and radium, the reactivity of certain metals such as Mo, Ni, Se or As, which are sometimes present in
121 significant quantities in the ore and are still present in the tailings, mean that these are also EOCs, distinct from those
122 belonging to the ^{238}U radioactive decay chain.

123 Previous characterization work on ore tailings stored in France showed that they consist mainly of minerals inherited
124 from the original ore, as well as a smaller fraction of minerals (gypsum, clay minerals, metal hydroxides) that have
125 been neo-formed during rapid diagenesis after deposition (Somot et al., 1997, 2000; Nos et al., 2013; Ballini et al.,
126 2017; Lestini et al., 2019). Consequently, mill tailings constitute a highly anthropized and complex reactive system
127 for investigation, wherein diagenesis and weathering phenomena are observed.

128 More generally, the mobility of uranium and radium in the environment has been the subject of considerable scientific
129 research (see Langmuir (1978) and Langmuir and Riese (1985)). Uranium has a complex chemistry mainly governed
130 in the natural environment by redox and pH conditions. Insoluble under reducing conditions, it has higher mobility
131 in an oxidizing environment, exacerbated under acid or alkaline conditions. Additionally, the presence of inorganic
132 (carbonate, sulfate, phosphate, silicate, etc.) or organic complexing agents can also increase the solubility of uranium
133 and hence its mobility in the environment. However, due to its concentration at trace level in the natural environment
134 (in the order of a few ppm), the mobility of uranium, even in hexavalent form, is strongly affected by sorption
135 reactions at the surface of clay minerals (Catalano and Brown Jr, 2005; Schlegel and Descostes, 2009; Bachmaf and
136 Merkel, 2011; Tayal et al., 2019) or metal hydroxides (Ames et al., 1983a; Waite et al., 1994; Walter et al., 2003)
137 frequently encountered in mining environments. Uranium can also in some cases be sorbed to organic matter
138 (Cumberland et al., 2016; Bordelet et al., 2018), or else form very poorly soluble phosphate minerals (Murakami et
139 al., 1997; Cretaz et al., 2013). Due to its very low elemental concentration ($1 \text{ Bq/L} \sim 1.21 \times 10^{-13} \text{ mol/L} \sim 27.3 \text{ pg/L}$),
140 ^{226}Ra is regarded as an ultra-trace element with a fairly simple aqueous speciation (Molinari and Snodgrass, 1990).
141 The geochemistry of ^{226}Ra in the natural environment is exclusively governed by interface reactions such as sorption
142 on clay minerals (Ames et al., 1983b; Tachi et al., 2001; Reinoso-Maset and Ly, 2016; Robin et al., 2017), metal
143 oxides and oxyhydroxides (Ames et al., 1983b; Nirdosh et al., 1984; Sajih et al., 2014), carbonates (Jones et al.,
144 2011), organic matter (Bordelet et al. (2018) and references included), but also co-precipitation within sulfate-bearing
145 minerals (Zhu, 2004; Curti et al., 2010; Zhang et al., 2014; Brandt et al., 2015; Lestini et al., 2019) such as gypsum
146 ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), celestine (SrSO_4) and barite (BaSO_4). Unfortunately, it is still difficult to directly access the location
147 of ^{226}Ra at the mineral scale, although recent work focusing on alpha autoradiography points to some promising
148 possibilities with observations at the micrometer scale (Sardini et al., 2016; Angileri et al., 2018). Often the only
149 approach put forward for identifying the ^{226}Ra carrier phases is the use of sequential leaching, a method which
150 frequently leads to interpretation bias (Bacon and Davidson, 2008).

151 This article presents the results of the long-term reactivity study on dynamic process tailings resulting from the
152 milling of ore at the La Crouzille mining division and stored at the Bellezane site (Haute-Vienne, France). To conduct
153 this study, a multi-scalar and multidisciplinary approach had been devised. This had been based on an investigation
154 of the site's history, allowing an understanding of the composition of the tailings storage on a macroscopic scale, on
155 chemical, radiological and mineralogical characterizations of the solid fraction of the U mill tailings, and on
156 porewater analyses. These data were complemented by thermodynamic equilibrium modeling to better understand
157 the water-rock interactions, which in a second step allowed the long-term mobility of U and ^{226}Ra to be assessed
158 through the development of a 1D predictive model of reactive transport. This study therefore presents unique findings
159 in relation to the characterization and understanding of the long-term geochemical evolution of U mill tailings some
160 25 years after their emplacement. The findings were based on multi-year studies (Descostes et al., 2013; Nos et al.,
161 2014; Ballini, 2017) carried out under the French National Radioactive Materials and Waste Management Plan
162 (PNGMDR ; (ASN, 2019)).

163 **2 La Crouzille Mining Division and the Bellezane site**

164 The mining division of La Crouzille is located in Haute Vienne (France), within a 20 km radius of the town of
165 Bessines-sur-Gartempe (Figure SI-1). This is a crystalline zone in the northwestern part of the Massif Central
166 (Bavoux and Guiollard, 2003), characterized by large granitic intrusions, particularly rich in uranium, and that were
167 formed between 360 and 290 m.y. ago during the Hercynian orogenesis. From west to east, the mining division
168 comprises the Brême massif, the St-Sylvestre massif and the Marche (or Guéret) massif (Scaillet et al., 1996).

169 Most of the deposits developed within the La Crouzille mining division are concentrated in the St-Sylvestre massif
170 and more precisely in the two-mica (biotite and muscovite) St-Sylvestre leucogranite (formed 318 ± 15 m.y. ago). Its
171 chemical composition is shown below in Figure 1. In this massif, veins of lamprophyres (vein-type microgranular
172 magmatic rock) with biotite, pyroxenes and peridots, microgranite veins, with biotite and plagioclase phenocrysts,
173 and episyenites (de-quartzified granites), sometimes highly mineralized, present as columns or clusters, are also
174 observed (Scaillet et al. (1996) and Kanzari et al. (2017) and references included).

175 Mineralization consists of silicates or uranium oxides (coffinite and uraninite) at depth and accompanied by surficial
176 weathering minerals such as phosphates or hydrated uranium oxides (autunite and gummite) (Barbier and Ranchin,
177 1969). The mean uranium content of the ores in the La Crouzille division ranged from 0.49‰ in the Daumart-
178 Margnac sector and 7‰ for the Henriette mine (Figure SI-1) (Paucard, 2007).

179 The Crouzille mining division was the principal uranium production area in France with about twenty separate mining
180 operations, representing a production of 27,000 tU in the form of ammonium diuranate (ADU) containing 75%
181 uranium, for nearly 15 Mt of ore processed. This mining activity generated in addition nearly 57 Mt of mine waste
182 rock and 22 Mt of process tailings (AREVA, 2004; Kanzari et al., 2017).

183 Between 1958 and 1993, the ore from the La Crouzille mining division (average grade 1.66 ‰) was processed by
184 the SIMO mill (Société Industrielle des Minerais de l'Ouest, 95% yield (Bavoux and Guiollard, 2003)) at Bessines-
185 sur-Gartempe by an acid extraction process, which was either heap leaching (8,614,000 tons of ore) or dynamic
186 leaching (14,839,000 tons of ore) depending on the ore grade (Bavoux and Guiollard, 2003). In the case of dynamic
187 leaching, the ore was crushed and then ground to a pulp with a granulometry of under $450 \mu\text{m}$ (Bavoux and Guiollard,

188 2003). The pulp was then treated by adding sulfuric acid at 65°C in the presence of sodium chlorate as an oxidizing
189 agent. After filtration, the solid waste was washed, neutralized with lime (CaO) and transferred to a storage pond.
190 The processes changed very little during the entire operation of the mill.

191 The process tailings produced by the SIMO mill were stored at the Bessines industrial site (Lavaugrassse) from 1958
192 to 1978 and in the former open-pit mine of Brugeaud until 1987. Subsequently, two tailings management facilities
193 (TMFs) were created with the erection of peripheral dams at the Montmassacrot site (between 1987 and 1990) and
194 at the Bellezane site (BZN) (between 1989 and 1993) (Figure SI-1). In total, 1,546,000t of mill tailings are stored at
195 the BZN site, 97% of which are the product of dynamic leaching and take the form of fine clayey sand with a particle
196 size of under 450 µm.

197 Before becoming a tailings disposal site, the BZN site was an active mining site between 1975 and 1992 with seven
198 open-pit mines of various sizes as well as underground workings. The open-pit workings were partially backfilled as
199 mining progressed with both waste rock and mill tailings. In the case of pit MCO 68, this was from February 1989
200 to July 1990, and then for pit MCO 105 from August 1990 to July 1993 (Figure 1). The final remediation of the site
201 took place in 1996, when the process tailings in MCO 105 and MCO 68 were covered over with a layer of waste rock
202 both for mechanical protection (against erosion, intrusion) and for radiological protection (to limit radiation emissions
203 and radon migration). The storage facility, as well as the remodeled areas of the entire site, were covered over in
204 1998 with a layer of topsoil and then revegetated (Figure 2). Today, the BZN site, consisting of a TMF and waste
205 rock disposal site, is subject to environmental monitoring. Drainage water is discharged, after treatment, into a stream
206 (Les petites Magnelles), a tributary of the river Gartempe.

207 From a hydrogeological point of view, previous work in this area showed that the process tailings are saturated and
208 that their permeability is very low, in the range of 10^{-9} to 10^{-8} m.s⁻¹ (Ledoux and Schmitt, 2010). This was confirmed
209 notably by the strong correlation between atmospheric pressure and the piezometric level of the piezometer implanted
210 in the tailings (Figure SI-2), such a correlation being typical of media with very low permeability (Fatmi et al., 2008).
211 Water movements are therefore very limited within the TMF.

212 The mill tailings stored in the two open-pit mines at the BZN site were described as homogeneous in terms of particle
213 size (< 450 µm), mineralogy and chemistry (Somot et al., 1997, 2000). In fact, the ores from the two mining
214 operations, processed at the SIMO mill, had very similar chemical and mineralogical compositions, while the mill
215 processes were not significantly modified between 1989 and 1993, during which period the tailings were stored at
216 the BZN site.

217

218 **3 Methods and materials**

219 **3.1 Core drilling and sampling strategy for solids**

220 A sonic percussion borehole was drilled in April 2011 in the downstream part of the MCO 105 pit for the BZN 1
221 survey. Tailings samples were collected over the entire height of the storage, with a recovery rate of ~ 80%. The
222 sampling was carried out in 1.5 m long runs on average, which were dry-subdivided into sections of 30 to 50 cm in
223 length. Drilling, cutting and sampling techniques were chosen to avoid water inflows and preserve the sediment
224 structure.

225 The samples are composed of brown and ochre fine-grain tailings, with locally darker brown and black layers and a
226 high degree of homogeneity of facies. Dose rate measurements using a CANBERRA INSPECTOR 1000 (LaBr)
227 radiometric probe approximately every 25 cm showed slight variability with depth, with values ranging from 0.4 to
228 0.7 $\mu\text{Sv/h}$ for the first samples taken from 0 to 7.5 m deep (mine waste rock used as solid cover) and higher values
229 ranging from 1.3 to 4.1 $\mu\text{Sv/h}$ for at higher depth (process tailings in the strict sense). After observing the facies and
230 analyzing the dose rate of each section, thirteen of core samples were selected at regular two-meter intervals to be
231 representative of the entire height of the tailings storage (Figure 3). Two sections exhibiting a radiometric peak and
232 one section corresponding to a radiometric drop were also selected. Each section was divided longitudinally into two
233 equal parts for dose rate measurement and lithological observations. A total of 16 sections were sampled for chemical
234 analysis, and for mineralogical and radiological characterization (Figure SI-3 and Table SI-1).

236 3.2 Analysis of the solid samples

237 Samples were characterized using different complementary analytical techniques. Considering the chemical,
238 mineralogical and granulometric homogeneity of the samples, these characterizations were performed in some cases
239 on a reduced number of samples.

241 3.2.1 Particle size distribution

242 Only one specimen (BZN_1_13.25-14.75m_2T) was used for particle size characterization. This sample was selected
243 on account of its relatively high U content (240 ppm) and is deemed to be representative of all the samples taken.
244 The characterizations were performed by dry sieving on a total mass of 630 g, to avoid the dissolution of soluble
245 minerals such as gypsum and to avoid altering the chemical composition distribution within each grading category.
246 The sieving thresholds applied were: 2 mm, 400 μm , 250 μm , 100 μm and 40 μm . Once separated, the different
247 grading families were weighed and then subjected to chemical and radiological analyses.

249 3.2.2 Elemental and radiological compositions

250 The samples were previously ground in an agate bowl. After being fused with LiBO_2 and dissolved in acid solution.
251 Major and trace elements concentrations were determined by ICP-OES (Thermo Elemental IRIS radial) and ICP-MS
252 (Perkin-Elmer Elan 6000), respectively. Loss of ignition (LOI) measurements were complementary performed.
253 Analytical uncertainties range from 1 to 15% for ICP-OES and from 5 to 15% for ICP-MS. Total CO_2 (uncertainty
254 $< 5\%$), C_{org} (uncertainty $< 20\%$) and S (uncertainty $< 2\%$) concentrations were determined with a Leco SC 144DR
255 apparatus by calcining the sample under oxygen stream at 1400°C in the presence or not of an oxidant (iron
256 phosphate). For C_{org} , the measurement was carried out after elimination of the carbonates with HCl. The total
257 inorganic carbon (TIC) content was calculated from the difference between the total CO_2 and C_{org} concentrations.

258 The ^{238}U , ^{234}Th and ^{226}Ra concentrations were also determined on the previously ground samples, after a one-month
259 waiting period so that daughters ^{214}Pb and ^{214}Bi would be in equilibrium with their parent. The measurements were
260 made by gamma-ray spectrometry according to the NF ISO 18589-3 standard (apparatus comprising Canberra COAX
261 type N type EGC 35-195-R, Canberra BEGe type BE5030P and DSG type NGC 4021).

262

263 3.2.3 Mineralogy

264 As the BZN samples were already relatively fine, no grinding was necessary prior to characterization by X-ray
265 diffraction. The characterizations were performed in parallel with a Bruker D8 diffractometer (CREGU, Nancy) and
266 an X'Pert Pro Panalytical (IMPMC-UPMC, Paris), both with Cobalt anode. Two types of samples were analyzed: on
267 the one hand, non-oriented bulk rock powders used to determine the predominantly present mineral phases and, on
268 the other hand, fractions < 2 μm collected by wet granulometric separation on bulk samples, in the form of oriented
269 deposits to more accurately determine the presence of clay minerals. These oriented preparations were then treated
270 with ethylene glycol and heated to 550°C for 3 hours.

271 Seven tailings samples were studied using a scanning electron microscope (SEM) on a thin section and/or in powder
272 form. The observations were made on a Hitachi FEG S4800 device coupled with a wavelength dispersion
273 spectrometer (WDS). For thin sections, a JEOL JSM7600F scanning electron microscope was also used.

274 Uranium (VI) carrier phases were identified directly on samples fixed in resin used to make the thin sections using
275 time-resolved laser-induced fluorescence spectrometry (TRLFS) (Vercouter et al., 2017). A sorbed U-doped
276 montmorillonite was used as U(VI) reference compound already studied by Tayal et al. (2019). Measurements were
277 made using an arrangement featuring a 266 nm nanosecond excitation laser and collection of luminescence emission
278 through an optical fiber connected to a monochromator and an intensified CCD camera (Othmane et al., 2016).

279

280 3.3 Porewater chemistry

281 The porewater from the process tailings was sampled in July 2013 in piezometer ES85 capturing the core of the
282 storage located near the BZN 1 borehole using a WATERRA pump. A complete purge of the piezometer was
283 performed the day before the sampling. A second (partial) purge was carried out just before sampling, until the
284 physico-chemical parameters were stabilized. The physico-chemical parameters were measured online using a
285 HORIBA probe (model W-22XD) for pH, redox potential and temperature, a WTW TetraCon 325 electrode for
286 conductivity and a WTW FDO 925 electrode for dissolved oxygen. All the probes were pre-calibrated.

287 On site, immediately after sampling, the samples were filtered through a 0.2 μm pore-size filter. The samples were
288 also immediately ultrafiltered through 10 kDa using BIOMAX membranes for analysis of anions, organic carbon
289 (C_{Org}), major cations, metals, U and ^{226}Ra to verify the presence of colloids. All samples were acidified for
290 conservation (HNO_3 pH 2) except for the anion and C_{Org} fractions. The alkalinity was also measured by titration with
291 sulfuric acid immediately after field filtration allowing the total inorganic carbon concentration (TIC) to be
292 recalculated. The samples were then analyzed for anions by ion chromatography (DIONEX ICS 5000 - DX 500,
293 standard NF EN ISO 10304-1), the sulfate and phosphate ions being determined by photometry (ThermoFisher
294 AQUAKEM 250 sequential analyzer, NF T 90-040 and NF EN ISO 6878 standards). The concentrations of the major
295 cations (Na, K, Ca, Mg) were determined by flame atomic absorption (AGILENT AA240, standards NF T90-020
296 and NF EN 7980). Si and trace elements (Al, As, Ba, Cu, Fe, Mn, Mo, Sc, Se, Sr, V) were assayed by ICP-AES
297 (VARIAN 720ES, standards NF EN ISO 11885 and 2 N) but also by ICP-MS (THERMO ELECTRON X7, standard
298 ISO 17294-2) for rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb) and U.
299 Dissolved total organic carbon was quantified on a Shimadzu TOC VCPN analyzer (standard 79 N). Lastly, aqueous

300 ²²⁶Ra activities were determined by gamma-ray spectrometry after a one-month waiting period (see Section 3.2.2
301 Elemental and radiological compositions).

302

303 **3.4 Reactive transport modeling**

304 Modeling was carried out using PhreeqC software (Parkurst and Appelo, 1999) to describe the speciation and
305 distribution of U and ²²⁶Ra in the porewater and tailings system in thermodynamic equilibrium, and to evaluate U
306 and ²²⁶Ra concentrations over the mid-term and long-term using predictive calculations according to a 1D model for
307 reactive transport.

308 The thermodynamic database used for the construction of the geochemical models was the LLNL database (llnl.dat
309 4023 2010-02-09) for PhreeqC. The ionic strength correction model used was the extended Debye-Huckel model,
310 considered sufficiently accurate to predict the activities of aqueous species up to ionic forces of 0.3 to 1 molal
311 (Bethke, 2007). Sorption of major elements and Ba onto ferrihydrite (HFO) was taken into account via the surface
312 complexation model of Dzombak and Morel (1990) and the constants already incorporated in the LLNL database.
313 Sorption of U and ²²⁶Ra and carbonates onto ferrihydrite was implemented in the database considering surface
314 complexation data from Mahoney et al. (2009) and Sajih et al. (2014). Cation exchange reactions on montmorillonite
315 of the major cations, uranium and radium 226 were incorporated considering a multi-site ion exchange model
316 (Reinoso-Maset et al., 2012a, 2012b; Reinoso-Maset and Ly, 2014, 2016). The sorption constants used are indicated
317 in Tables SI-2 and SI-3. The incorporation of ²²⁶Ra into a solid solution (Ba,Ra)SO₄ was considered using the
318 concentrations of ²²⁶Ra, Ba and SO₄²⁻ measured in the tailings porewater and the total contents of Ba and Ra in the
319 tailings. The solid/solution distribution coefficient (D) for Ra, under thermodynamic equilibrium conditions is
320 expressed as follows:

$$321 \quad D = \frac{\frac{[Ra]_{solid}}{[Ba]_{solid}}}{\frac{[Ra]_{solution}}{[Ba]_{solution}}} = \frac{f_{BaSO_4} \cdot \gamma_{Ra} \cdot K_S^0_{BaSO_4}}{f_{RaSO_4} \cdot \gamma_{Ba} \cdot K_S^0_{RaSO_4}} \quad (1)$$

322 $K_S^0_{BaSO_4}$ and $K_S^0_{RaSO_4}$ are the respective solubility constants of BaSO₄ and RaSO₄, γ and f respectively representing
323 the activity coefficients of Ba, Ra in the aqueous solution and in the solid solution. Assuming a regular, diluted solid
324 solution, the activity coefficients in the solid solution are defined as follows: $\ln f_{BaSO_4} = 0$ and $\ln f_{RaSO_4} = a_0$, a_0 being
325 a parameter reflecting the deviation from ideality (Curti et al., 2010). A solid-solution model was therefore
326 implemented, with a Guggenheim mean parameter a_0 of 1.27 in agreement with values reported in Brandt et al. (2015)
327 and Vinograd et al. (2013) (e.g. $a_0 = 1.0 \pm 0.4$). The molar fraction in the solid solution was calculated and led to a
328 molar fraction of ²²⁶Ra in the solid solution of 4.6×10^{-7} . This results in a distribution coefficient of 0.21 in agreement
329 with values already reported in Lestini et al. (2019).

330 The geometry of the 1D transport model amounted to a column of 25 cells 1 m high, representing a vertical section
331 (height 25 m) of the process tailings in the open-pit mine MCO 105 under saturated conditions. The initial conditions
332 of the water-tailings system are described in Section 5.1 and correspond to the steady state of the pore solutions with
333 the mineral paragenesis observed in the tailings. The transport parameters were taken from Ledoux et Schmitt (2010),
334 namely a porosity of 0.33, a permeability of $5 \times 10^{-8} \text{ m.s}^{-1}$ (high assumption) and a hydraulic load gradient of 0.16,
335 which means a low flow velocity in the tailings of $8 \times 10^{-8} \text{ m.s}^{-1}$. It therefore requires 99 years to pass through the 25
336 m of tailings. In this simplified configuration, the phenomena of dispersion and molecular diffusion had been

337 disregarded, only the advective transport of the solutions being taken into account. Water percolates from the top to
338 the bottom of the column. The composition of the percolating solution (Table 1) is based on analyses of samples
339 taken in 2008 from the superficial granitic aquifer (ES60; Ledoux and Schmitt (2010)). The water is weakly
340 mineralized, containing sodium bicarbonate, of low ionic strength ($I = 1.69 \cdot 10^{-3}$ mol/L), slightly acidic ($\text{pH} = 6.31$)
341 and oxidizing ($E_h = 319$ mV/SHE). It is close to the solubility equilibrium for some aluminosilicates, including
342 smectites, feldspars and muscovite, quartz polymorphs, aluminum hydroxides, ferrihydrite, and barite and therefore
343 with the initial mineral assemblage used in the model (see Section 5.1 Current distribution of U and ^{226}Ra). Lastly, it
344 is under-saturated with respect to all uranium-carrying phases with a uranium concentration ($1.7 \cdot 10^{-8}$ mol/L) three
345 orders of magnitude lower than that of the tailings porewater ($1.19 \cdot 10^{-5}$ mol/L). In addition, the ^{226}Ra specific activity
346 is 0.2 Bq/L, which represents one third of the specific activity measured in the tailings.

347 The modeling was carried out over a total period of 230,000 years in order to better assess the long-term reactivity
348 of the tailings and in particular the processes at the interfaces regulating the aqueous concentrations of U and ^{226}Ra .
349 This time span is naturally longer than 16,000 years, i.e. 10 times the radioactive half-life of ^{226}Ra . A correction for
350 the radioactive decay of ^{226}Ra was performed retrospectively. Finally, production of ^{226}Ra from the residual stock of
351 U in the tailings was not considered.

352

353 **4 Geochemical and mineralogical characterization of the mill tailings**

354 **4.1 Composition of the porewaters**

355 The waters taken from the core of the tailings were weakly acidic ($\text{pH} = 6.35$), weakly oxidizing ($E_h = 138$ mV/SHE)
356 and exhibited high ionic strength (0.13 mol/L; electrical conductivity = 7630 mS/cm). The analyses displayed a
357 satisfactory ionic balance of 6.2 and 5.8% respectively for the fraction filtered at 0.2 μm and 10 kDa, allowing these
358 results to be exploited (Table 1). These waters had a sulfated-magnesian facies ($[\text{SO}_4]_{\text{tot}} = 43$ mmol/L ;
359 $[\text{Mg}]_{\text{tot}} = 33$ mmol/L) with a calcium bicarbonate component ($\text{TIC} = 25$ mmol/L ; $[\text{Ca}]_{\text{tot}} = 13$ mmol/L)). In addition
360 to chloride ions (8.5 mmol/L) and sodium ions (8.9 mmol/L), iron and manganese were also observed at significant
361 concentrations (7.9 mmol/L and 1 mmol/L respectively). The concentrations of uranium and ^{226}Ra were
362 $12 \cdot 10^{-6}$ mol/L and $7 \cdot 10^{-14}$ mol/L (0.58 Bq/L) respectively.

363 Figure SI-4 shows the concentration ratio of both 0.2 μm and 10 kDa fraction for each EOC. Concentration ratios
364 close to 1 (taking into account the measurement uncertainty) indicate an absence of colloidal phases in the sample.
365 Examination of the ratios between the two fractions also shows that uranium and ^{226}Ra are mainly present in dissolved
366 form. In the case of ^{226}Ra , the large variation in the ratio is due to the uncertainty of the measurement of this element
367 (40%), which nevertheless remains at low concentration. However, exceptions are observed for nitrates ($\sim 10^{-6}$ - 10^{-5}
368 mol/L) and copper ($\sim 10^{-9}$ - 10^{-8} mol/L) due to the cleaning protocol of the ultrafiltration device (successive rinses with
369 HNO_3 , distilled water, basic solution to remove organic matter, distilled water) and to the pollution from the
370 ultrafiltration system, respectively. Nonetheless, both elements concentration in each fraction remain at trace level.

371 4.2 Mill tailings

372 4.2.1 Chemical composition

373 The chemical composition of the mill tailings was very homogeneous over all the samples taken as shown in Figure
374 4. The samples were mainly composed of Si, Al, K, Ca, Fe, S, Na and Mg in accordance with the initial composition
375 of the ore. The average element contents measured are given in Table SI-4, as well as the minimum and maximum
376 levels. Levels of P, Ti and Mn were an order of magnitude lower (less than 1 %, by weight of oxide). The total CO₂
377 contents were also fairly low in the order of 0.5%. C_{Org} contents were also quite low (0.28%), reflecting TIC (Total
378 Inorganic Carbon) contents in the order of 0.22%. Concentrations of trace elements are available in Supplementary
379 Information (Table SI-4).

380 The average concentrations measured are quite close to those measured within the mineralized or non-mineralized
381 granites of the Saint-Sylvestre Massif, as shown in Figure 1. The only differences are in the measured concentrations
382 of S, Ca, TIC and LOI, which are much lower in the reference and mineralized granites than in the tailings (CaO: 0.9-
383 0.5% vs. 3.4-3.3% ; S: 0.0015-0.05% vs. 1.8-1.5% ; TIC : ~0.03-0.1% vs. 0.22-0.6 % ; LOI : ~0.7-3.3% vs. 9.5-
384 8.2%).

385 Ca and S concentrations are consistent with the presence of gypsum (CaSO₄.2H₂O) and to a lesser extent of calcite,
386 in agreement with the mineralogical characterizations presented below. This is illustrated in Figure 5a, where S and
387 TIC concentrations are indicated as a function of Ca content (expressed in mol/100g). A good correlation is observed
388 between S and Ca contents, with a S/Ca molar ratio slightly below 1, i.e. slightly below the S/Ca molar ratio in
389 gypsum (CaSO₄.2H₂O). On the other hand, the molar ratio (S+ TIC)/Ca is very close to 1, this excess of Ca being
390 interpreted by the distribution of Ca within other phases such as carbonated minerals (calcite). Additionally, the good
391 correlation LOI/S evidenced the presence of gypsum (see Figure 5b). Indeed, this mineral is strongly hydrated and
392 can therefore be first approximated using the simple parameter of LOI. Sulfur is also present as sulfides, but in much
393 smaller proportions (see Section 4.2.4 Mineralogical characterization).

394 These enrichments in Ca, S and TIC are due to the initial presence of a neutralizing limewash slurry in the process
395 tailings. The additional calcium reacts with the residual sulfur from the sulfuric acid leach to form gypsum (hydrated
396 mineral) which is consistent with the high Ca, S and LOI levels and mineralogical observations. The addition of lime
397 has also resulted, by increasing the pH, in the formation of carbonate precipitates in the slurries, by reacting with
398 CO₂ from the air, a source of carbon.

399 All the results of the chemical and radiological characterizations are presented in the form of an element correlation
400 matrix in Supplementary Information (Table SI-5). The correlation coefficients calculated confirm the presence of
401 two fractions: the first enriched in Si and Na ($R_{SiO_2-Na_2O} = 0.74$) corresponding to the residual ore, and a second
402 enriched in Ca ($R_{SiO_2-CaO} = -0.92$), Mg ($R_{SiO_2-MgO} = -0.83$), Fe ($R_{SiO_2-Fe_2O_3} = -0.93$), S ($R_{SiO_2-S} = -0.90$) and water content
403 ($R_{SiO_2-H_2O} = -0.92$) and LOI ($R_{SiO_2-LOI} = -0.94$) which is interpreted as tracing the presence of neo-formed minerals
404 including gypsum ($R_{S-CaO} = 0.94$, $R_{S-H_2O} = 0.87$, $R_{S-LOI} = 0.92$).

405 The other main correlations highlighted concern REE-type trace elements with Zr, Ti and P₂O₅ consistent with the
406 presence of accessory heavy minerals such as zircon, titanium oxide and monazite (see Section 4.2.4 Mineralogical
407 characterization).

408

4.2.2 U and ²²⁶Ra contents

The U and ²²⁶Ra concentrations measured were relatively constant for all the mill tailings samples (see Table SI-4) with mean values of 169 ± 61 ppm and 23 ± 15 Bq/g respectively. The significantly higher concentrations of U (292.4 and 239.3 ppm) were found at the highest dose rate values (at a depth of 9 and 14 m; see Figure 3). The measured values are consistent with the yields (90-95%) and average U content of the ore milled at the SIMO plant (1.66 ‰). Furthermore, the ²²⁶Ra activities measured are also of the same order of magnitude as those expected for an ore with an average grade of 1.66 ‰ at secular equilibrium before processing in the mill (20.7 Bq/g). An examination of the profiles of the [²³⁸U]/[²²⁶Ra] activity ratio, calculated from the ²³⁴Th activity measurements (assimilated to ²³⁸U activity), can be interpreted in terms of U extraction efficiency, but may also illustrate the presence of unprocessed ores and/or differential migration of the U and ²²⁶Ra (Figure 4). As the U was extracted during mining operations, the observed [²³⁸U]/[²²⁶Ra] ratio is logically low. The two most superficial samples (at depths of about 1 and 4 m) were close to radioactive equilibrium ([²³⁸U]/[²²⁶Ra] ~1 with U concentrations less than or equal to 30 ppm). Then, below 7 m in depth, the activity ratio was low and fluctuated little, ranging from 0.04 to 0.08. The cover over the tailings repository consists of mine waste rock whose [²³⁸U]/[²²⁶Ra] activity ratio is close to equilibrium, and therefore higher than that of the process tailings. The low and homogeneous [²³⁸U]/[²²⁶Ra] values observed in the tailings confirm respectively that the extraction of U during the mill process was effective and that in principle there was no differential migration of U and ²²⁶Ra.

The element correlation matrix (Table SI-6) also provides some insight into the distribution of ²²⁶Ra and U. Indeed, ²²⁶Ra concentrations were positively correlated with those of U ($R_{226\text{Ra-U}} = 0.80$), which is consistent with a fraction of ²²⁶Ra associated with refractory uranium minerals (see Section 4.2.4 Mineralogical characterization). However, the difference in concentrations between ²²⁶Ra and the other chemical elements analyzed does not allow for clear identification of reliable elemental correlations. Thus, considering Ba and Fe, which are in principle the chemical elements tracing the carrier phases at the origin of ²²⁶Ra retention (barite, ferric oxyhydroxides), no correlation was found ($R_{226\text{Ra-Ba}} = 0.11$ and $R_{226\text{Ra-Fe}_2\text{O}_3} = 0.51$), except with Mn ($R_{226\text{Ra-MnO}} = 0.76$). U concentrations on the other hand were correlated with those of Fe ($R_{\text{U-Fe}_2\text{O}_3} = 0.75$), As ($R_{\text{U-As}} = 0.80$) Mn ($R_{\text{U-MnO}} = 0.81$) and to a lesser extent with those of Ca ($R_{\text{U-CaO}} = 0.70$) and S ($R_{\text{U-S}} = 0.68$). They were also anticorrelated to Si ($R_{\text{U-SiO}_2} = -0.69$) and Na ($R_{\text{U-Na}_2\text{O}} = -0.61$) concentrations. The observed correlations between the concentrations of Mn, U and ²²⁶Ra reflect the high affinity of these elements with respect to ferric oxyhydroxides ($R_{\text{Fe}_2\text{O}_3\text{-MnO}} = 0.76$ and $R_{\text{Fe}_2\text{O}_3\text{-As}} = 0.91$). Thus, Mn would indicate the presence of ferric oxyhydroxides known for their retention properties for both As and Mn (Dzombak and Morel, 1990; Root et al., 2007).

These elemental correlations do not strictly allow to identify the U and ²²⁶Ra bearing minerals, as the volumes analyzed are too large to differentiate minerals unambiguously. It is more reasonable to attempt to associate U and ²²⁶Ra with the two previously identified fractions, that is, on the one hand, the inherited fraction of the ore (predominantly SiO₂ and Na₂O) and, on the other hand, the neo-formed fraction (enriched in CaO, S, Fe₂O₃). In this manner, ²²⁶Ra appears to be preferentially in the neo-formed fraction while uranium, as confirmed by the results of the particle size characterization, appears to be in both fractions.

4.2.3 Chemical composition of each particle size fraction

The majority of the particles had a size less than or equal to 400 μm (91% by mass) as shown in Figure SI-5. This result is consistent with the nature of dynamic process tailings, which are mainly composed of fine sands and fines (term used here to include silt and clay grades). This result should be considered as indicative because only one particle size analysis was conducted. Nevertheless, the study of the chemical composition of each granulometric class points to an enrichment of the smallest particle fractions with respect to LOI and Ca, S, Fe contents (LOI: from 12.7 to 17.4%; CaO: from 1.83 to 6.60%; S: from 0.65 to 3.48%; Fe_2O_3 : from 2.67 to 4.64%) associated with a decrease in Si, Na and K contents (SiO_2 : from 64.6 to 48.5%; Na_2O : from 1.57 to 1.24%; K_2O : from 6.72 to 4.70%), as observed in the overall analysis. The enrichments observed in TiO_2 and P_2O_5 are interpreted as a small increase in heavy minerals such as titanium oxides and monazite. Elemental enrichment was also visible for Ba (from 781 to 1190 ppm) as well as ^{226}Ra (from 15.7 to 65.8 Bq/g). Uranium concentration was higher in the 2000 μm fraction and to a lesser extent in the finest fraction. This results in a decrease in the $^{238}\text{U}/^{226}\text{Ra}$ activity ratio in the finest particle size fractions (from 0.29 to 0.05). These results, are interpreted as a concentration of ^{226}Ra mainly associated with barite type neo-formed or inherited reactive phases found in the finest fraction of the tailings dominated by gypsum while uranium is distributed within both fractions (inherited and neo-formed).

4.2.4 Mineralogical characterizations

Characterization by X-ray diffraction (XRD) confirmed the homogeneity of the set of samples which was consistent with the chemical characterizations. Representative diffractograms on total rock and fine fraction are presented in Figure 6. They underlined the presence principally of the minerals constituting the ore, namely quartz, potassium feldspar, plagioclases and micas, but also of the phases due to weathering of the ore (smectite, chlorite and kaolinite) and inherited from the milling process, such as gypsum. Iron oxides were observed in smaller quantities. Gypsum was not observed in the fraction below 2 μm . This is explained by the dissolution of this highly soluble mineral during the extraction of the fine fraction by wet process. The XRD did not detect any U-carrier phase.

Elemental and micromorphological observations using SEM (Figure 7) confirmed the results of the XRD characterizations. They highlighted the presence of the St-Sylvestre granite primary minerals, but also a fairly rapid diagenesis at the scale of the storage duration of the mill tailings. This was evidenced by the observation of weathering phases of inherited minerals such as the iron oxyhydroxides which had been neo-formed mainly within phyllosilicates (Figure 7). The accessory minerals were also visible at this scale of observation, namely zircons, barite, monazites and apatite-type rare earth phosphates. Occurrences of barite in the presence of neo-formed gypsum are neo-formed barite resulting from the neutralization slurries. This neo-formed barite coexists with inherited barites since the reference and the mineralized St-Sylvestre granites already contain significant levels of Ba in the form of barite (110 and 591 ppm respectively in the granites versus 839 ppm in the tailings samples) (Barbier and Ranchin, 1969).

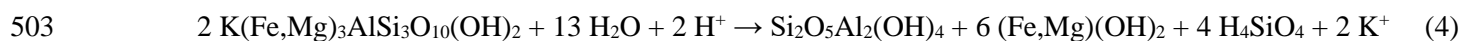
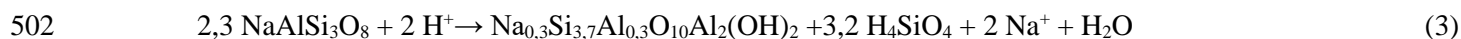
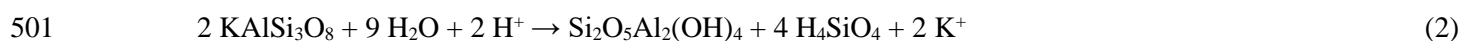
The uranium carrier phases were mainly either of the uraninite or coffinite type, generally at the micrometer scale, preserved within resistant minerals (quartz) or accessory minerals such as phosphates and zircons. These were inherited phases that had withstood the milling process. Their dimensions were smaller than the release mesh produced by grinding at 450 μm . Micromorphological analysis also indicated that sulfide-type minerals were generally not accessible to fluids.

485 *4.2.5 Evidence of the reactivity of clay minerals*

486 The mineralogical and elemental characterizations by XRD revealed the presence both of minerals inherited from
 487 the mineralized granites, and of sulfated, oxyhydroxide-type and also clayey neo-formed phases (in particular
 488 kaolinite and smectite). In this section, a focus is proposed on the neo-formation of clay minerals and their important
 489 U and ²²⁶Ra retention properties (Schlegel and Descostes, 2009; Reinoso-Maset et al., 2012; Reinoso-Maset and Ly,
 490 2014, 2016; Robin et al., 2017; Tayal et al., 2019).

491 The use of ternary diagrams makes it possible to highlight the weathering of feldspars (and micas) as well as the
 492 formation of kaolinite and smectite type clays and oxides using only the elemental concentrations determined in the
 493 solid samples. The poles Al₂O₃ - (CaO+Na₂O) - K₂O commonly used (Nesbitt and Young, 1984) could not be used
 494 because of the presence of gypsum in the samples. For this reason, results were plotted in Figure 8 on a (K₂O+Na₂O)
 495 - ([Al₂O₃-(Na₂O+K₂O)]/2) - ([Fe₂O₃+MgO+MnO]/3) diagram allowing for the consideration of an alkaline pole
 496 (representing feldspars) - (Na,K)AlSi₃O₈, an aluminous pole (representative of kaolinite - Si₂O₅Al₂(OH)₄) and
 497 finally a ferromagnesian pole (representative of micas - K(Fe,Mg)₃AlSi₃O₁₀(OH)₂). As a reminder, the weathering of
 498 feldspars and micas results in a depletion of alkaline elements (K and Na) and the formation of kaolinite and to a
 499 lesser extent smectite, schematically summarized below according to the respective balanced equations:

500



504

505 The data from the BZN tailings samples exhibited limited scatter, consistent with their homogeneity (Figure 8). Other
 506 analyses from samples from the St-Sylvestre massif are also documented (Boekhout et al., 2015; Kanzari et al., 2017).
 507 This is a non-weathered granite, an episyenite considered representative of the mineralizations, and a granitic waste
 508 rock subjected to varying stages of weathering since its first emplacement. In particular, the mineralogical and
 509 petrographic observations on these latter, more weathered samples, indicated the presence of smectite and kaolinite.
 510 The dots representing the tailings align well with the weathering profile ranging from the sound granites to the most
 511 weathered mine waste rock. They confirm the presence of clay minerals in greater quantities in the process tailings
 512 than in the ore.

513 The interpretation of the chemistry data led to consideration of the U within the minerals inherited from the ore, here
 514 in the form of uranium oxides and coffinite, but also within neo-formed minerals. As no uranium-carrying mineral
 515 phase was clearly identified, the presence of uranium sorbed to the surface of the smectite was investigated by
 516 TRIFS, a technique that can only detect the environments of U (VI). The superposition of the experimental spectra
 517 of the BZN_1_13.25-14.75m_2T sample with that acquired on the U-doped reference smectite confirmed the
 518 presence of U also sorbed to the surface of the smectite (Figure 9). Uranium also has a high affinity for ferric
 519 oxyhydroxides. However, these phases could not be investigated because iron is known to inhibit U(VI) fluorescence.

520

5 Long-term Mobility of U and ²²⁶Ra in Mill Tailings

Two types of modeling were performed. Firstly, the distribution of U and ²²⁶Ra was investigated in order to describe the diagenesis conditions observed today. This modeling was carried out in static mode, i.e. by considering the physico-chemical equilibria (saturation indexes, SI) regulating the chemical composition of the porewaters in contact with the tailings. In a second step, the mobility of the U and ²²⁶Ra was assessed using 1D reactive transport models simulating the long-term evolution of the tailings under leaching by inflow-water.

5.1 Current distribution of U and ²²⁶Ra

On the basis of the characterizations of the porewaters and tailings, it was shown that the majority (more than 99%) of the U and ²²⁶Ra was trapped in the solid fraction (Figure 10). However, the geochemical and mineralogical study of tailings alone was often insufficient to identify the compartments carrying U and ²²⁶Ra within the tailings, and thus to assess their mobility. Moreover, there was no unambiguous marker for these compartments that would allow them to be easily identified and quantified. Microscopic observations revealed the presence of some resistant uranium minerals (uraninite and coffinite) trapped mainly within quartz. The additional characterizations by TRLFS allowed us to determine that a part of the U is also sorbed to the smectite. However, this technique did not allow the sorption of U to the HFOs to be evidenced. It was impossible to perform this type of analysis for ²²⁶Ra because of its low elemental concentration (~ 700 ppt). However, its speciation can be studied indirectly by sequential leaching. These complex experiments are subject to significant analytical bias. The compartments targeted are not completely independent of each other and there may be elemental recombination phenomena during a wash, leading to distortion in yield results (Bacon and Davidson, 2008). Therefore, thermodynamic equilibrium modeling was performed to study the distribution of U and ²²⁶Ra in the BZN tailings.

The chemical composition of the porewater measured in the piezometer showed that the BZN tailings porewater was close to equilibrium with quartz polymorphs (SI = 0.2), aluminosilicates and especially smectite (SI = 0.1), calcite (SI = 0.0), ferrihydrite (SI = -0.4) and gypsum (SI = -0.1), and slightly supersaturated with barite (0.5). This is consistent with the mineralogy of the tailings previously described. The mineral assemblage composed of chalcedony (29%), potassium feldspar (35%), Ca-montmorillonite (25%), ferrihydrite (0.6 to 1.1% as per model discussed in the paragraph below), gypsum (9%), calcite (0.5%), and barite (0.15%), was used to describe the chemical reactivity of the solid-solution system within the BZN tailings throughout the interaction processes, and to simulate the chemical composition of the tailings porewater over time. The proportions of the mineral phases in the equilibrium assemblage were calculated from the elemental composition of the tailings. Thus, Si and Al were divided between clays, chalcedony, potassium feldspar (representing all the feldspars and muscovite) and the Ca-montmorillonite (representing all the clay minerals). Mg and K were attributed to the Ca-montmorillonite and potassium feldspar respectively. Na was artificially transferred to the sodium feldspars. Fe was attributed to ferrihydrite, while S, Inorganic C and Ba were attributed to gypsum, calcite and barite respectively. Sorption of major elements and traces (U and ²²⁶Ra) to the ferrihydrite and montmorillonite had also been taken into account in the reactive paragenesis. Thus, the calculated composition of the water in equilibrium with this mineralogical assemblage, given in Figure SI-6 and Table 1 was very close to that of the porewater analyzed.

The mean U concentration measured in the solid was 160 ppm, of which 83 ppm (calculated with a yield of 95% and an initial content of 1.66‰) could be borne by highly insoluble resistant phases as highlighted by the preceding

559 mineralogical characterizations. Therefore, a low model (Min) taking into account the presence of resistant phases
560 and a high model (Max) not taking them into account were presented. The only difference between these two models
561 was the concentration of ferrihydrite. For the high model, the quantity of iron was carried exclusively by ferrihydrite
562 while for the low model, the iron was distributed between pyrite (FeS_2) and ferrihydrite, respecting the sulfur balance.
563 The quantity of ferrihydrite was 0.6% for the high model and 1.1% for the low model.

564 Thus, the speciation calculation carried out in the BZN porewaters indicated that uranium in solution was found
565 exclusively in hexavalent form at a concentration of 1.2×10^{-5} mol/L. Due to the high fugacity of CO_2 , carbonate
566 complexes were in the majority ($\text{UO}_2(\text{CO}_3)_3^{4-}$: 78.5 % ; $\text{UO}_2(\text{CO}_3)_2^{2-}$: 21 % ; UO_2CO_3 : 0.5 %). However, calcium-
567 uranyl-carbonate ternary complexes were not included in the model due to the high degree of uncertainty about their
568 formation constant. Analysis of the saturation indices suggested that the U concentration was not constrained by any
569 equilibrium with a pure mineral phase, as no uranium phase was in equilibrium. Therefore, surface sorption of clay
570 minerals and HFOs was considered to explain the U concentrations measured in the solid fraction of the tailings and
571 the porewaters in accordance with the mineralogical and TRLFS characterization. The amount of sorbed U was
572 calculated by considering water in equilibrium with reactive mineral paragenesis and including the sorption
573 mechanisms. In this way, the concentration in the solid phase (in equilibrium with the imposed concentration in
574 solution of 1.2×10^{-5} mol/L) was correctly reproduced (160 ppm), of which 20 to 37% was sorbed to the clay minerals
575 and 63 to 80% was sorbed to the HFOs (Figure 10) according to the model.

576 As with the U, the specific activity of the ^{226}Ra present in the process-resistant phases was calculated and was
577 approximately 1 Bq/g. The concentration in ^{226}Ra , present at ultra-trace concentration in the environment, could not
578 be constrained by the solubility of a pure ^{226}Ra phase. Therefore, other mechanisms such as the co-precipitation of
579 ^{226}Ra in barite, sorption of ^{226}Ra to HFOs and clay minerals were taken into account in order to reproduce the ^{226}Ra
580 specific activity in the solid. All of the ^{226}Ra and Ba present in the solid tailings were considered to be associated
581 with the solid solution $(\text{Ba,Ra})\text{SO}_4$. Under these conditions, estimation of the ^{226}Ra concentration in porewater gave
582 0.68 Bq/L (Table 1) while over 97.2% of the ^{226}Ra stock was associated with the solid solution of $(\text{Ba,Ra})\text{SO}_4$, with
583 clay minerals and HFOs respectively accounting for 2.8 % and 4.10^{-5} % (Figure 10). Finally, the concentration of
584 SO_4 imposed by the solubility balance of gypsum explained the predominance of ^{226}Ra in the form of the aqueous
585 complex RaSO_4 . The latter therefore promoted equilibrium with the solid solution $(\text{Ba,Ra})\text{SO}_4$.

586 These calculations confirmed the distribution of U and ^{226}Ra in the mill tailings, with over 99.9% of the U and the
587 ^{226}Ra in the solid fraction, divided regardless of the model between the resistant minerals, the clay minerals, iron
588 hydroxides, and, in the case of ^{226}Ra , in the barite. The concentrations of U and ^{226}Ra in solution, reproduced
589 according to the chemical equilibria with the minerals mentioned above, constituted a very small stock in the order
590 of 10^{-4} %.

591

592 **5.2 Evolution of U and ^{226}Ra distribution over time**

593 A 1D reactive transport model to simulate the effect of percolation of granitic water within the tailings was run over
594 a period of 230,000 years to evaluate the long-term reactivity of the U and ^{226}Ra and thus their mobility.

595 5.2.1 *Evolution of the geochemical system*

596 The variations in the chemical composition of the different compartments (aqueous, surfaces and mineral phases) of
597 the last cell of the column modeled during the percolation of the granitic water are presented in Figure 11.

598 The percolation of weakly mineralized granitic water within the Bellezane mill tailings led, as expected, to a
599 significant decrease in the ionic strength of the porewater, down to an ionic strength of the same order of magnitude
600 as that of the granitic waters (Figure 11a). The facies of the porewater, initially sulfated-magnesian, evolved as the
601 equilibrium between the solid phase, the liquid phase, and the reactive surfaces changed and gradually converged
602 with the facies of the percolating granitic water. The principal minerals from the mineral paragenesis did not undergo
603 any significant dissolution or precipitation during the simulation period (Figure 11c). Only the gypsum and then the
604 calcite were fully dissolved. The dissolution of the gypsum and the progressive dissolution of calcite led to a slight
605 increase in pH from 6.3 to 7.2 (Figure 11b). In a second step, when the gypsum was completely dissolved (23,000
606 years), the pH increased to 8.5 for the entire calcite dissolution period, i.e. up to about 100,000 years, then reduced
607 to a pH of around 6.6 at 150,000 years. This last decrease in pH was related to cation exchange reactions on the
608 surface of clay minerals and more particularly to the preferential desorption of Ca, resulting from the dissolution of
609 the gypsum and calcite, to the detriment of protons (Figure 11d). Finally, this slow decrease in pH was explained by
610 the low concentrations of major ions in granitic water, not allowing sufficiently rapid redistribution of the initially
611 sorbed cation populations in favor of H^+ , K^+ and Mg^{2+} . This was also verified to a lesser extent for the Ca sorbed to
612 the ferric oxyhydroxides and also for the carbonates.

613

614 5.2.2 *Uranium mobility*

615 The modification of the chemical equilibria resulting from the percolation of granitic water within the tailings
616 generated a redistribution of U between the different compartments (sorption to clay minerals, sorption to iron
617 oxyhydroxides, resistant uranium-bearing minerals, all of these minerals having been evidenced within the tailings).
618 The evolution of this distribution within the last cell of the column over time is given in Figure 11e and f for the two
619 models previously discussed (low model and high model). The "total solid" part represents the sum of the fractions
620 sorbed to the clay minerals and ferric hydroxides as well as the U contained in the resistant phases when these are
621 taken into account (Min model).

622 Percolation of weakly mineralized granitic water with low uranium concentration within the BZN tailings was not
623 sufficient to leach the uranium from the solid fraction, even if the uranium-bearing phases that were resistant to the
624 process were not taken into account (low model), and despite the prevailing oxidizing conditions. Irrespective of the
625 model considered, the U concentration in the solid was in the order of 160 ppm throughout the simulation period and
626 varied only slightly (1.8% decrease in the total amount of U in the solid). The uranium was thus sequestered
627 alternatively by two traps: sorption to ferrihydrite and sorption to clay minerals (Figure 11f). U sorption to iron
628 oxyhydroxides was predominant throughout the dissolution of gypsum and calcite (Figure 11c). The fraction sorbed
629 to the iron oxyhydroxides then decreased as the pH decreased (Figure 11b) while the fraction sorbed to the clay
630 minerals increased (Figure 11f). Therefore, as a function of pH, the evolution of the sorbed U fractions was anti-
631 correlated, the U being trapped alternatively on the iron oxy-hydroxides and clay minerals. The increase in pH and

632 the increase in the concentration of calcium in solution generated inhibited the sorption of uranium to clay minerals
633 during this period.
634 Dissolved U equilibrium concentrations decreased significantly in several stages in accordance with its retention on
635 the iron oxyhydroxides and clay minerals. Thus, after a little over 150 years, concentrations reached $\sim 10^{-6}$ mol/L,
636 then decreased during the gypsum dissolution phase ($\sim 8 \times 10^{-8}$ mol/L up to 23,000 years), and again during the
637 progressive dissolution of the calcite ($\sim 6 \times 10^{-8}$ mol/L up to 100,000 years; Figure 11e). When all the calcite was
638 dissolved and the pH was returned to pH 6.6 (150,000 years), the dissolved U concentration was stabilized at 10^{-8}
639 mol/L, which is close to the U concentration of the percolation solution.

640

641 5.2.3 Radium 226 mobility

642 Radioactive decay mainly governs the long-term evolution of ^{226}Ra mobility. The simulation period considered here,
643 230,000 years, goes well beyond ten radioactive periods of ^{226}Ra . However, in order to better understand the role of
644 each of the phases of ^{226}Ra sequestration, and to study the influence of ^{226}Ra in the percolation waters, several models
645 were performed without taking into account the radioactive decay. The main results are also presented in Figures 11g
646 and h.

647 Whichever model is considered (*e.g.* Min model or Max model), the ^{226}Ra always remained sequestered over time.
648 Indeed, the high sulfate concentration resulting from the dissolution of gypsum allowed the non dissolution of barite.
649 However, the solid solution $(\text{Ba,Ra})\text{SO}_4$ entered equilibrium with the percolation water, showing a low level of ^{226}Ra
650 activity. This therefore explained the decrease in the specific activity of the ^{226}Ra within the barite, in favor of sorption
651 to the clay minerals (Figure 11h). Therefore, these retention mechanisms maintained a low aqueous concentration of
652 ^{226}Ra , systematically below that measured in this study (< 0.68 Bq/L) during 150,000 years (~ 100 radioactive decay);
653 see Figure 11g for modeling results.

654 This mechanism was accelerated once the gypsum was completely dissolved (23,000 years), with SO_4 concentrations
655 no longer allowing the RaSO_4 complex to be predominant and more conducive to the establishment of the solid
656 solution $(\text{Ba,Ra})\text{SO}_4$. The aqueous concentration of ^{226}Ra became almost negligible. The decrease in pH to 6.6 after
657 the complete dissolution of the calcite and the desorption of Ca^{2+} ions (150,000 years), also led to a slight desorption
658 of ^{226}Ra which was in turn co-precipitated within the residual barite. The solid solution $(\text{Ba,Ra})\text{SO}_4$ again constrained
659 the ^{226}Ra solution concentration, which then increased to values close to the concentrations initially observed (~ 1.4
660 Bq/L).

661 Additional modeling was performed with percolation water not containing ^{226}Ra . These models yielded the same
662 results as those presented above (see Figure SI-7) indicating that the redistribution of ^{226}Ra and in particular its re-
663 dissolution after 150,000 years was mainly governed by the initial source term here consisting of the mill tailings.

664 On this basis, the results of the modeling were then corrected for the radioactive decay for each compartment
665 investigated (Figure 11i and j). As expected, ^{226}Ra activities decreased more rapidly, with a consistently verified
666 distribution between barite and clay minerals and concentrations in solution in the order of natural background noise
667 after three radioactive periods.

668 All these results (Figures 11g - 11j) indicated that the minerals with retention properties with respect to ^{226}Ra , present
669 in the ultra-trace concentration, were in surplus: barite, clay minerals and ferric hydroxides. The ^{226}Ra was easily

trapped as a function of the chemical evolution of the system and in particular the pH. When radioactive decay was taken into account, the specific activity of ^{226}Ra in the tailings was in the order of 1 Bq/g from 5,000 years onwards, while the concentration in solution was less than 0.2 Bq/L from 1,800 years onwards (Figures 11i and 11j).

5 Conclusions

This multi-technical and multi-scalar study of the Bellezane mill tailings confirmed their chemical stability more than 25 years after emplacement thanks to rapid diagenesis. They remained homogeneous from the point of view of chemical, mineralogical and radiological composition. Indeed, the minerals inherited from the ore (quartz, potassic feldspar, plagioclases and micas) were observed in association with their initially present or neo-formed weathering products (mainly clay minerals such as smectite, chlorite and kaolinite as well as iron oxyhydroxides), and coexisting with neo-formed minerals following milling of the ore and neutralization of the tailings before their emplacement, such as in the case of gypsum (and to a lesser extent barite also present in the ore). All these minerals are effective traps for retention of U and ^{226}Ra . The residual uranium (160 ppm) and ^{226}Ra (25 Bq/g) in the solid phase after treatment represented in fact more than 99% of the total stock leading to concentrations in the porewaters of 12 $\mu\text{mol/L}$ and 0.58 Bq/L respectively for U and ^{226}Ra .

The long-term chemical reactivity of mill tailings could be described using a thermodynamic approach including solubility equilibria and also sorption and coprecipitation reactions in the case of ^{226}Ra . The modeling carried out in this study confirmed the surplus presence of mineralogical traps (smectite, ferric oxyhydroxides and barite in the specific case of ^{226}Ra) which, as the porewater chemistry evolves under the dissolution of gypsum and calcite, will maintain the concentrations of U and ^{226}Ra in solution at low levels, even under oxidizing conditions, normally favorable to the migration of U(VI). In addition, the low permeability of the mill tailings stored within the former Bellezane open-pit mines led to mobility, in the case of the ^{226}Ra , being governed mainly by radioactive decay, since the estimated flow rates within the tailings are in the region of $8.10^{-8} \text{ m.s}^{-1}$.

These results will in the future be complemented by more detailed characterization of the tailings, in particular by X-ray absorption spectroscopy and alpha autoradiography coupled with sequential leaching experimentation.

6 Acknowledgements

The authors would like to thank ORANO Mining's AMF department (Bessines sur Gartempe, France) for providing access to the Bellezane site and for their assistance in carrying out all the sampling work. Thanks also to Martine Gérard of IMPMC for her valuable expertise in the characterization of clay minerals.

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877 **8 Figure and Table captions**

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879 according to Boekhout et al. (2015) and Kanzari et al. (2015)).

880 Figure 2. Bellezane site in (a) operation, (b) during backfilling of pits MCO 105 and 68 with tailings (red color), and (c) after remediation.
881 Tailings core collected during this study in (d). The location of the BZN 1 borehole in the MCO 105 pit is given in (c).

882 Figure 3. Dose rate measured on core as a function of depth. The grey dots represent the samples that have undergone full characterization.

883 Figure 4. Elemental chemical composition of BZN tailings, $[U]_{\text{solid}}$, $[^{238}\text{U}]_{\text{solid}}/[^{226}\text{Ra}]_{\text{solid}}$ mass activity ratio and $[^{226}\text{Ra}]_{\text{solid}}$ as a function of
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890 Figure 7. SEM images of Bellezane tailings. In the center, an overall view completed by details of inherited phases and secondary phases
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907 **9 Supplementary Information Figure and Table captions**

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911 characterization.

912 Figure SI-4. Ratios of concentrations measured in the porewater fraction filtered at 10 kDa and 0.2 μm , sampled in piezometer ES85.

913 Figure SI-5. Particle size distribution (a), $[\text{}^{238}\text{U}]/[\text{}^{226}\text{Ra}]$ mass activity ratio (b), major (c) and trace (d) element concentrations in each of the
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919 figures.

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924 (Reinoso-Maset et al., 2012a and 2012b).

925 Table SI-4. Mean (C_{mean}), minimum (C_{min}) and maximum (C_{max}) elemental levels measured in BZN samples. Mean values are accompanied
926 by the standard deviations. C_{org} and LOI denote organic C content and loss on ignition respectively.

927 Table SI-5. Trace-level element concentrations measured in mill tailings samples (D. L. stands for detection limit).

928 Table SI-6. Elemental correlations calculated from the chemical and radiological characterizations of the mill tailings.

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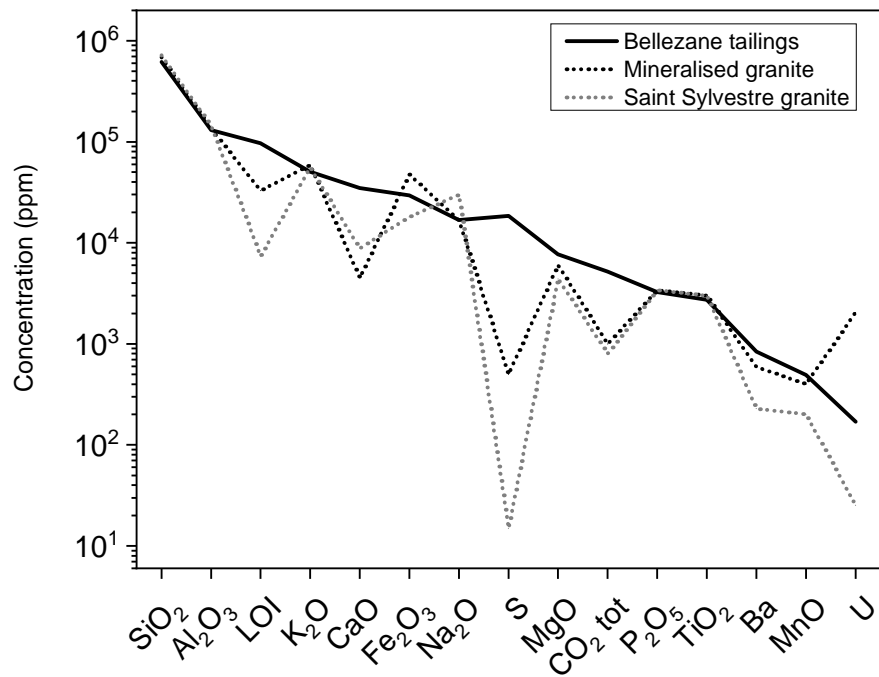


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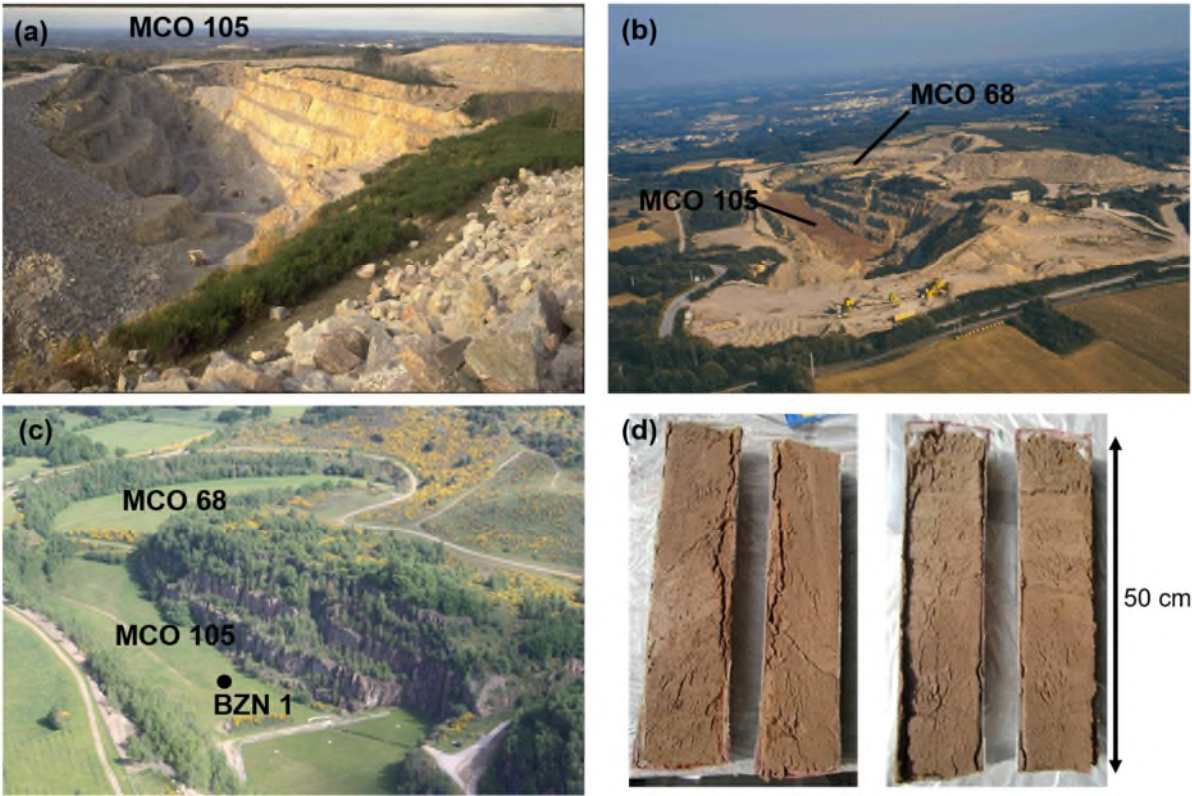


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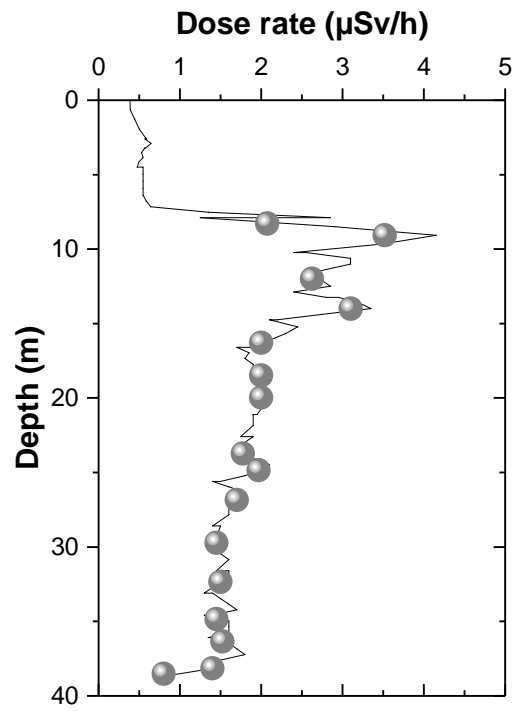


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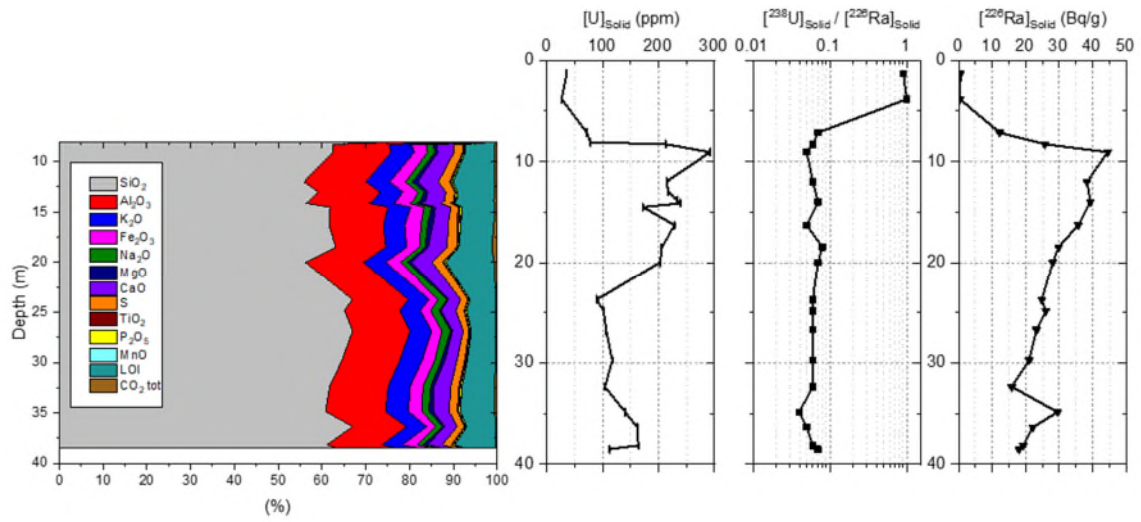


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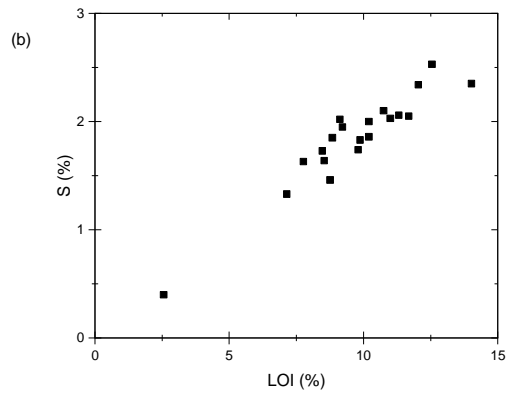
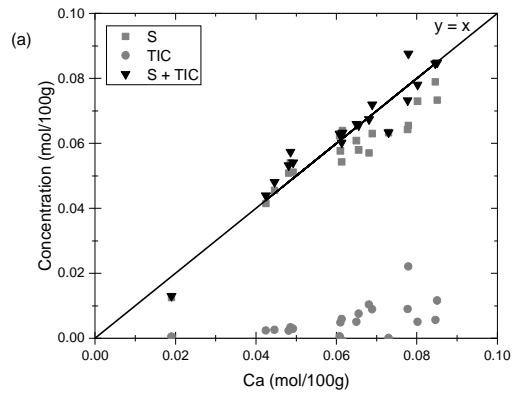


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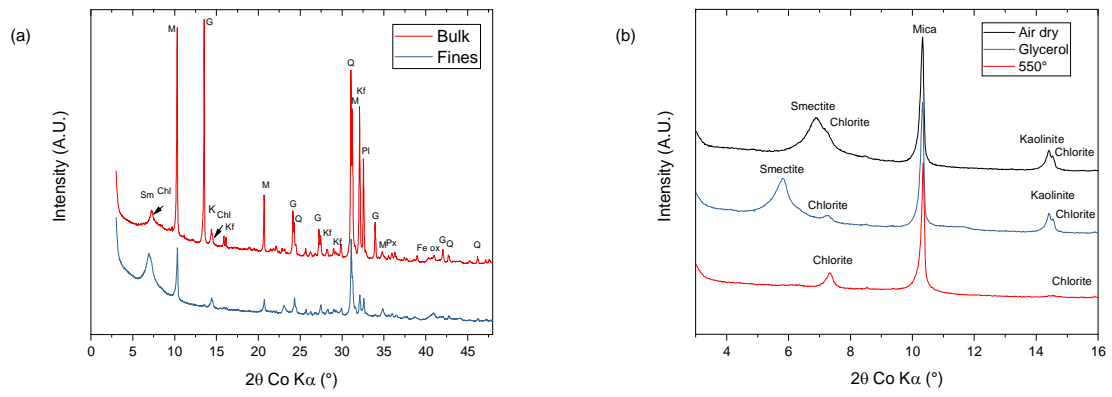


Figure 6. (a) Comparisons of X ray diffraction patterns of the bulk and the clay fraction (<math><2\ \mu\text{m}</math>) and (b) clay mineralogy on oriented air-dried, glycolated and heated of tailing sample BZN_1_13.25-14.75m_3T. Abbreviations: Sm: smectite, Chl: Chlorite, G: Gypsum, K: Kaolinite, M: Mica, Q: Quartz, Kf: K-felspar, Pl: Plagioclase, Fe ox: Fe oxide, Px: Pyroxene.

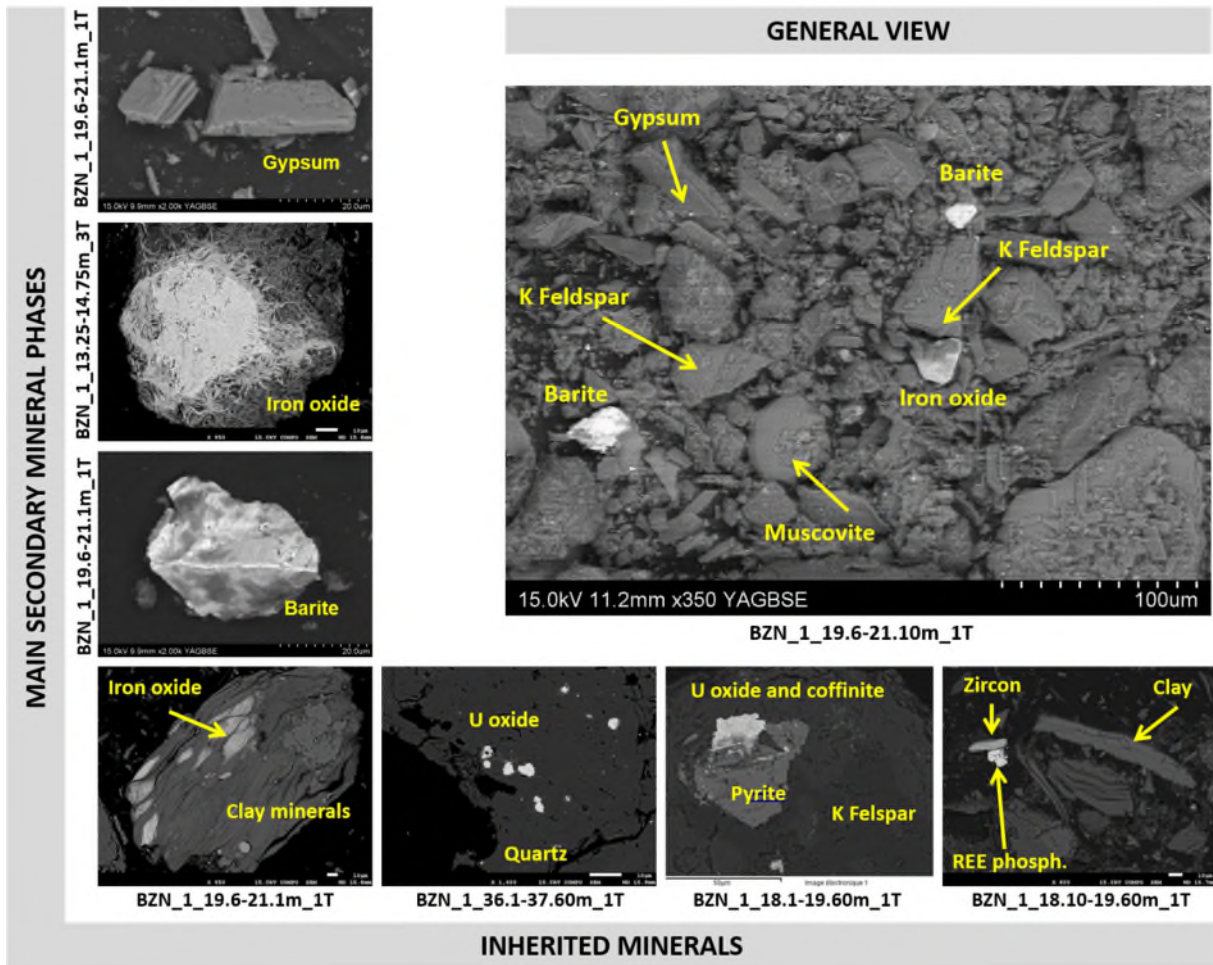


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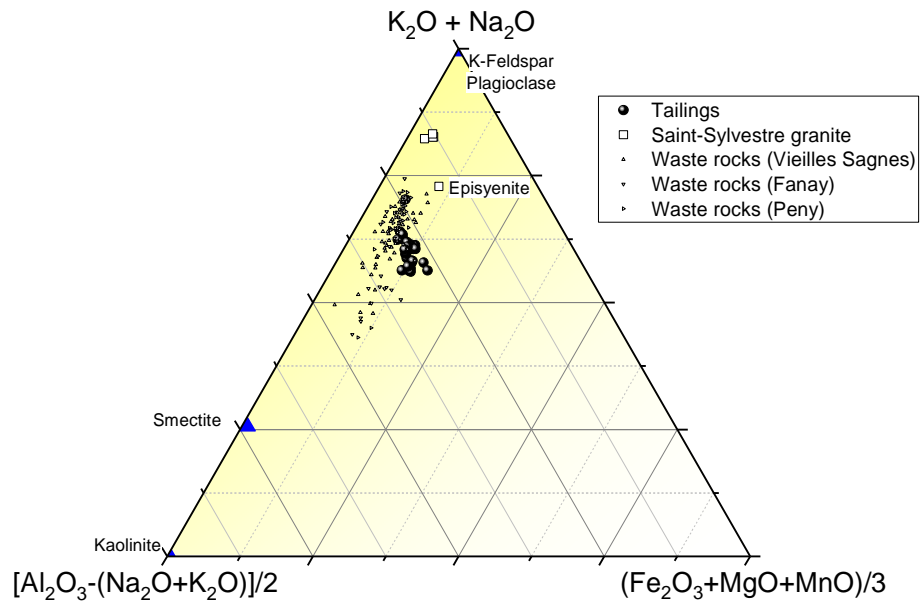


Figure 8. Ternary diagram (K_2O+Na_2O) - ($[Al_2O_3-(Na_2O+K_2O)]/2$) - ($[Fe_2O_3+MgO+MnO]/3$) showing the weathering of feldspars to clay minerals in BZN samples. Additional data from Boekhout et al. (2015) and Kanzari et al. (2017) for waste rocks are also plotted.

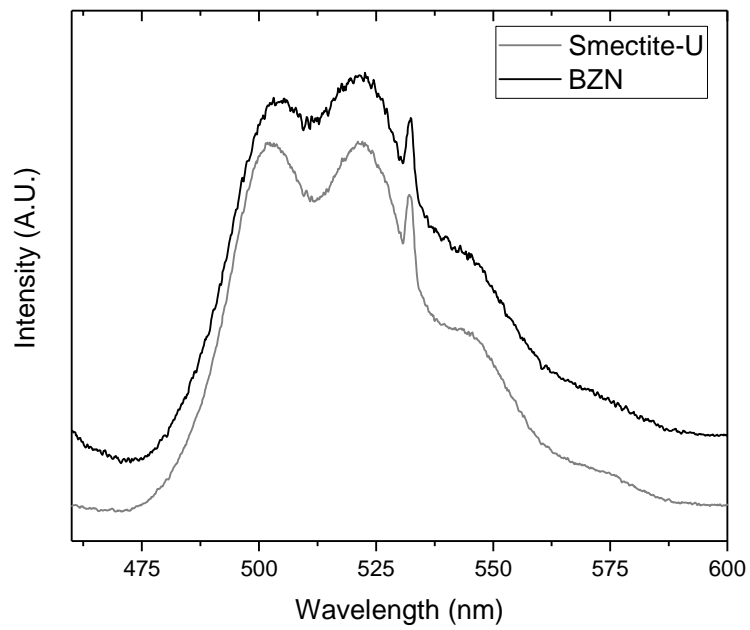


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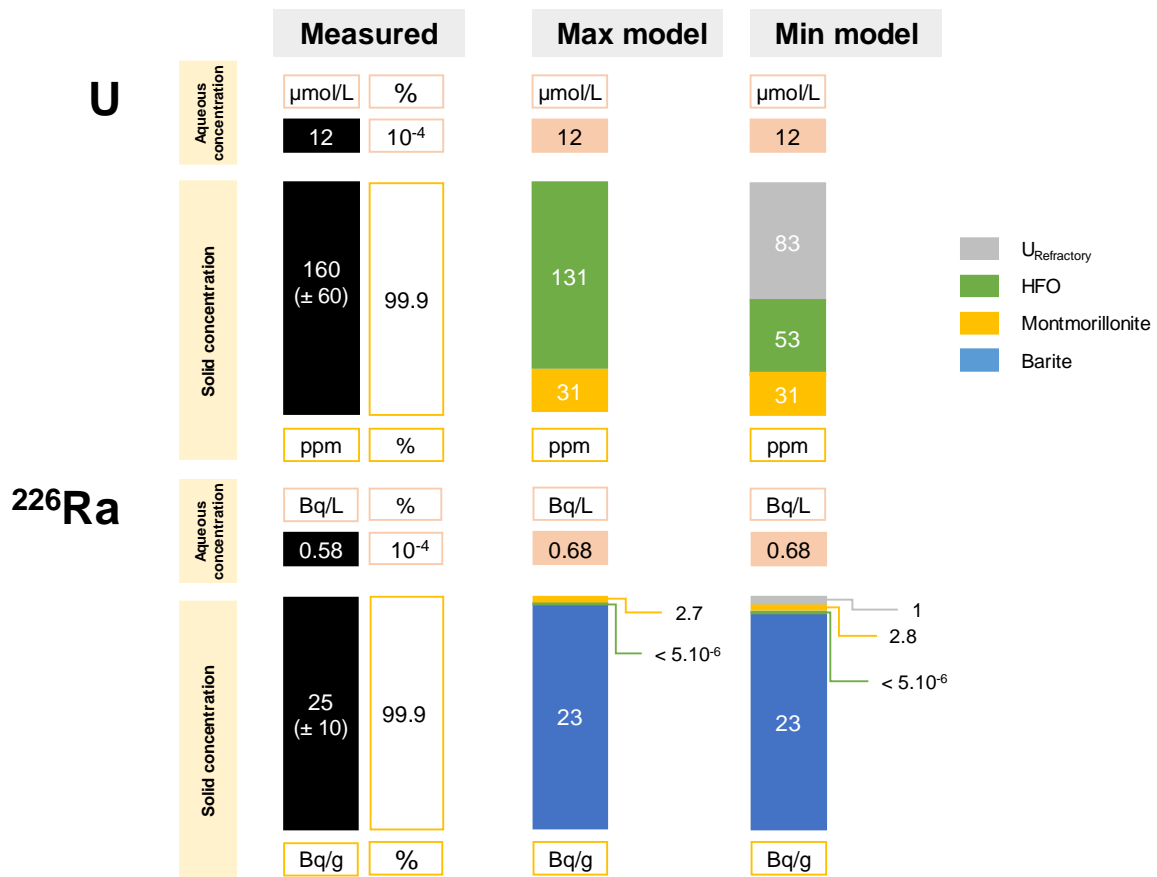


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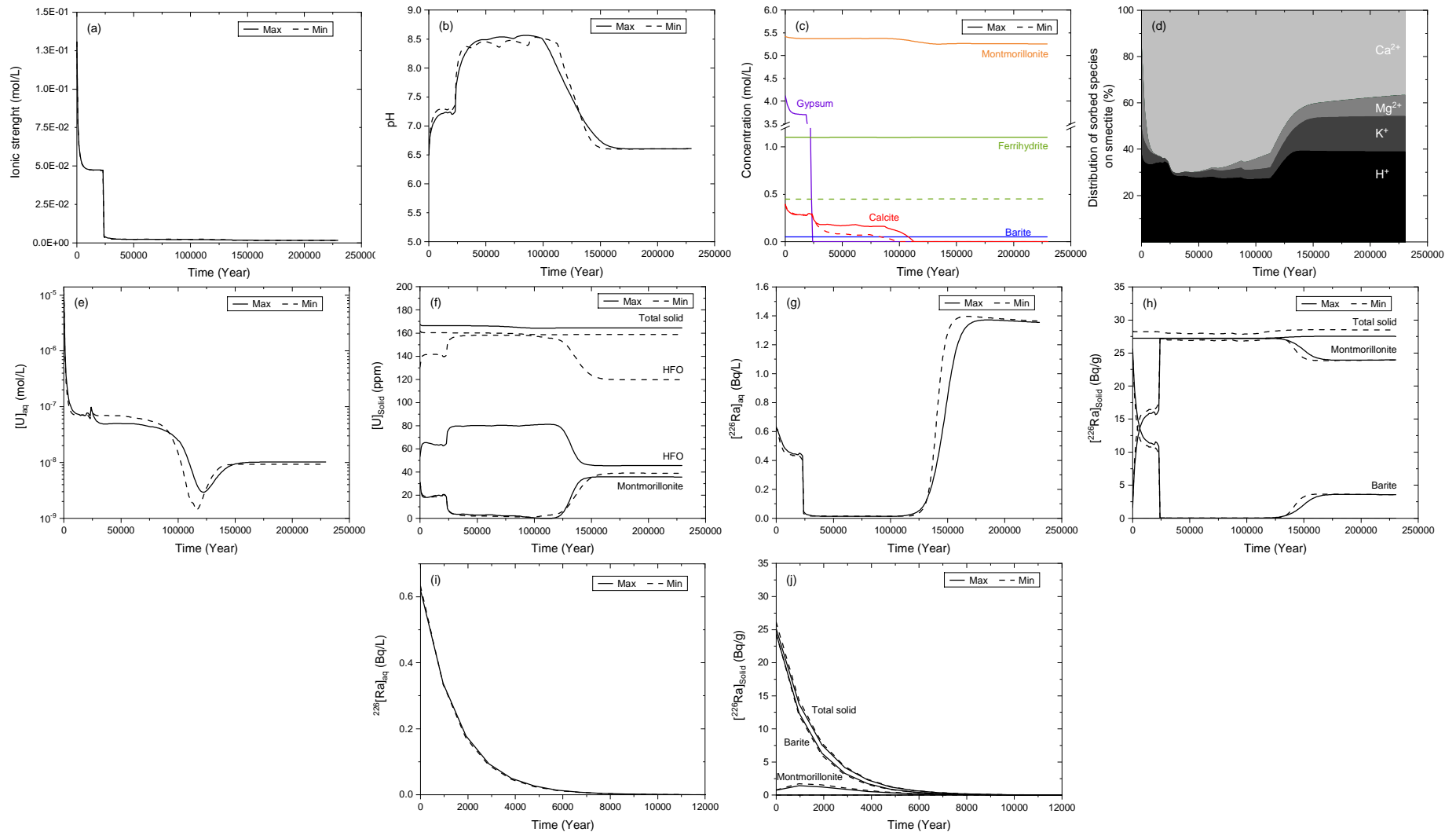


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Table 1. Chemical composition of the ES85 porewater solution (measured and modeled) and the granitic water (ES60; from Ledoux and Schmitt, 2010) percolating in the tailings column. All the concentrations are given in mol/L, except ²²⁶Ra concentration in Bq/L.

	ES85- Measured	ES85- Modeled	ES60
pH	6.35	6.49	6.31
Eh (mV/SHE)	138	185	319
T (°C)	12	12	13.8
Ionic strength	0.13	0.13	1.69 10 ⁻³
Anions			
[Cl] _{tot}	8.5x10 ⁻³	8.5x10 ⁻³	1.8x10 ⁻⁴
[F] _{tot}	7.8x10 ⁻⁴	7.8x10 ⁻⁴	7.4x10 ⁻⁵
[NO ₃] _{tot}	1.2x10 ⁻³	1.2x10 ⁻³	
[SO ₄] _{tot}	4.3x10 ⁻²	4.3x10 ⁻²	2.3x10 ⁻⁴
[PO ₄] _{tot}	7.6x10 ⁻⁸	7.6x10 ⁻⁸	6.3x10 ⁻⁷
[Si] _{tot}	1.5x10 ⁻⁴	9.4x10 ⁻⁵	2x10 ⁻⁴
TIC	2.5x10 ⁻²	2.6x10 ⁻²	6.6x10 ⁻⁴
Cations			
[Na] _{tot}	8.9x10 ⁻³	8.9x10 ⁻³	2.5x10 ⁻⁴
[K] _{tot}	1.7x10 ⁻³	1.6x10 ⁻³	3.8x10 ⁻⁵
[Mg] _{tot}	3.3x10 ⁻²	3.3x10 ⁻²	1.4x10 ⁻⁴
[Ca] _{tot}	1.3x10 ⁻²	1.5x10 ⁻²	2.8x10 ⁻⁴
[Sr] _{tot}	3.8x10 ⁻⁶	3.8x10 ⁻⁶	
[Ba] _{tot}	1.0x10 ⁻⁷	3.8x10 ⁻⁸	2.83x10 ⁻⁷
Metals			
[Al] _{tot}	7.0x10 ⁻⁵	3.2x10 ⁻⁵	6.9x10 ⁻⁷
[Mn] _{tot}	1.0x10 ⁻³	1.0x10 ⁻³	
[Fe] _{tot}	7.9x10 ⁻³	7.9x10 ⁻³	1x10 ⁻⁵
[²²⁶ Ra] _{tot}	0.58	0.68	0.2
[U] _{tot}	1.2x10 ⁻⁵	1.2x10 ⁻⁵	1.7x10 ⁻⁸
<i>Elec. Bal. (% err)</i>	6.24%	6.06%	6.83%

SUPPLEMENTARY INFORMATIONS: A MULTI-SCALAR STUDY OF
THE LONG-TERM REACTIVITY OF URANIUM MILL TAILINGS
(BELLEZANE, FRANCE)

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BESANCON^{1,3}, A. BOIZARD⁴, M. CATHELINÉAU⁴, C. PEIFFERT⁴, T. VERCOUTER⁵, E. VORS⁵,
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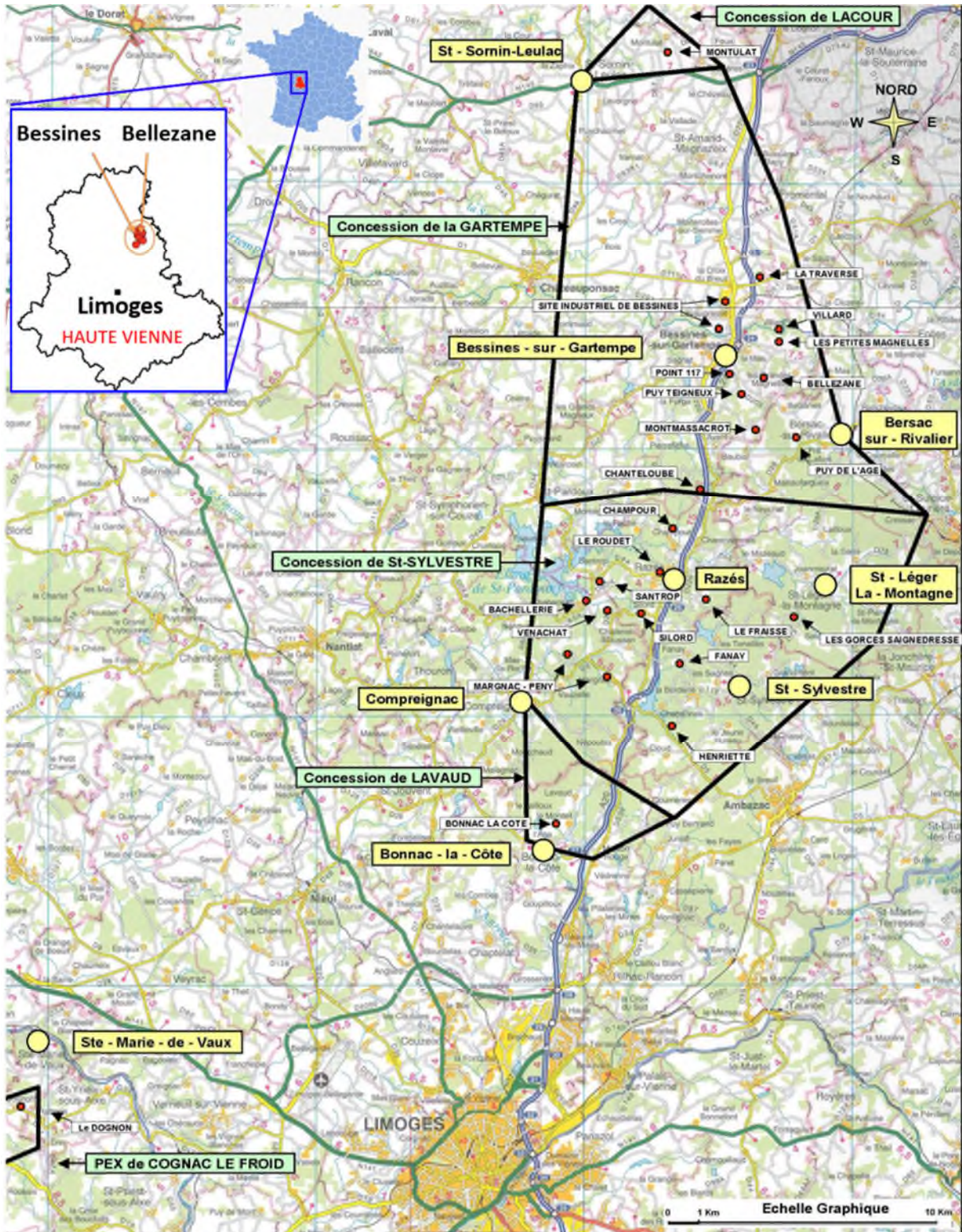


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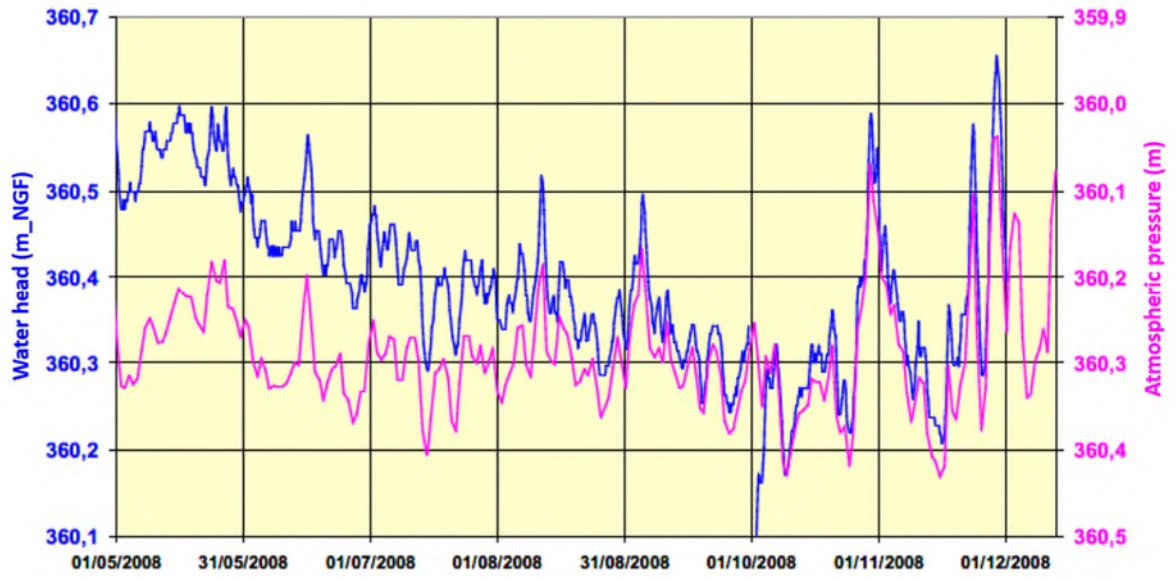


Figure SI-2. Correlation between the piezometric height measured at ES85 and atmospheric pressure (Ledoux and Schmitt, 2010).

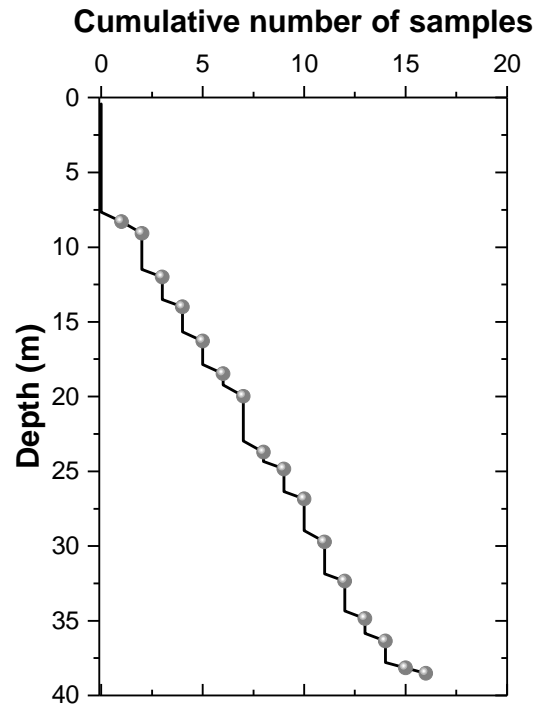


Figure SI-3. Cumulative number of samples as a function of depth. The grey dots represent the samples that have undergone full characterization.

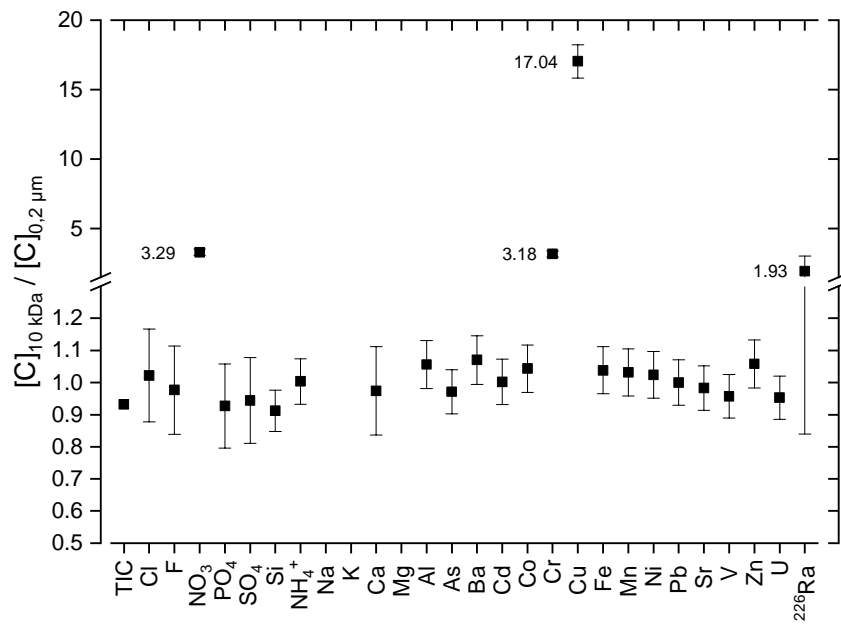


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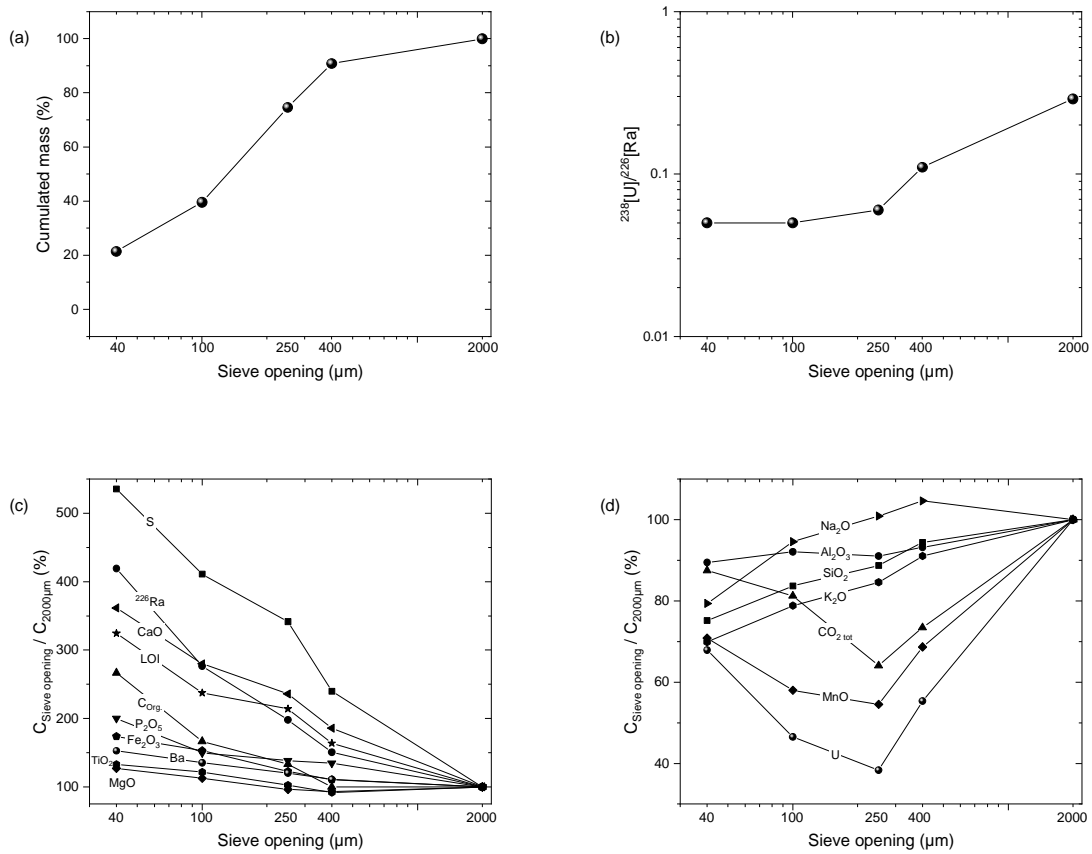


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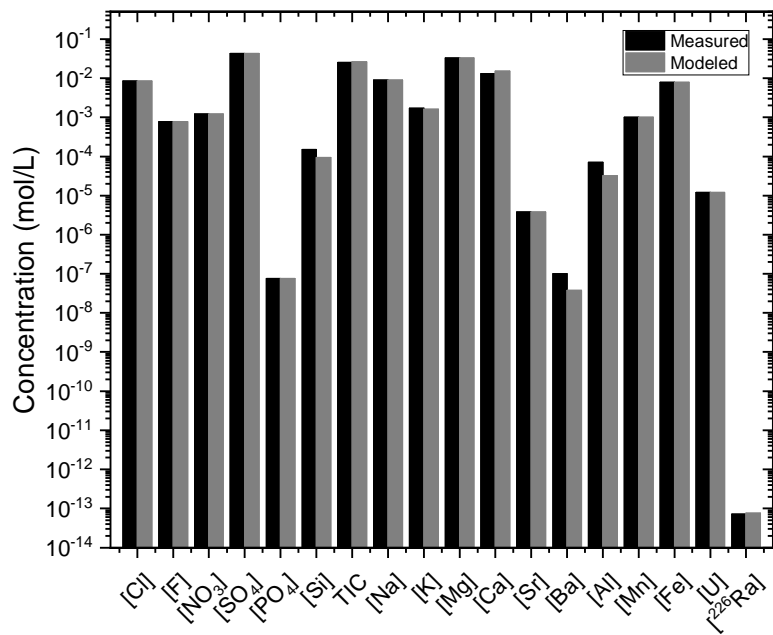


Figure SI-6. Comparison between measured and modeled ES85 porewater concentrations.

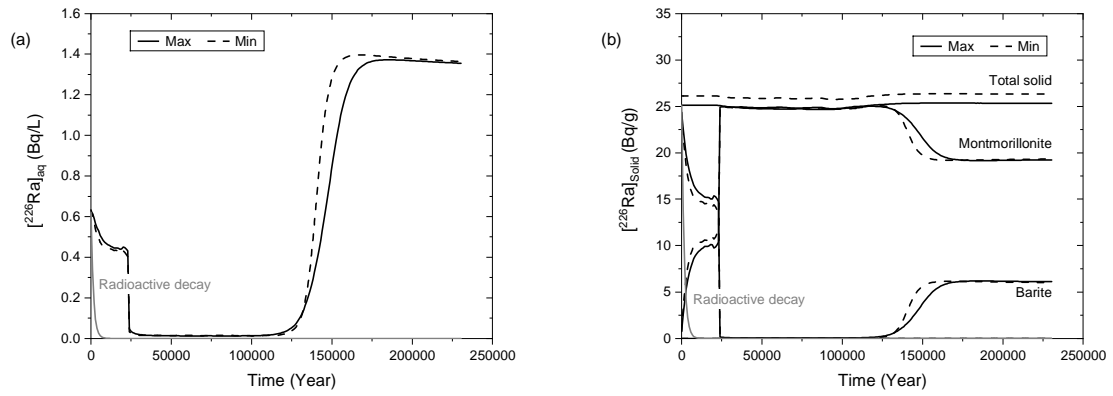


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TableaSI-1. Summary of the characterization analyses carried out for all the samples studied.

Sample name	Mean depth (m)	Chemistry	Radiological characterization	Mineralogical characterization	Particle-size distribution	TRLFS
BZN 1_Carotte 1	1.30		X			
BZN 1_Carotte 3	3.85		X			
BZN 1_Carotte 5	7.15		X			
BZN_1_7.90-10.25m_1T	8.30	X	X	X		
BZN_1_7.90-10.25m_2T	9.10	X	X	X		
BZN_1_11.75-13.25m_1T	12.00	X	X	X		X
BZN_1_13.25-14.75m_1T	13.50	X		X		
BZN_1_13.25-14.75m_2T	14.00	X	X	X	X	
BZN_1_13.25-14.75m_3T	14.50	X		X		
BZN_1_14.75-16.60m_3T	16.30	X	X	X		
BZN_1_18.10-19.60m_1T	18.50	X	X	X		
BZN_1_19.60-21.10m_1T	20.00	X	X	X		
BZN_1_22.60-24.10m_2T	23.70	X	X	X		
BZN_1_24.10-25.60m_2T	24.90	X	X	X		
BZN_1_25.60-27.10m_3T	26.90	X	X	X		
BZN_1_28.60-30.10m_2T	29.70	X	X	X		
BZN_1_31.60-33.10m_2T	32.40	X	X	X		
BZN_1_34.60-36.10m_1T	34.90	X	X	X		
BZN_1_36.10-37.60m_1T	36.40	X	X	X		
BZN_1_37.60-38.70m_2T	38.20	X	X	X		
BZN_1_37.60-38.70m_3T	38.50	X	X	X		

Table SI-2. Sorption constants of U, ²²⁶Ra and CO₃²⁻ on ferrihydrite added to the PHREEQC database (_w and _s stands for weak and strong binding sites respectively).

		Lg k	Reference
²²⁶Ra	$\text{HFO_sOH} + \text{Ra}^{2+} = \text{HFO_sOHRa}^{2+}$	6.66	Sajih et al. 2014
	$\text{HFO_wOH} + \text{Ra}^{2+} = \text{HFO_wORa}^{+} + \text{H}^{+}$	-5.67	
U	$\text{HFO_sOH} + \text{UO}_2^{2+} = \text{HFO_sOUO}_2^{+} + \text{H}^{+}$	3.73	Mahoney et al. 2019
	$\text{HFO_wOH} + \text{UO}_2^{2+} = \text{HFO_wOUO}_2^{+} + \text{H}^{+}$	2.53	
	$\text{HFO_wOH} + \text{UO}_2^{2+} + \text{CO}_3^{2-} = \text{HFO_wOUO}_2\text{CO}_3^{-} + \text{H}^{+}$	9.03	
	$\text{HFO_wOH} + \text{UO}_2^{2+} + 2 \text{CO}_3^{2-} = \text{HFO_wOUO}_2(\text{CO}_3)_2^{3-} + \text{H}^{+}$	15.28	
	$\text{HFO_wOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{HFO_wOUO}_2\text{OH} + 2 \text{H}^{+}$	-5.11	
CO₃²⁻	$\text{HFO_wOH} + \text{CO}_3^{2-} + \text{H}^{+} = \text{HFO_wOCO}_2^{-} + \text{H}_2\text{O}$	12.78	Mahoney et al. 2019
	$\text{HFO_wOH} + \text{CO}_3^{2-} + 2 \text{H}^{+} = \text{HFO_wOCO}_2\text{H} + \text{H}_2\text{O}$	20.37	

Table SI-3. Site concentration and selectivity coefficients of cation exchange reactions for montmorillonite added to the PHREEQC database (Gaines-Thomas convention) (Reinoso-Maset et al., 2012a and 2012b).

	Site				
	>X1	>X2	>X3	>X4	>X5
	Site concentration (mmol/g clay)				
	6.20x10 ⁻¹	1.50x10 ⁻¹	1.40x10 ⁻¹	1.50x10 ⁻¹	4.10x10 ⁻⁴
Selectivity coefficient					
H ⁺ /Na ⁺	-2.2	-12.5	-12.5	-12.5	7.3
H ⁺ /K ⁺	0.75	-1.4	-4.4	-7.2	
2H ⁺ /Ca ²⁺	0.1	-2.5	-11.5	-17.5	
2H ⁺ /Mg ²⁺	0.1	-2.5	-11.5	-17.5	
2H ⁺ /UO ₂ ²⁺		-0.475	-3.44		
2H ⁺ /Ra ²⁺		-2.37	-6.55	-10.17	

Table SI-4. Mean (C_{mean}), minimum (C_{min}) and maximum (C_{max}) elemental levels measured in BZN samples. Mean values are accompanied by the standard deviations. C_{org} and LOI denote organic C content and loss on ignition respectively.

	C_{mean}	C_{min}	C_{max}
<i>Major elements(%)</i>			
SiO₂	61.9 ± 4.4	55.4	73.2
Al₂O₃	13.1 ± 0.8	11.2	14.5
K₂O	5.04 ± 0.27	4.61	5.57
CaO	3.48 ± 0.93	1.07	4.77
Fe₂O₃	2.94 ± 0.61	1.50	3.76
Na₂O	1.68 ± 0.29	1.26	2.61
S total	1.85 ± 0.45	0.40	2.53
MgO	0.77 ± 0.26	0.32	1.19
P₂O₅	0.33 ± 0.05	0.24	0.42
TiO₂	0.27 ± 0.07	0.16	0.46
MnO	0.05 ± 0.02	0.03	0.09
CO₂ total	0.52 ± 0.25	0.24	1.23
C_{org}	0.08 ± 0.04	0.03	0.20
LOI	9.69 ± 2.39	2.56	14.02
<i>Traces (ppm)</i>			
Ba	839±609	294.9	2502
U	169±61	77.7	292.4
<i>²²⁶Ra (Bq/g)</i>			
²²⁶Ra	23±15	0.3	44.5

Table SI-5. Trace-level element concentrations measured in mill tailings samples (D. L. stands for detection limit).

	BZN / 7.9- 10.25m / 1T A	BZN / 7.9- 10.25m / 1T B	BZN / 7.9- 10.25m / 2T	BZN / 11.75- 13.26m / 1T	BZN / 13.26- 14.75m / 1T	BZN / 13.26- 14.75m / 2T A	BZN / 13.26- 14.75m / 2T B	BZN / 13.26- 14.75m / 3T	BZN / 14.75- 16.60m / 3T	BZN / 18.10- 19.60m / 1T	BZN / 19.60- 21.10m / 1T	BZN / 22.60- 24.10m / 2T
As	42.32	143.50	146.60	146.40	146.00	176.70	172.80	91.26	147.20	156.30	173.30	78.71
Ba	294.90	530.90	848.70	1026.00	508.20	539.00	1062.00	987.10	2463.00	389.20	961.50	399.70
Be	16.53	24.65	19.20	22.38	20.40	22.71	22.28	17.50	18.13	18.21	22.42	19.07
Bi	3.17	10.60	7.85	3.15	3.49	3.40	2.97	3.52	4.02	9.45	3.06	5.74
Cd	0.94	2.89	2.34	0.37	0.25	0.68	0.29	0.24	0.26	3.78	0.29	0.23
Ce	39.62	54.58	57.86	77.08	63.74	56.87	81.00	77.99	90.90	43.61	67.72	49.30
Co	5.84	10.77	10.82	5.77	3.38	4.53	5.32	6.86	9.60	14.69	5.03	4.88
Cr	21.04	23.91	19.63	37.90	17.84	18.38	41.28	55.17	74.01	24.00	36.35	20.02
Cs	25.58	31.99	28.47	31.73	37.69	37.82	31.92	30.84	29.20	21.27	34.09	28.34
Cu	169.70	238.10	221.80	19.34	22.13	51.40	18.14	24.62	45.83	335.60	19.50	51.77
Dy	1.68	2.86	2.97	3.06	2.78	2.99	3.19	3.31	4.53	2.80	2.96	2.20
Er	0.61	1.02	1.02	1.09	0.98	1.15	1.16	1.22	1.83	0.96	1.06	0.77
Eu	0.45	0.83	0.77	0.91	0.66	0.69	0.95	1.06	1.51	0.79	0.90	0.49
Ga	21.81	25.21	26.10	27.63	27.76	28.02	28.21	24.07	22.32	21.46	25.90	24.94
Gd	2.65	4.63	4.84	5.29	4.62	4.74	5.32	5.27	6.34	4.29	4.89	3.48
Ge	1.72	2.75	2.77	2.83	3.08	2.92	2.93	2.28	2.28	2.31	2.81	2.01
Hf	2.30	3.19	3.36	4.33	3.49	3.37	4.52	4.88	5.81	2.58	3.97	2.85
Ho	0.25	0.43	0.44	0.46	0.41	0.48	0.48	0.50	0.72	0.41	0.45	0.33
In	0.09	0.15	0.16	0.12	0.12	0.13	0.12	0.11	0.11	0.17	0.13	0.14
La	18.79	26.00	27.05	36.83	30.40	27.30	40.28	39.33	51.29	20.26	33.22	22.72
Lu	0.08	0.12	0.11	0.12	0.12	0.13	0.13	0.14	0.23	0.11	0.13	0.09
Mo	0.65	0.59	0.69	0.85	0.87	0.87	0.96	0.70	1.35	0.94	0.93	0.83
Nb	10.66	13.06	13.40	16.05	14.47	14.74	16.37	16.40	17.39	10.46	14.92	15.17
Nd	18.14	26.08	27.87	36.64	30.16	27.37	37.88	36.81	43.17	21.86	32.47	24.07
Ni	18.09	12.21	9.68	15.22	7.95	8.33	14.83	19.92	27.10	13.59	13.23	10.18
Pb	109.35	335.51	310.21	120.50	131.97	194.88	120.56	90.61	124.11	421.95	115.88	77.42
Pr	4.59	6.45	6.80	8.96	7.46	6.67	9.39	8.97	10.44	5.21	7.81	5.81
Rb	379.60	381.90	391.00	398.00	396.70	399.10	416.10	377.80	340.40	336.70	379.40	430.40
Sc	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.
Sb	1.10	4.19	4.17	3.17	3.30	3.17	3.24	2.13	5.97	4.12	2.76	1.56
Sm	3.85	5.89	6.23	7.61	6.48	5.99	7.61	7.58	8.70	5.33	6.81	5.23
Sn	20.05	20.02	16.76	15.85	23.17	19.95	16.47	16.96	16.21	15.95	25.06	24.40
Sr	79.16	96.11	103.50	151.30	105.80	109.70	158.50	181.30	271.60	78.33	151.00	72.80
Ta	2.38	2.97	2.73	2.66	2.88	3.00	2.67	2.70	2.72	2.11	2.80	3.69
Tb	0.36	0.63	0.66	0.69	0.61	0.64	0.71	0.70	0.90	0.60	0.65	0.49
Th	14.10	17.03	19.48	22.78	20.98	19.22	23.47	21.16	19.74	14.76	19.14	18.63
Tm	0.08	0.13	0.13	0.14	0.13	0.15	0.15	0.16	0.26	0.13	0.14	0.11
U	77.65	212.50	292.40	214.30	217.10	233.20	239.30	171.70	228.40	205.90	202.70	88.83
V	12.71	37.09	30.23	28.02	16.53	21.39	28.78	30.98	39.68	35.83	24.93	16.87
W	402.40	47.91	20.17	18.53	14.91	20.05	17.54	19.60	37.12	50.02	18.17	14.32
Y	8.12	14.44	14.85	14.20	13.40	16.81	14.90	15.40	21.58	14.16	13.91	10.16
Yb	0.55	0.83	0.82	0.90	0.82	0.95	0.95	1.01	1.63	0.80	0.87	0.66
Zn	273.00	514.10	397.90	107.90	92.04	169.00	102.80	77.51	84.43	577.00	89.47	80.26
Zr	79.63	113.00	115.30	156.60	120.10	114.30	161.30	180.00	221.00	91.85	143.80	95.01

	BZN / 24.10-25.60m / 2T	BZN / 25.60-27.10m / 3T	BZN / 28.60-30.10m / 2T	BZN / 31.60-33.10m / 2T	BZN / 34.60-36.10m / 1T	BZN / 36.10-37.60m / 1T	BZN / 37.60-38.70m / 2T	BZN / 37.60-38.70m / 3T
As	89.70	80.31	111.90	107.30	136.50	86.91	154.00	110.40
Ba	317.50	505.00	711.70	697.40	750.80	532.10	2502.00	752.60
Be	20.72	20.73	19.48	18.80	19.76	19.42	19.34	17.14
Bi	6.06	4.49	3.88	2.98	2.41	5.89	3.89	3.14
Cd	0.31	0.19	0.28	0.35	0.21	0.44	0.19	0.29
Ce	52.47	54.69	61.96	69.74	70.16	53.80	75.07	65.74
Co	4.58	3.81	5.64	5.55	4.83	5.25	8.09	4.83
Cr	17.76	14.99	39.36	42.68	49.87	24.23	59.48	30.81
Cs	28.41	26.77	43.35	33.85	39.18	30.38	42.55	30.79
Cu	45.66	41.23	36.78	26.83	22.93	46.31	42.34	23.38
Dy	2.57	2.21	3.10	3.59	3.53	2.20	4.32	2.96
Er	0.97	0.78	1.18	1.38	1.32	0.77	1.78	1.09
Eu	0.53	0.46	0.85	0.94	0.91	0.56	1.18	0.75
Ga	24.28	25.65	26.54	25.87	25.79	25.13	25.03	26.01
Gd	4.00	3.64	4.55	5.34	5.51	3.52	5.91	4.72
Ge	2.00	2.28	2.43	2.27	2.50	2.01	2.71	2.64
Hf	2.88	3.39	4.08	4.45	3.86	3.04	4.92	4.23
Ho	0.39	0.33	0.48	0.56	0.55	0.32	0.71	0.45
In	0.14	0.14	0.12	0.14	0.12	0.16	0.12	0.11
La	23.95	25.70	32.45	34.64	34.13	25.42	42.30	32.05
Lu	0.11	0.09	0.14	0.16	0.15	0.09	0.22	0.13
Mo	0.50	0.53	0.57	0.65	0.76	0.87	1.41	0.59
Nb	15.76	16.33	16.00	16.29	14.88	15.16	17.31	15.91
Nd	25.34	26.06	29.48	33.72	33.86	26.34	35.67	31.45
Ni	9.62	8.14	13.35	15.53	12.99	9.95	20.56	11.15
Pb	71.92	72.79	106.93	109.69	78.38	106.83	109.42	109.96
Pr	6.10	6.41	7.23	8.13	8.20	6.40	8.64	7.53
Rb	440.10	446.80	412.50	401.70	402.30	450.10	390.30	413.50
Sc	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.
Sb	1.49	1.68	2.35	2.31	1.93	2.43	5.93	2.56
Sm	5.63	5.62	6.37	7.31	7.46	5.49	7.75	6.65
Sn	24.67	23.21	24.43	21.03	21.45	24.38	23.29	18.25
Sr	73.86	75.72	132.80	138.00	125.40	82.83	205.50	127.20
Ta	4.03	3.61	3.13	3.12	2.99	3.64	3.12	2.77
Tb	0.55	0.48	0.65	0.75	0.75	0.48	0.86	0.65
Th	20.33	21.58	18.11	22.23	22.62	19.28	19.24	22.86
Tm	0.13	0.11	0.16	0.18	0.18	0.10	0.25	0.14
U	101.30	106.10	116.90	103.70	140.10	161.70	163.90	111.90
V	15.96	17.11	23.51	23.62	23.17	15.38	30.75	20.74
W	24.52	24.13	23.53	18.22	13.17	18.78	32.36	14.32
Y	12.61	10.15	14.88	17.64	17.14	9.90	22.53	13.87
Yb	0.84	0.67	0.98	1.11	1.06	0.65	1.56	0.88
Zn	79.37	73.36	86.52	123.10	75.55	105.40	77.83	102.90
Zr	94.98	112.60	145.10	157.20	137.30	104.70	180.90	148.70

