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1 Retention of arsenic, chromium and boron on an outcropping  
2 clay-rich rock formation (the Tégulines Clay, eastern France)

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12 **Abstract**

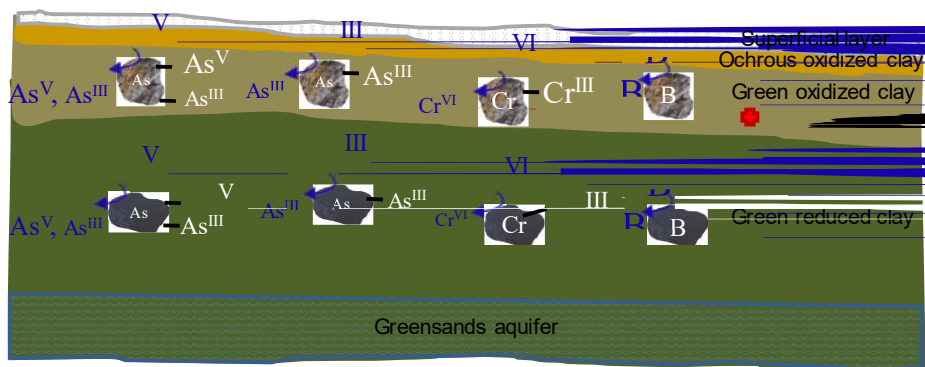
13 The retention behavior of three toxic chemicals, As, Cr and B, was investigated for an outcropping  
14 rock formation, the Albian Tégulines Clay (France, Aube). At a shallow depth, Tégulines Clay is  
15 affected by weathering processes leading to contrasted geochemical conditions with depth. One of the  
16 main features of the weathering is the occurrence of a redox transition zone near the surface. Batch  
17 sorption experiments of As(V), As(III), Cr(VI) and B were performed on samples collected at two  
18 depths representative either of oxidized or reduced mineral assemblages. Batch sorption experiments  
19 highlighted a distinct behavior between As, Cr and B oxyanions. Cr(VI) retention behavior was  
20 dominated by redox phenomena, notably its reduction to Cr(III). The *in-situ* redox state of the  
21 Tégulines Clay samples has a significant effect on Cr retention. On the contrary, As(V) reduction into  
22 As(III) is moderate and its retention slightly affected by the *in-situ* redox state of the Tégulines Clay.  
23 As(V) retention is higher than As(III) retention in agreement with literature data. B retention is strongly  
24 related to its natural abundance in the Tégulines clay samples. Distribution coefficient of B corrected  
25 from its natural content is expected to be very low for *in-situ* conditions. Finally, the retention and  
26 mobility of these oxyanions were affected by clay mineralogy, natural abundance, and reducing  
27 capacity of the Tégulines Clay.

28 **Keywords:** *Oxyanions retention, Tégulines Clay, redox environment, arsenic, chromium, boron.*

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29 Graphical abstract



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34 **1. Introduction**

35 Inorganic toxic chemicals occur in various forms (e.g., cations, oxyanions, and ligands). Among them,  
36 the oxyanionic forms are subject of high interest, because of their high mobility. In neutral conditions,  
37 the capacity of soils and sediments to retain anions and oxyanions is low compared to cations,  
38 because rock retention capacity is generally controlled by the presence of clay minerals and Fe and  
39 Mn oxyhydroxides, whose surface are negatively charged under most environmental conditions  
40 (Sparks, 2005). Limited retention through chemical reduction (Li and Bowman, 2001) or sorption on  
41 iron oxyhydroxides or clay minerals (Fendorf et al., 1997; Li, 1999) and oxidation by Mn oxides (James  
42 and Bartlett, 1983a; James and Bartlett, 1983b; Wu et al., 2018) have been reported in the literature  
43 for oxyanions. Therefore, the mobility of toxic chemicals is closely linked to the mineralogy of the  
44 sediments and to their oxidation-reduction (redox) potential. The variations of those parameters are  
45 significant in the critical zone, and may lead to discrepancies in the prediction of the behavior of toxic  
46 chemicals. The behavior of metals (Cu, Zn, Fe, Mn, Hg, Mo, etc.) in such a context has been  
47 extensively studied in the literature (Evans, 1989; Lynch et al., 2014; Nagajyoti et al., 2010; Poggio et  
48 al., 2009; Wuana and Okieimen, 2011) and references therein). In contrast, the mobility of inorganic  
49 toxic chemicals, with oxyanionic forms ( $\text{AsO}_4^{3-}$ ,  $\text{H}_2\text{AsO}_3^-$ ,  $\text{HAsO}_3^{2-}$ ,  $\text{AsO}_3^{3-}$ ,  $\text{B(OH)}_4^-$ ,  $\text{CrO}_4^{2-}$ ), sometimes  
50 combined with redox sensitivity (As(V)/As(III), Cr(VI)/Cr(III)) is less well understood.

51 The behavior of As and Cr depends on their oxidation state, which influences their solubility and the  
52 adsorption-desorption reactions on mineral surfaces. In the soil and water environment, inorganic As is  
53 mainly present in two oxidation states: arsenate (As(V)), which is predominant in oxidized  
54 environments, and arsenite (As(III)), which is predominant in reduced environments (Adriano, 1986;  
55 Arai, 2010; Gorny et al., 2015). Redox transformation rates for inorganic As species are slow, so As(V)  
56 and As(III) often co-exist in soil solutions (Masscheleyn et al., 1991; Tallman and Shaikh, 1980). The  
57 less toxic and less mobile oxidation state is As(V) (Arai, 2010; Goldberg and Johnston, 2001; Gulens  
58 et al., 1979; Penrose, 1974; Smedley and Kinniburgh, 2002). Usually, the extent of As uptake is  
59 positively correlated with clay mineral and extractable Fe and Al contents (Arai, 2010; Walsh and  
60 Keeney, 1975; Wauchope and McDowell., 1984). As(V) sorption on Al and Fe oxyhydroxides and on  
61 clay minerals exhibit sorption maxima in the pH range 3–7, while As(III) is retained between pH 7 and  
62 9 (Goldberg, 2002; Goldberg and Johnston, 2001; Goldberg and Suarez, 2012; Jain and Loeppert,

2000). The mobility of As is thus a function of its oxidation state, the pH conditions and of the soil mineralogy. Cr is also a redox metal that can be encountered as Cr(III) or Cr(VI) in the environment (Gorny et al., 2016). These two oxidation states have contrasting toxicity and mobility: Cr(III) has very low toxicity and mobility in soils, while Cr(VI) is toxic and readily transported. The low Cr(III) solubility ( $1.7 \cdot 10^{-7} \text{ mol L}^{-1}$  at pH 7 with respect to  $\text{Cr(OH)}_{3(s)}$ ) limits its mobility and availability, while Cr(VI) is highly soluble in water (Ma and Hooda, 2010; Nakayama et al., 1981) and is mainly present in the environment as oxyanion species ( $\text{HCrO}_4^-$  at pH < 6.5 and  $\text{CrO}_4^{2-}$  at pH > 6.5). Thus, the greatest risk associated with the presence of Cr(III) is its potential oxidation to Cr(VI), and this makes the presence of Cr(III) an environmental risk in the presence of fluctuant redox conditions (Fendorf, 1995; Ma and Hooda, 2010; Taghipour and Jalali, 2015). Manganese oxides, fly ash and hydroxyapatite affect Cr bioavailability by oxidizing Cr(III) to Cr(VI) (Bartlett and James, 1979; Pansar-Kallio et al., 2001), while organic matter immobilizes Cr. Cr(VI) retention is higher at pH 7, because oxyanions are easily absorbed at positively charged sites on soil minerals. Indeed, the point of zero charge (pH<sub>zpc</sub>) for Fe- and Al- oxides varies from 7 to 10 (Alloway, 1995) generating positively charged adsorbent surface attracting anions. At higher pH than 8, a competition with OH<sup>-</sup> hinders the sorption of oxyanions (Ma and Hooda, 2010). Considering their distinctive toxicity, determining Cr redox states, in the critical zones, such as close to aquifer, is of prime importance. B has no redox reactivity. B concentration in soils is controlled by adsorption reactions (Goldberg, 1997). B sorption capacity is strongly related to the organic and inorganic carbon content of the soil, as well as to the Fe oxyhydroxides (Goldberg et al., 2004) and to calcite content (Hemming et al., 1998). The highest B adsorption on clay minerals, organic matter, and calcite is produced at pH 8–10, while the highest sorption is reported at pH 7–9 on Al and Fe oxyhydroxides (Goldberg, 1997). This sorption is a two-step process with adsorption followed by incorporation. In clay minerals, B may replace Si and Al in tetrahedral sites (Couch and Grim, 1968; Fleet, 1965; Goldberg, 1997), while B uptake in calcite requires a change in B coordination from tetragonal ( $\text{B(OH)}_4^-$ ) to trigonal ( $\text{B(OH)}_3$ ) to be incorporated in its structure (Hemming et al., 1998; Mavromatis et al., 2015).

In many countries, environmental impact of toxic chemicals has to be considered for the implementation of industrial facilities. The assessment of the toxic chemical environmental impact for a given facility requires evaluating the mobility of the various toxic chemicals potentially involved in the industrial activity in its surrounding environment. Numerical evaluations of the migration of the

93 identified toxic elements from the industrial facilities toward the biosphere necessitate a good  
94 parametrization of their retention behavior. Long live low activity level (LL-LL) wastes include radium  
95 bearing wastes as well as toxic chemicals such as As, Cr and B not only from the nuclear power  
96 sector but also from the chemical industry (rare earth element extraction) and from cleanup waste  
97 radioactive contaminated sites (old industrial plants, laboratories...). The repository concept currently  
98 studied in France for LL-LL waste consists in a shallow depth repository (< 30 m) in a clay-rich  
99 geological formation. Since 2013, the Tégulines Clay, an Albian sedimentary formation in the eastern  
100 part of the Paris basin is currently under study for feasibility purposes. s , The ability of the Tégulines  
101 Clay to retain chemical elements, such as As, Cr and B was investigated. Due to its vicinity with the  
102 surface, the Tégulines Clay is affected by weathering processes inducing redox contrasts with depth  
103 (Lerouge et al., 2018). Such redox contrasts can potentially affect the mobility of sensitive redox  
104 chemical elements in the Tégulines Clay. Indeed, oxidized environment would sustain highly mobile  
105 oxyanions in the sediments (e.g.  $\text{CrO}_4^{2-}$ ) while reduced environment would lead to their reduction and  
106 immobilization. Therefore, the retention behavior of As, Cr and B on samples originating from two  
107 depths with distinct redox environments was considered in this study to assess the mobility of these  
108 oxyanions and quantify the retention capacity of the Tegulines Clay.

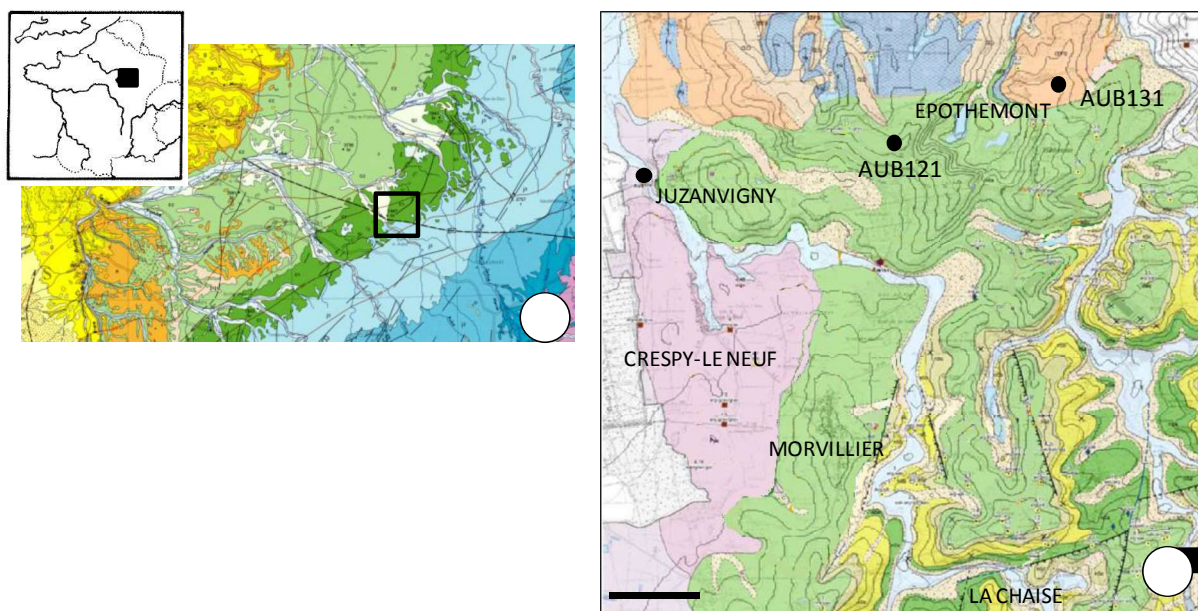
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## 110 **2. Context of the study and samples**

### 111 *2.1. Geological setting*

112 The marine Gault Clay Formation outcrops as an 8–10 km wide and 80-km long band of terrane  
113 oriented NE-SW through the Aube Department, in the eastern part of the Paris Basin (France)  
114 (Amédéo et al., 2017; Lerouge et al., 2018). The Gault Clay is represented by Tégulines Clay in the  
115 study area of Brienne Le Chateau. Its thickness varies from 65-75 m to ~10 m. The Tégulines Clay is  
116 covered by thin (0.7 to 6 m thick) surficial layers of soils or alluvium. The mineralogy of the Tégulines  
117 Clay is mainly constituted by clay minerals (35-65 % including muscovite and/or illite, chlorite,  
118 kaolinite) associated with a quartz-feldspar silty fraction (18–58 wt.%), and carbonates (0–30 wt.%).  
119 Carbonates are essentially represented by calcite with minor dolomite. Ankerite and siderite were  
120 detected as well in the formation. Accessory minerals include pyrite, celestite, gypsum, phosphates  
121 nodules, and iron oxides. As the formation is being subjected to weathering with the occurrence of

122 oxidation phenomena, the mineralogy of the Tégulines Clay evolves with depth (see section 4.1 and  
 123 Lerouge et al. (2018) for further details). Sulfur and iron bearing minerals are mainly affected by  
 124 weathering that influences the mobility of the traces due to mineralogical modifications (see section  
 125 4.1).



126

127 **Fig. 1. Geological map (a) of the eastern part of the Paris Basin showing the investigated area;**  
 128 **(b) zoom of the area studied and location of the boreholes.**

## 129 2.2. Sampling

130 In order to define the impact of weathering processes on the As, Cr, and B distribution among minerals  
 131 and on the retention capacity of Tégulines Clay, two core samples were selected according to depth.  
 132 The AUB00976 sample was collected at 7.70 m depth of the borehole AUB121 crosscutting about 70  
 133 m of Tégulines Clay and the AUB00307 sample at 21.20 m depth of the borehole AUB131  
 134 crosscutting ~25-30 m of Tégulines Clay (Fig. 1). The AUB00976 and AUB00307 samples are  
 135 considered as representative of the oxidized and reduced zones, respectively.

136 The two samples were packed and sealed within 10 to 30 minutes after their coring in double layer  
 137 aluminum bags under vacuum to prevent any oxidation. Prior to packing, the samples were cut in  
 138 rectangles parallel to the axis of the drill core to avoid any contamination by the drill mud. The  
 139 aluminum bags were then opened in a glovebox under a nitrogen atmosphere. The blocks were  
 140 roughly cut with a spatula covered with polytetrafluoroethylene, transferred in airtight containers and

141 frozen for 24 h at -45 °C. Finally, samples were freeze dried to remove water, then milled in an agate  
142 mortar, and sieved at 100 µm.

### 143 3. Materials and methods

#### 144 3.1. Mineral characterization

##### 145 3.1.1. X-ray diffraction (XRD)

146 XRD measurements were carried out on bulk-rock powder with a SIEMENS D5000 X-ray  
147 diffractometer with  $\text{CoK}\alpha$  radiation ( $\lambda = 1.79026 \text{ \AA}$ ) operating at 50 kV and 50 mA. Samples were  
148 prepared using the RTS method (Zhang et al., 2003), and analyzed in step mode between 4 to 84° 2 $\theta$ ,  
149 with a counting time of 18 s per 0.04° step of 2 $\theta$ . ICDD references for the different minerals of  
150 relevance for the present study are: quartz (00-046-1045), calcite (00-005-0586), muscovite (01-084-  
151 1302), kaolinite (01-078-1996), pyrite (00-042-1340), dolomite (01-084-2065), chlorite (00-046-1323),  
152 and microcline (01-084-1455).

##### 153 3.1.2. Electron microprobe

154 Elemental mapping was carried on a CAMECA SXFiveFE electron microprobe equipped with a  
155 Schottky Field-Emission Gun (FEG) (CAMECA, Gennevilliers – France), using an acceleration voltage  
156 of 25 kV and beam current of 40 nA for Fe, Ca, and Mn, and an accelerating voltage of 25 kV and a  
157 beam current of 288 nA for As and S.  $\text{AsL}\beta$  was measured on large thallium acid phthalate (LTAP),  
158  $\text{SK}\alpha$  and  $\text{CaK}\alpha$  on large pentaerythritol (LPET),  $\text{MnK}\alpha$  on large lithium fluoride (LLIF), and  $\text{FeK}\alpha$  on  
159 lithium fluoride (LiF).

160 Fully quantitative compositional spot analyses of silicates (clay minerals, feldspar), carbonates, pyrite,  
161 sulfates (gypsum and celestite), phosphates, and iron-hydroxides were carried out at BRGM using a  
162 Cameca SXFive electron microprobe with an accelerating voltage of 20 kV and a beam current of 100  
163 nA.  $\text{NaK}\alpha$ ,  $\text{AsL}\alpha$  and  $\text{SrL}\alpha$  were measured on LTAP,  $\text{MgK}\alpha$ ,  $\text{AlK}\alpha$  and  $\text{SiK}\alpha$  on TAP,  $\text{SK}\alpha$ ,  $\text{CaK}\alpha$ ,  $\text{KK}\alpha$   
164 on PET,  $\text{CrK}\alpha$  and  $\text{MnK}\alpha$  on LPET, and  $\text{FeK}\alpha$  on LiF. Counting times on peaks and backgrounds were  
165 10 s for Na, Mg, S, and Mn, 30 s for Al, Si, Ca, K, Cr, and Fe, and 60 s for As. The system was  
166 calibrated with a variety of natural minerals (albite for Na, andradite for Si and Ca, pyrite for Fe and S,  
167 orthoclase for K), synthetic oxides ( $\text{MgO}$  for Mg,  $\text{Al}_2\text{O}_3$  for Al,  $\text{MnTiO}_3$  for Ti, and  $\text{SrSO}_4$  for Sr), metal



168 alloy (AsGa for As) and pure elements (Cr). Matrix corrections were made with the phi-rho-Z  
169 computing program PAP (Pouchou and Pichoir, 1984).

### 170 3.2. *Natural contents and distribution of As, Cr, and B among phases in Tégulines Clay*

171 The natural abundance of As, Cr, and B in the samples was measured after a tri-acid attack on bulk  
172 powder (HCl, HNO<sub>3</sub>, HF) by ICP-MS, and their distribution among the chemical reservoirs was  
173 discriminated after sequential extractions. Sequential extractions were made on triplicates of each  
174 sample in a glove box following the method developed by Claret et al. (2010), modified after Tessier et  
175 al. (1979) (see Supplementary information A for details on extractants and mineralogical targets).

### 176 3.3. *Pore water extracted by squeezing*

177 Pore water was extracted from the clay samples by squeezing according to a method adapted from  
178 Fernández et al. (2014). A modification of the water sampling circuit was made for extracting the pore  
179 water at anoxic conditions, preserving its redox state. In addition, pore water chemistry was calculated  
180 following the method developed by Gaucher et al. (2009) for the Callovian-Oxfordian host rock, a  
181 claystone which is studied for the disposal of high level radioactive waste. The squeezing  
182 measurements were carried out only on the reduced sample, which was less exposed to atmospheric  
183 perturbations than the oxidized sample. The pore water was, therefore, not or less disturbed by rock  
184 oxidation. The mass of the core sample was measured before and after squeezing. The initial mass of  
185 core samples ranged between 300 and 500 g. Extractions were carried out at 10 MPa over seven  
186 days.

### 187 3.4. *Analysis of the aqueous phases*

188 The measurement of pH in batch solutions was carried out with a Metler Toledo, SevenMulti pH meter  
189 using NIST 1.7, 4, 7, and 9 buffers. Inductively coupled plasma atomic emission spectroscopy (ICP-  
190 AES, Jobin Yvon) or mass spectroscopy (ICP-MS, Thermo Fisher Scientific) were used to measure B,  
191 As, Ca, K, Mg, Na, and Si concentrations. Chloride anions were analyzed by ionic chromatography  
192 (HPLC, Dionex). The elemental concentrations in solution were determined with a relative uncertainty  
193 of 3 %. Alkalinity was measured using a Titrand 905 and a Dosino 800 equipped with a 5 mL syringe  
194 (Metrohm) to inject the HCl solution ( $10^{-3}$  mol L<sup>-1</sup>) in the sample. The alkalinity was then calculated with

195 the Gran method (Gran, 1952). As speciation was determined using High-performance liquid  
196 chromatography (HPLC) coupled with an AFS-HG (Atomic Fluorescence Spectrometry-hydride  
197 generation) called Xcalibur (Thermo Fisher) or by ICP. In the first case, the solution is analyzed  
198 straightaway (typically within 15 min), while in the second case, As(V) was separated from As(III) on  
199 resin (Biorad AG 1X8, 50-100 Mesh), and then As(V), As(III), and total As were analyzed to check the  
200 results consistency. The recovery percentage was  $100 \pm 5$  %. Ultraviolet/visible spectrophotometry  
201 (UV-VIS) of Cr(VI) was done conforming to the ISO 11083 international standard with an ATI Unicam  
202 UV2 spectrophotometer.

### 203 3.5. *Preparation of the synthetic water*

204 The synthetic pore water was prepared with boiled and outgassed Millipore Milli-Q® 18 MΩ water and  
205 using  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , KCl, NaCl,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaHCO}_3$  analytical grade salts  
206 (Supplementary information B). The preparation was done in a glove box with an atmosphere closed  
207 to the field, and equilibrated with carbonates (99 %  $\text{N}_2$  / 1 %  $\text{CO}_2$ ). The synthetic pore water chemistry  
208 was based on pore water chemistry modeled in Tégulines Clay from the drilling campaigns described  
209 in Lerouge et al. (2018), following the procedure given by Gaucher et al. (2009) for the Callovian-  
210 Oxfordian clay rock. *In situ* pore water measured by squeezing (Lerouge et al., 2018) was consistent  
211 with the model and validated it. Synthetic pore water was used in this study for the equilibration and  
212 “batch” sorption tests in order to reach the steady state concentrations of major elements faster than  
213 by addition of Milli-Q® 18 MΩ water and avoid mineral dissolution.

### 214 3.6. *Determination of natural contents of As, Cr and B release from Tégulines Clay and sorption* 215 *tests*

216 All the experiments were done in a glove box under anoxic conditions to avoid on one hand the  
217 oxidation of the sediments, and on the other hand the oxidation of the redox sensitive toxic elements.  
218 Once the pore water had been prepared, the desired volume was equilibrated with a suitable sediment  
219 mass in a polypropylene copolymer (PPCO) container for at least 24 h under agitation. Once the time  
220 limit had been reached, the agitation was stopped, the solution was decanted for 30 min, and then the  
221 supernatant was sampled, filtered at 0.1  $\mu\text{m}$ , and acidified with 20  $\mu\text{L}$  of  $\text{HNO}_3$  suprapur®.

222 Three types of experiments were conducted for best understanding of the behavior of As, Cr, and B in  
223 the Tégulines Clay rock formation. They consisted of: (i) kinetics equilibration experiments, which  
224 aimed at determining the equilibrium concentration of As, Cr, and B in the pore water, as well as  
225 determining the kinetics of equilibration between the sediments and the solution; (ii) batch sorption  
226 tests, which aimed at determining the As, Cr, and B distribution coefficients on the sediments; and (iii)  
227 kinetics sorption experiments, which aimed at determining the kinetics of As and Cr sorption on the  
228 sediments. Thus, As, Cr, or B were only spiked in the solutions for the (ii) and (iii) experiments.

229 To determine the natural release of As, Cr, and B from the Tégulines Clay, and thus the equilibrium  
230 concentrations, kinetic experiments were completed over 49 days at a solid to liquid ratio ( $R_{SL}$ ) of 1 g  
231  $L^{-1}$ . Measurements were performed on independent experiment samples at 8, 9, 26, 42, and 49 days.  
232 For each contact time, three replicates were analyzed. In addition, equilibration experiments were  
233 done at an  $R_{SL}$  ranging from 0.001 to 0.1  $kg L^{-1}$ , and with pH values in the range of 7.2–7.4, to better  
234 constrain the natural source.

235 Sorption tests were conducted at an  $R_{SL}$  of 10  $g L^{-1}$ . Mother solutions containing the element of  
236 interest (As, Cr, or B) were prepared with analytical grade salts (using  $Na_2HAsO_4 \cdot 7H_2O$ ,  $NaAsO_2$ ,  
237  $Na_2CrO_4$  or  $Na_2B_4O_7 \cdot 10H_2O$ ). Then, an aliquot was introduced into a vial containing the sediment  
238 suspension in order to reach the initial target concentration. The solution and the sediments were kept  
239 in contact for at least four days. Sampling of the reacted sediments and solution was the same as the  
240 one described for the equilibration tests.

241 Kinetic sorption experiments were made for redox sensitive elements (As and Cr) at the following  
242 sample time: 1, 7, 15, and 30 days. The method was the same as the one described above. Two  
243 Cr(VI) concentrations have been tested ( $5.1 \cdot 10^{-6}$  and  $4.8 \cdot 10^{-5} \text{ mol } L^{-1}$ ) due to the high concentration  
244 decrease observed with the lowest concentration, while only one was tested for As(V) ( $2.5 \cdot 10^{-5} \text{ mol } L^{-1}$ ).  
245 Two replicates were made for each sample time. The fact that the added concentrations remain  
246 under the solubility of potential phases was checked with Phreeqc program (Parkhurst and Appelo,  
247 2013) using the Thermoddem (Blanc et al., 2012) and ThermoChimie databases (Giffaut et al., 2014).

## 248 4. Results

### 249 4.1. *Mineral and chemical characterization of oxidized and reduced Tégulines Clay samples*

250 The AUB00307 sample of Tégulines Clay consisted of ~57 wt.% clay minerals, ~9 wt.% carbonates,  
251 and 32 wt.% quartz-feldspar (Table 1). The AUB00976 sample consisted of ~56 wt.% clay minerals,  
252 ~16.5 wt.% carbonates, and 26 wt.% quartz-feldspar (Table 1). Variation in carbonate content and  
253 quartz-feldspar content was essentially due to the position of the sample in the clay formation (Fig. 2  
254 a). The clay fraction was quite similar in the both samples, and essentially consisted of illite/mica and  
255 illite-smectite mixed layers with minor amounts of kaolinite and chlorite. The carbonate fraction was  
256 essentially composed of calcite with minor amounts of dolomite and siderite. Pyrite was detected by  
257 XRD in the AUB00307 reduced sample, but not in the AUB00976 oxidized sample.

258 Complementary microscopic optical observations indicated that a large part of the calcite occurs as  
259 bioclasts (ammonites, foraminifers) (Fig. 3d & g), micrite disseminated in the clay matrix, and minor  
260 microsparite filling some bioclasts or cementing quartz grains. Diagenetic glauconite was frequently  
261 observed as 20 to 50  $\mu\text{m}$ -sized aggregates, always green in color in the AUB00307 sample (Fig. 3f &  
262 h), but green to brownish in color in the AUB00976 sample (Fig. 3c). Pyrite usually occurred as < 10  
263  $\mu\text{m}$  sized framboids disseminated in the clay matrix and as a filling in bioclasts and bioturbations (Fig.  
264 3g & h). In the AUB00976 sample, pyrite was replaced by brownish iron oxyhydroxides (Fe-Ox) and  
265 gypsum. Gypsum also occurred as 100-500  $\mu\text{m}$  sized euhedral grains (Fig. 3e). As expected, the  
266 mineral assemblage of the AUB00976 sample gave evidence of oxidation (glauconite changes, pyrite  
267 dissolution, iron hydroxides and gypsum precipitation) while AUB00307 remained reduced (glauconite  
268 still green, pyrite, no iron hydroxides or gypsum).

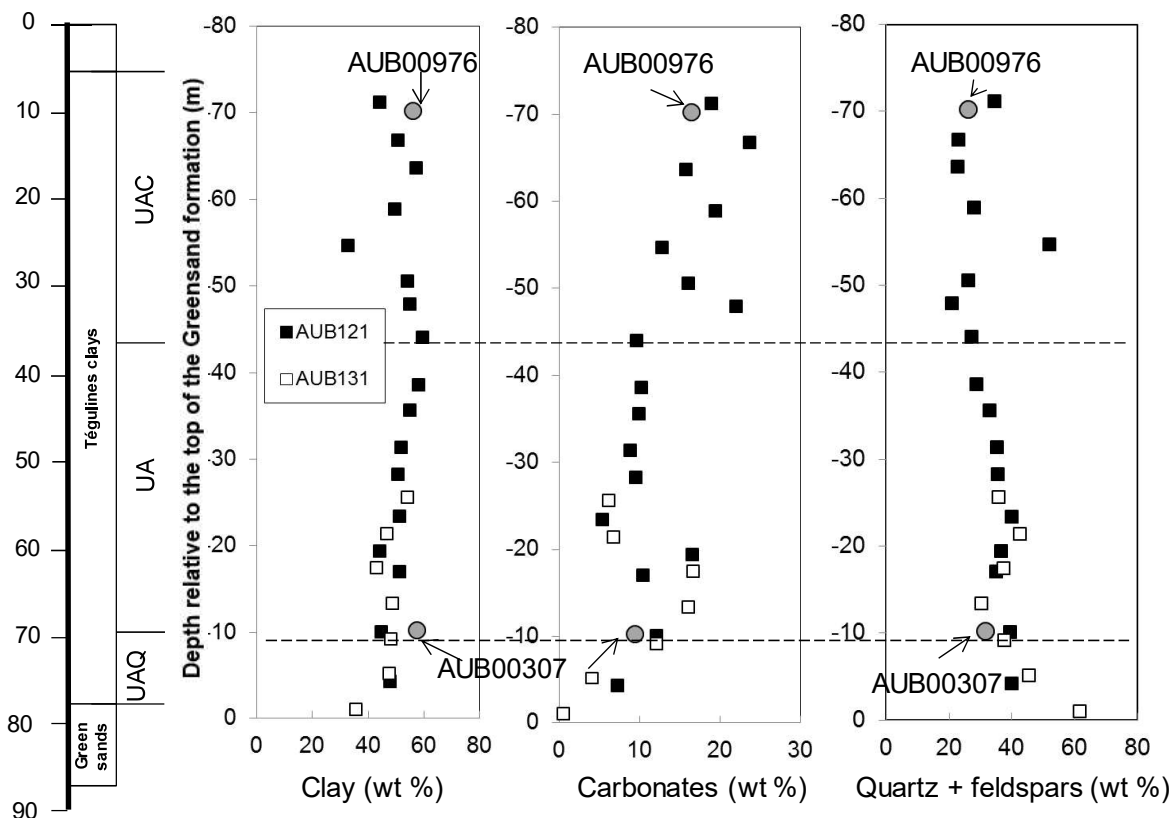
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270  
 271 **Table 1** Quantification of the mineralogical composition of the oxidized sample (AUB00976) and  
 272 reduced sample (AUB00307) by XRD (data in wt.%). Names in italics refer to the drilling described in  
 273 Fig. 1 and in Lerouge et al. (2018).

		<b>AUB00976</b>	<b>AUB00307</b>
		<i>(AUB121)</i>	<i>(AUB131)</i>
<b>Depth</b>		7.8–7.95 m	21.75–21.93 m
<b>Phyllosilicates</b>	Chlorite/vermiculite	3.8	1.3
	Illite/mica	20.2	22.7
	Illite/Smectite interstratified	24.0	21
	Kaolinite	8.0	12.4
	Sum	56.0	57.4
<b>Carbonates</b>	Calcite	16.2	8.9
	Dolomite/ankerite	0.2	0.2
	Siderite	0.1	0.3
	Sum	16.5	9.4
<b>Tectosilicates</b>	Feldspar	3.5	3.8
	Quartz	22.6	27.9
	Sum	26.1	31.7
<b>Oxides</b>	Anatase	0.7	0.8
	Rutile	0.3	0.1
<b>Sulfurs</b>	Pyrite	0	0.4

274

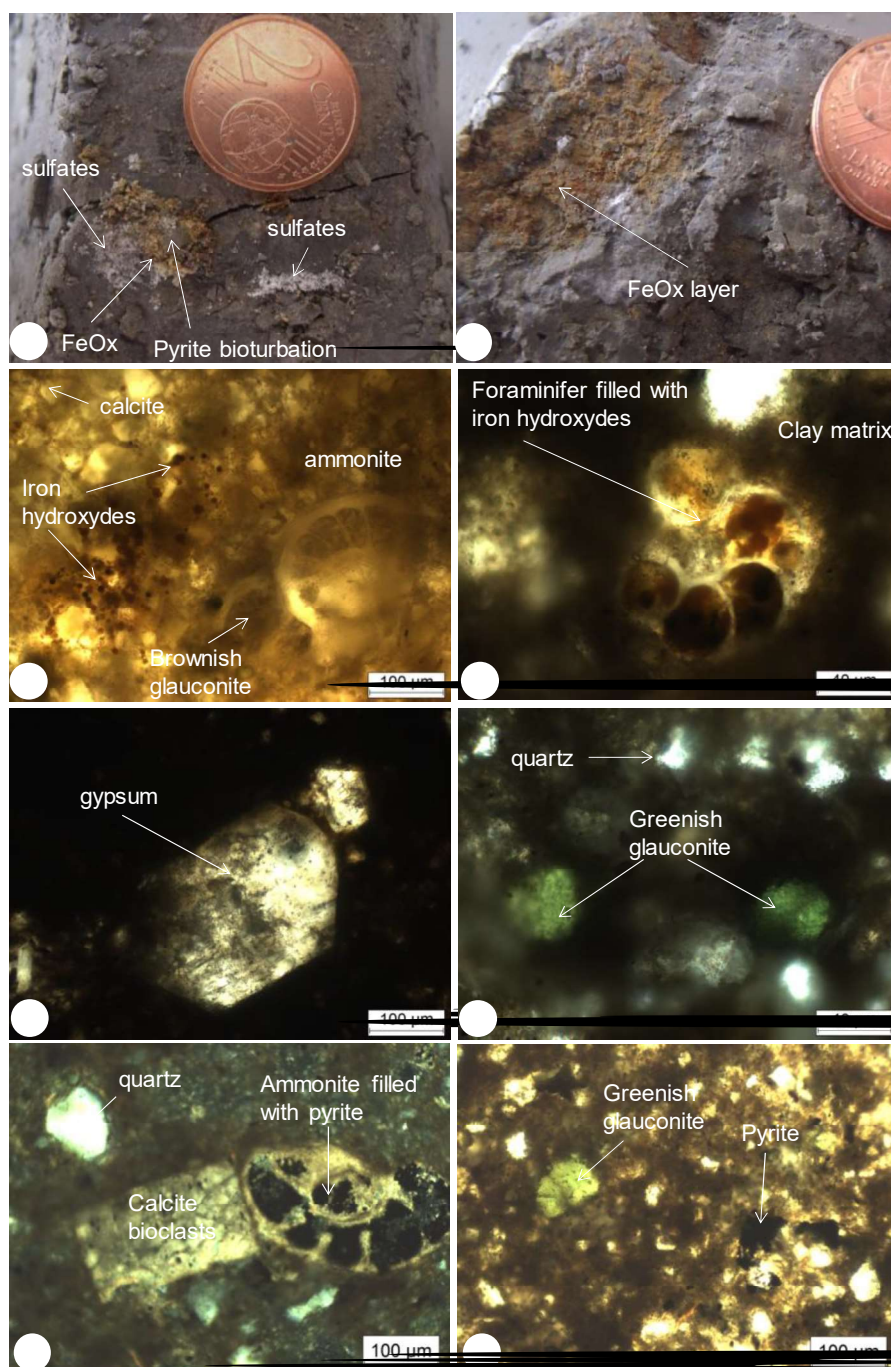
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277

278 **Fig. 2. Profiles of clay minerals, carbonates, and quartz + K-feldspar contents as a function of**  
 279 **depth relative to the top of the greensands. Dashed lines indicate the limits of the three units**  
 280 **defined in the Tégulines Clay. The positions of the two samples are indicated in each profile**  
 281 **according to the Figure 2 in Lerouge et al. (2018).**

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285  
 286 **Fig. 3. Photographs of: (a) oxidized sample in which pyrite bioturbation, FeOx and sulfates can**  
 287 **be observed; (b) FeOx layer in oxidized sample; and photomicrographs (in transmitted light) of:**  
 288 **(c) calcite, ammonite, iron hydroxides and altered brownish glauconite (oxidized sample); (d)**  
 289 **foraminifer filled with iron hydroxides in the clay matrix (oxidized sample); (e) gypsum**  
 290 **(oxidized); (f) well preserved rounded, green mass of glauconite and quartz (reduced); (g)**  
 291 **quartz, calcite and ammonite filled with pyrite (reduced sample); (h) well preserved rounded,**  
 292 **green mass of glauconite and pyrite (reduced sample).**

293 4.2. *Distribution of trace elements (As, Cr, B) among phases of Tégulines clay samples*

294 Sequential extractions were conducted in order to determine the natural distribution of the studied  
295 elements among the mineral phases (Fig. 4), and bulk (As, Cr, B) contents of studied samples were  
296 compared with bulk (As, Cr, B) element contents of tégulines Clay from drilling campaigns described in  
297 Lerouge et al. (2018) (Fig. 5).

298 The abundance of As in the exchangeable fraction was low ( $< 0.3\%$ ) in the two samples (Fig. 4a).  
299 Similarly, As was only present in trace amounts in carbonates ( $0.7 \pm 0.2\%$  and  $0.8 \pm 0.03\%$  for  
300 reduced and oxidized samples, respectively), and in Fe and Mn oxyhydroxides ( $1.0 \pm 0.2\%$  and  $0.9 \pm$   
301  $0.1\%$  for reduced and oxidized samples, respectively). In contrast, organic matter was a larger  
302 reservoir of As for the reduced sample ( $11.4 \pm 1.2\%$ ) than for the oxidized sample ( $1.4 \pm 0.1\%$ ). In  
303 both samples, the residual fraction was the main As reservoir. The As contents did not vary  
304 significantly with depth in the Tégulines Clay, but varied between boreholes (Fig. 5). The As  
305 concentrations measured in the reduced sample ( $21.2 \pm 3.9 \mu\text{g g}^{-1}$ ) were higher than those measured  
306 in the oxidized sample ( $13.9 \pm 0.8 \mu\text{g g}^{-1}$ ), although both remained in the range of values for the  
307 Tégulines Clay ( $51 \pm 31 \mu\text{g g}^{-1}$ ) (Fig. 4).

308 The total Cr concentrations were  $111.1 \pm 8.7 \mu\text{g g}^{-1}$  in the reduced sample and  $117.2 \pm 15.2 \mu\text{g g}^{-1}$  in  
309 the oxidized sample, and was found to be heavily concentrated in the residual fraction (Fig. 4b). Those  
310 values were close to the average concentrations reported in the Tégulines Clay for Cr ( $109 \pm 37 \mu\text{g g}^{-1}$ )  
311 (Fig. 5). The highest extraction yields were obtained in the fraction corresponding to organic matter  
312 ( $2.4 \pm 0.2\%$  in the reduced sample and  $1.6 \pm 0.2\%$  in the oxidized sample). It is noteworthy that Fe  
313 and Mn oxyhydroxides retained an order of magnitude more Cr in the reduced sample ( $0.80 \pm 0.04\%$ )  
314 than in the oxidized sample ( $0.07 \pm 0.02\%$ ).

315 The B concentrations were  $96.5 \pm 4.7 \mu\text{g g}^{-1}$  and  $117.3 \pm 5.6 \mu\text{g g}^{-1}$  for the reduced and oxidized  
316 samples, respectively. Those values were close to the average concentrations reported in the  
317 Tégulines Clay for B ( $111 \pm 22 \mu\text{g g}^{-1}$ ) (Fig. 5). In both samples almost all of the B ( $> 98\%$ ) was  
318 concentrated in the residual fraction (Fig. 4c).

319 Electron microprobe analyses of pyrite, iron hydroxides, gypsum, celestite, calcite, glauconite, and  
320 clay matrix indicated that As was essentially detected in pyrite ( $628 \pm 240 \mu\text{g g}^{-1}$ ,  $n = 27$ ), iron-

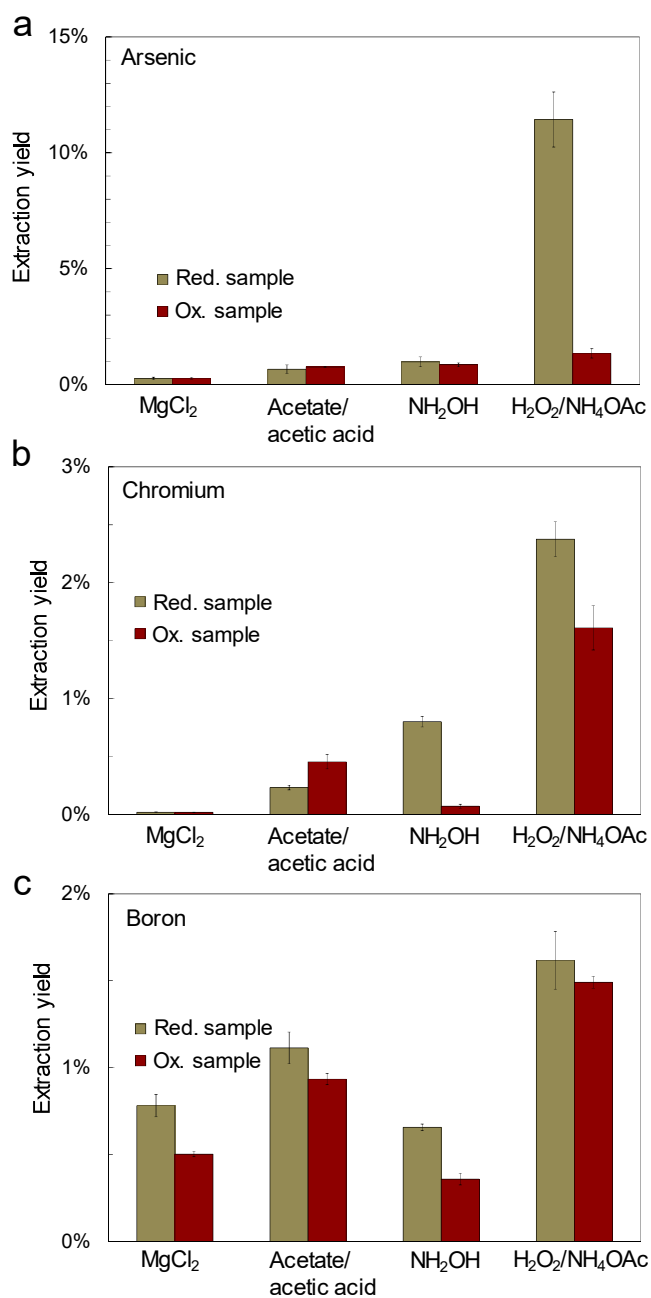


321 hydroxides ( $211 \pm 307 \mu\text{g g}^{-1}$ ,  $n = 20$ ), and gypsum ( $170 \mu\text{g g}^{-1}$ ), whereas Cr was detected essentially  
322 in glauconite ( $564 \pm 288 \mu\text{g g}^{-1}$ ,  $n = 30$ ), clay matrix ( $188 \pm 33 \mu\text{g g}^{-1}$ ,  $n = 20$ ), and also in phosphates  
323 ( $114 \pm 106 \mu\text{g g}^{-1}$ ,  $n = 5$ ). Additionally, iron hydroxides produced from oxidation of pyrite were richer in  
324 As ( $609 \pm 181 \mu\text{g g}^{-1}$ ,  $n = 9$ ) than iron hydroxides in the clay matrix (As was below the detection limit of  
325  $150 \mu\text{g g}^{-1}$ ).

326 Complementary X-ray dot mapping of As from a zone of oxidized pyrite surrounded by iron hydroxides  
327 and gypsum using the electron microprobe confirmed that As occurs as a trace element in pristine  
328 pyrite, secondary gypsum, and iron hydroxides, but not in the clay matrix (Fig. 6).

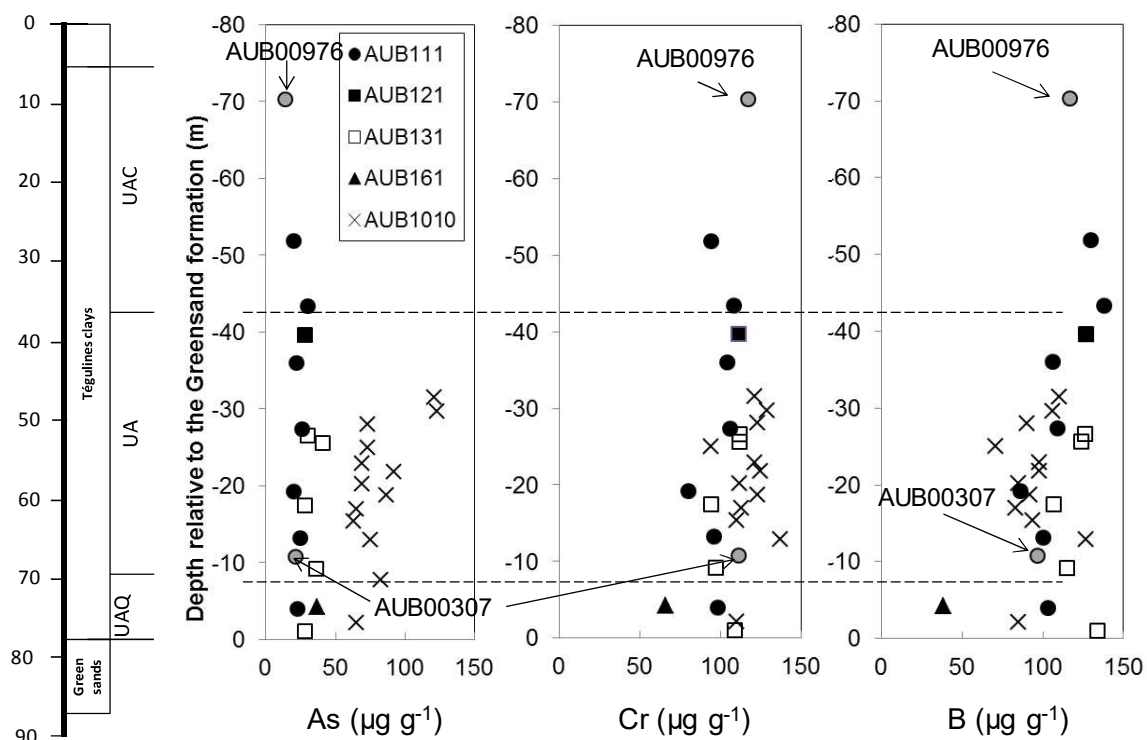
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331

332 **Fig. 4. Percentages of As (a), Cr (b), and B (c) at each step of the sequential extraction of the**  
 333 **reduced (AUB00307) and the oxidized (AUB00976) Tégulines clay samples. The four fractions**  
 334 **correspond to exchangeable, carbonate, Fe-Mn-oxyhydroxides, and organic matter, while the**  
 335 **residual fraction is not shown. The error bars were calculated using three replicates of the**  
 336 **experiments.**

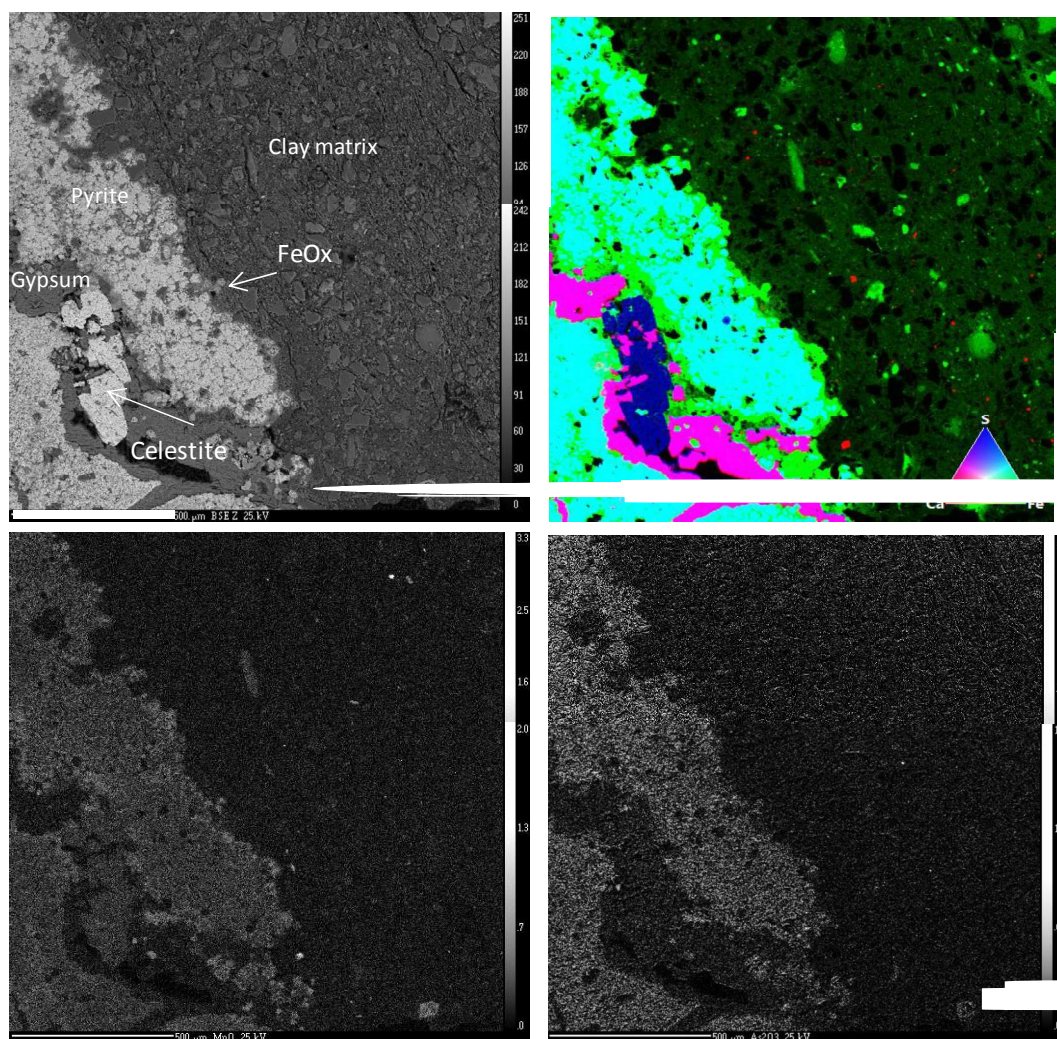


337

338 **Fig. 5. Profiles of As, Cr and B contents as a function of depth relative to the top of the**  
 339 **greensands. Dashed lines indicate the limits of the three units defined in the Tégulines Clay.**  
 340 **The positions of the two samples are indicated in each profile according to the Figure 2 in**  
 341 **Lerouge et al. (2018).**

342

343



344

345 **Fig. 6. Reactive assemblage observed in the transition redox zone (AUB1010, depth 8.25 m)**  
 346 **showing early diagenetic celestite and pyrite partially oxidized into iron oxides and gypsum: (a)**  
 347 **BSE image; (b) Ca- Fe-S ternary RGB map; (c) Mn X-ray dot map; and (d) As X-ray dot map.**

#### 348 4.3. Chemical composition of pore waters extracted by squeezing

349 Pore waters were extracted by squeezing technique from the reduced sample (Table 2). The pH value  
 350 of the extracted pore waters was measured at 7.7, and a carbonate alkalinity value at 3.7 meq L<sup>-1</sup>. The  
 351 calculated ionic strength was 0.1. The concentrations of Ca, Mg and sulfate were the greatest in the  
 352 pore waters. The S<sub>2</sub>O<sub>3</sub><sup>2-</sup> concentration (0.20 mmol L<sup>-1</sup>) is consistent with the reduced state of the  
 353 sample. Both Fe and Al were systematically below the detection limit (0.01 mmol L<sup>-1</sup>).

354

355

356 **Table 2.** Pore water chemistry measured after squeezing of the reduced sample (in mmol L<sup>-1</sup>).

Anions	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	F <sup>-</sup>	
(mmol L <sup>-1</sup> )	1.47	26.02	0.20	0.002	< 0.016	0.018	0.034	
Cations	Si	Na	K	Mg	Ca	Ba	Sr	Fe
(mmol L <sup>-1</sup> )	0.2	2.78	1.38	16.87	16.57	< 0.002	0.42	< 0.005
Trace elements	As	B	Cd	Cr	Cu	Hg	Mn	Zn
(μmol L <sup>-1</sup> )	0.01	148	0.003	0.029	58	0.015	29	31

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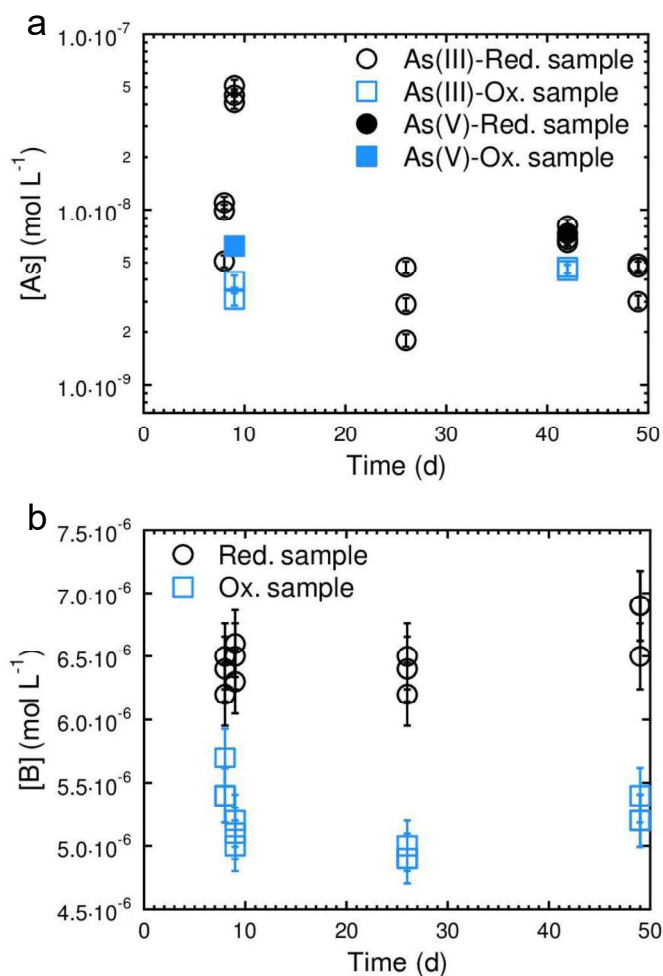
#### 358 4.4. *Sample equilibration and element natural release in solution*

359 Equilibration experiments revealed that in the two samples, As is principally released in solution as  
 360 As(III) (Fig. 7), which was detected in all replicates of equilibration tests made with the reduced  
 361 sample. As(V) was only detected at 9 and 42 days in two replicates with the oxidized sample. The  
 362 detected values remained lower than As concentration in the pore water ( $10^{-8}$  mol L<sup>-1</sup>, see Fig. 7 and  
 363 Table 2 for pore water value) although two replicates evidenced higher concentration after 8 days of  
 364 equilibration. The concentrations remained almost stable during the experiments pleading for a quick  
 365 equilibration of the system with labile As.

366 The measured Cr concentrations in solution (i.e. Cr<sub>total</sub> and Cr(VI)) remained negligible in the time  
 367 scale investigated here ( $< 1.9 \cdot 10^{-9}$  mol L<sup>-1</sup>), and therefore, they were lower than those found in the  
 368 squeezed pore water ( $2.9 \cdot 10^{-8}$  mol L<sup>-1</sup>, see Table 2).

369 The measured B concentrations were constant with time and were similar in the two samples. The  
 370 values were 30 times lower than those for the squeezed pore water ( $1.5 \cdot 10^{-4}$  mol L<sup>-1</sup>).

371

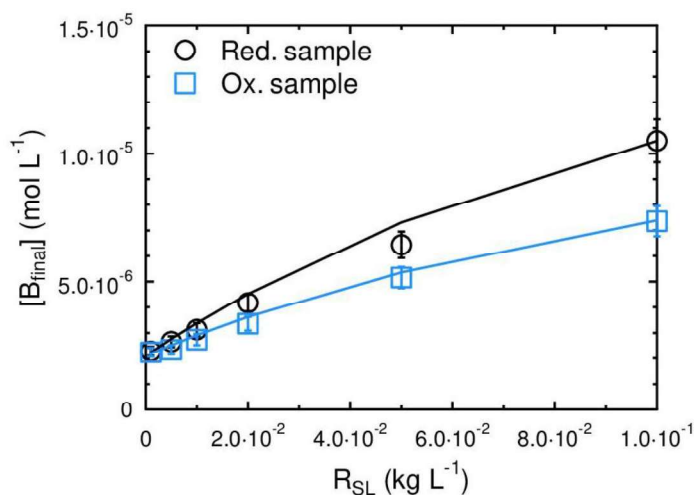


372

373 **Fig. 7. As (a) and B (b) concentrations during the kinetic equilibration of the oxidized sample**  
 374 **(AUB00976) and reduced sample (AUB00307) of Tégulines Clay. Analytical uncertainties are 4**  
 375 **%, and As and B quantification limit (QL) were  $7 \cdot 10^{-10} \text{ mol L}^{-1}$  and  $4.6 \cdot 10^{-8} \text{ mol L}^{-1}$ , respectively.**  
 376 **For a same time, the different circles and squares were replicates.**

377 Cr was undetectable ( $< 1.9 \cdot 10^{-9} \text{ mol L}^{-1}$ ) in the equilibration tests performed from 0.001 to 0.1 kg L<sup>-1</sup>,  
 378 while As concentrations ranged from  $2 \cdot 10^{-9}$  to  $8 \cdot 10^{-9} \text{ mol L}^{-1}$ , and were independent of the solid to  
 379 liquid ratio ( $R_{SL}$ ). In contrast, B concentrations increased with  $R_{SL}$  (Fig. 8). The B concentrations  
 380 remained slightly higher in reduced samples as compared to oxidized samples, consistent with the  
 381 kinetics experiments (Fig. 7). The boron released in solution as a function of the solid/liquid ratio  
 382 enabled determination of the labile concentration for each sample, as well as the initial distribution  
 383 coefficient (see Section 5.3).

384



385

386 **Fig. 8. B concentrations in solution (mol L<sup>-1</sup>) are a function of the solid to liquid ratio (R<sub>SL</sub> in kg**  
 387 **L<sup>-1</sup>). The solid lines represent the fits obtained according to Equation 7 (see section 5.3).**

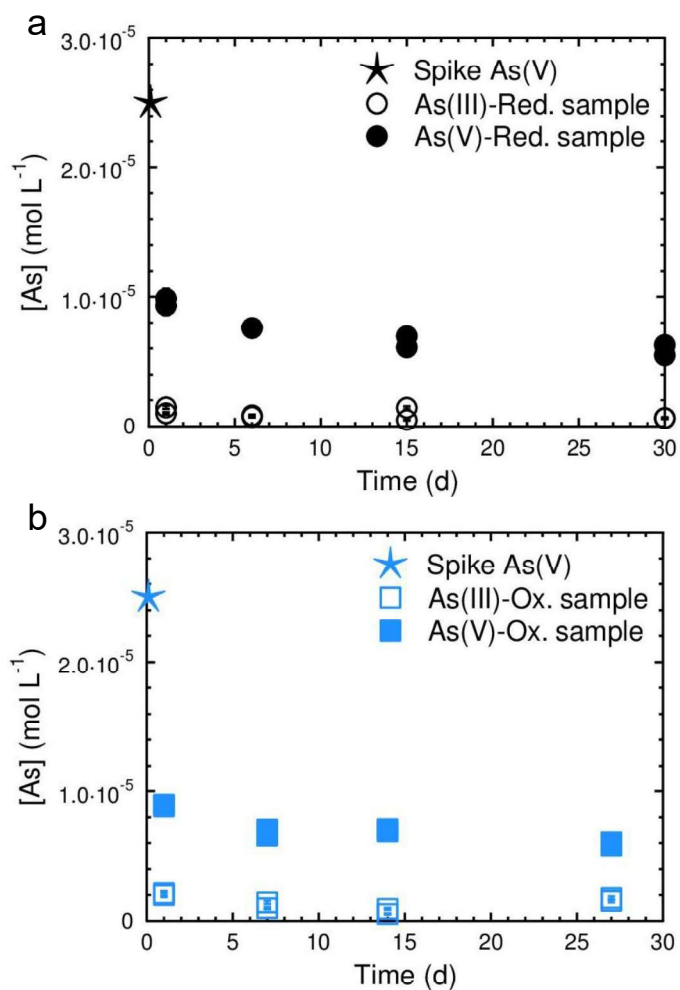
388 4.5. Sorption experiments on Tégulines Clay

389 4.5.1. Arsenic

390 As in solution remained mostly in its As(V) form in solution while in contact with the reduced or  
 391 oxidized samples of Tégulines Clay (Fig. 9). An initial reduction occurred and led to the formation of  
 392 As(III), but this seemed to stop after one day of reaction. Within 1 day, 60 % of the As was adsorbed,  
 393 before the sorption slowed down according to a first order law. At the end of the experiments, 25 % of  
 394 the As was still present in solution.

395 Upon adsorption, As(V) was reduced to As(III), and the release of As(III) in solution was revealed  
 396 during the equilibration tests. Thus, sorption tests with As(III) were done in order to better constrain the  
 397 rock capacity to retain this form of As. The results showed a slightly higher As retention on the  
 398 oxidized sample than on the reduced sample (Supplementary information C). In both cases, the  
 399 retention was significant and ranged from 20 to 60 % for the oxidized sample and from 15 to 50 % for  
 400 the reduced sample.

401



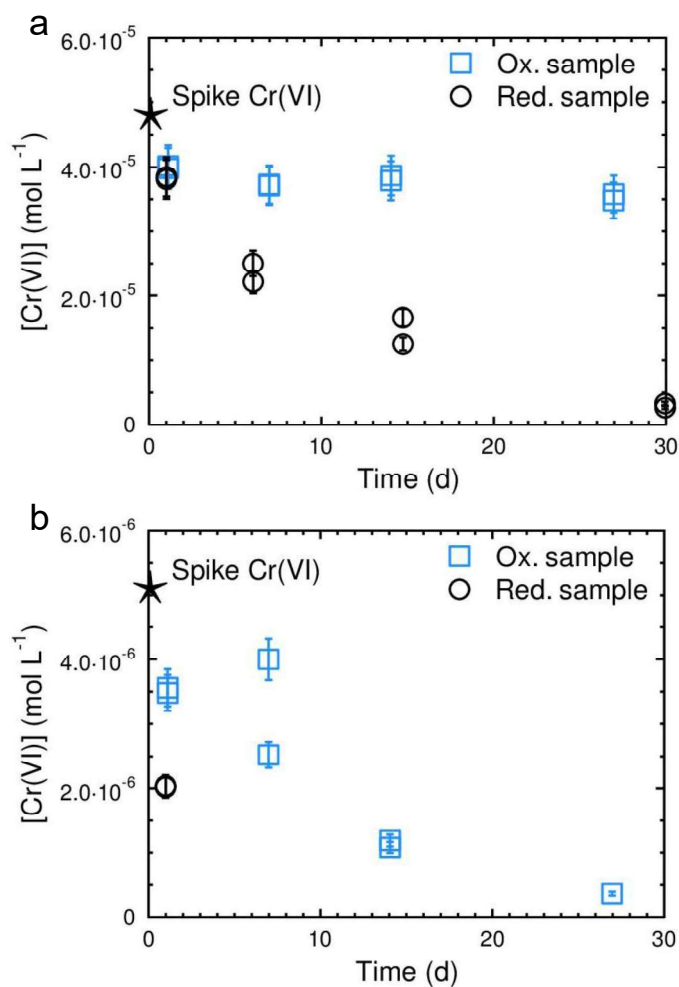
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403 **Fig. 9. As speciation (As(V) and As(III)) in the kinetic experiment of sorption with an initial**  
 404 **concentration of  $2.5 \times 10^{-5} \text{ mol L}^{-1}$  in contact with: (a) the reduced sample (AUB00307); (b) the**  
 405 **oxidized sample (AUB00976).**

#### 406 4.5.2. Chromium

407 Cr sorption experiments were performed using Cr(VI), because it is its expected form during its  
 408 release from the (LL-LL) radioactive waste. The introduction of  $4.8 \times 10^{-5} \text{ mol L}^{-1}$  Cr(VI) in a suspension  
 409 was followed by a fall of Cr(VI) in solution until  $2.7 \times 10^{-6} \text{ mol L}^{-1}$  (Fig. 10a). This decrease occurred  
 410 within 30 d of the interaction with the reduced sample, and represented a loss of 95 % of the Cr(VI),  
 411 while only 20 % was removed in the case of the oxidized sample (Fig. 10a). The difference was higher  
 412 for the lowest tested concentrations ( $5.1 \times 10^{-6} \text{ mol L}^{-1}$ ). In contact with the reduced sample, Cr(VI) was  
 413 removed from the solution between 1 and 6 days (Fig. 10b), while only 25 % ( $3.7 \times 10^{-7} \text{ mol L}^{-1}$ ) of the  
 414 Cr(VI) remained in solution in contact with the oxidized sample (Fig. 10b).





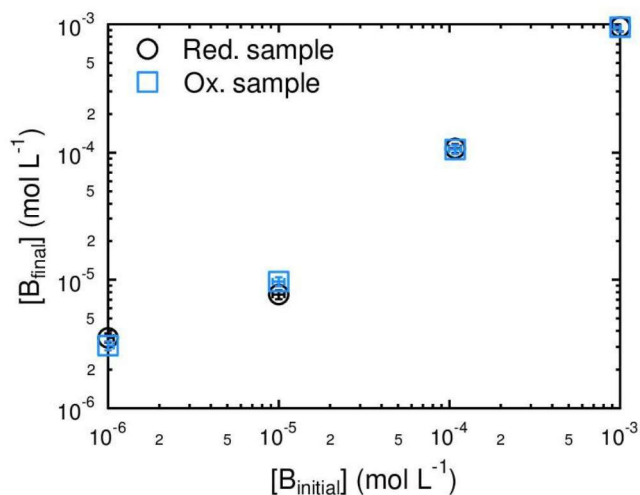
415

416 **Fig. 10. Comparison of Cr(VI) concentrations in the kinetic experiments of sorption with an**  
 417 **initial concentration of: (a)  $4.8 \times 10^{-5} \text{ mol L}^{-1}$ ; (b)  $5.1 \times 10^{-6} \text{ mol L}^{-1}$  in contact with the reduced**  
 418 **sample (AUB00307) and the oxidized sample (AUB00976) of Tégulines Clay.**

419 4.5.3. *Boron*

420 Sorption experiments of B showed few differences between initial and final B concentrations in  
 421 solution (Fig. 11a). Experiments conducted at an initial concentration that is lower than the value  
 422 measured in equilibration tests ( $2.2 \cdot 10^{-6} \text{ mol L}^{-1}$ ) would be expected to lead to higher final values than  
 423 the initial ones, confirming the high lability of B in our samples. In addition, the retention on both the  
 424 Teguline Clay were similar.

425



426

427 **Fig. 11. Initial and final B concentrations in sorption tests with the oxidized sample (AUB00976)**  
 428 **and the reduced sample (AUB009307) of Tégulines Clay.**

## 429 5. Discussion

### 430 5.1. Natural distribution coefficient ( $R_{D,Nat}$ ) of As, Cr and B in the Tégulines Clay

431 This study revealed that As, Cr, and B are naturally present in the Tégulines Clay (in Reduced and  
 432 oxidized samples). These elements were released in the pore water in different amounts (Table 2)  
 433 depending on their abundance and the carrier phases. A natural element sediment-solution  
 434 partitioning coefficient called natural distribution coefficient ( $R_{D,Nat}$ ) was calculated from those  
 435 measurements (Table 3) according to the equation 1:

$$436 \quad R_{D,Nat} = \frac{C_{sediment,Nat}}{C_{pore\ water}} \quad (1)$$

437 where  $C_{Pore\ water}$  is the pore water concentration of the toxic element in mol L<sup>-1</sup> given in the Table 2, and  
 438  $C_{sediment,Nat}$  is the concentration of this toxic element in the sediments in mol kg<sup>-1</sup> determined with the  
 439 sequential extractions (section 4.2).

440 High natural distribution coefficients were calculated for As and Cr (~2 10<sup>4</sup> L kg<sup>-1</sup> for As, and ~7.5 10<sup>4</sup>  
 441 L kg<sup>-1</sup> for Cr), which confirm the affinity of those elements for the sediment phases in Tégulines Clay  
 442 (Table 3). In the meantime, the natural  $R_D$  of boron is three orders of magnitude lower (~60 L kg<sup>-1</sup>),  
 443 and indicates the high lability of this element.

444 **Table 3** Natural distribution coefficient  $R_{D,Nat}$  in  $L\ kg^{-1}$  calculated with the pore water chemistry ( $mol\ L^{-1}$ ) given in  
 445 the Table 2 and the sediment natural concentration ( $mol\ kg^{-1}$ ) in reduced and oxidized samples of Tégulines Clay  
 446 determined with sequential extractions (section 4.2)

	As		Cr		B	
	oxidized	reduced	oxidized	reduced	oxidized	reduced
$C_{Pore\ water}$ ( $mol\ L^{-1}$ )	$1.00\ 10^{-8}$	$1.00\ 10^{-8}$	$2.90\ 10^{-8}$	$2.90\ 10^{-8}$	$1.48\ 10^{-4}$	$1.48\ 10^{-4}$
$C_{sediment,Nat}$ ( $mol\ kg^{-1}$ )	$2.83\ 10^{-4}$	$1.86\ 10^{-4}$	$1.48\ 10^{-3}$	$1.56\ 10^{-3}$	$1.29\ 10^{-3}$	$1.57\ 10^{-3}$
$R_{D,Nat}$ ( $L\ kg^{-1}$ )	$1.9\ 10^4$	$2.8\ 10^4$	$7.4\ 10^4$	$7.8\ 10^4$	73	60

447

448 5.2. Influence of the labile fraction on the distribution coefficient ( $R_D$ )

449 The retention of an element of interest by a sediment was calculated through a distribution coefficient  
 450 ( $R_D$  in  $L\ kg^{-1}$ ), defined as the ratio between the concentration of the element sorbed on the sediment  
 451 ( $C_{sorb}$  in  $mol\ kg^{-1}$ ) over the element concentration remaining in the liquid ( $C_{final}$  in  $mol\ L^{-1}$ ) according to  
 452 Equation 2:

$$453 \quad C_{sorb} = C_{final} R_D \quad (2)$$

454 However, the squeezing and equilibration experiments revealed that the three elements of interest  
 455 present in the sediments were partly released in solution. Thus, the natural labile concentrations on  
 456 the sediments ( $C_{labile,ini}$  in  $mol\ kg^{-1}$ ) must be considered in the calculation, depending on the results  
 457 obtained during equilibration experiments. Therefore,  $C_{sorb}$  must be calculated according to Equation  
 458 3:

$$459 \quad C_{sorb} = C_{labile,ini} + \frac{C_{added} - C_{final}}{R_{SL}} \quad (3)$$

460 where  $C_{added}$  is the added concentration in the retention experiments in  $mol\ L^{-1}$ ,  $C_{final}$  is the element  
 461 concentration at the end of the retention tests in  $mol\ L^{-1}$  and  $R_{SL}$  is the solid/liquid ratio in  $kg\ L^{-1}$ . This  
 462 relationship modifies the distribution coefficient calculation, and is given by the relation 4:

$$463 \quad R_D = \frac{C_{labile,ini} + \frac{(C_{added} - C_{final})}{R_{SL}}}{C_{final}} = \frac{R_{D,ini} C_{pore\ water} + \frac{(C_{added} - C_{final})}{R_{SL}}}{C_{final}} \quad (4)$$

464 where  $C_{\text{pore water}}$  is the pore water measured by squeezing, and  $R_{D,\text{ini}}$  is the initial  $R_D$  that considers the  
 465 natural labile abundance of an element on the sediments. In the case of equilibration,  $C_{\text{added}}$  is equal to  
 466 zero, so Equation 4 becomes:

$$467 \quad R_{D,\text{eq}} = \frac{R_{D,\text{ini}} C_{\text{pore water}} \frac{C_{\text{final}}}{R_{\text{SL}}}}{C_{\text{final}}} \quad (5)$$

468 Equations 4 and 5 are used to calculate the initial  $R_{D,\text{ini}}$  that has to be considered for  $R_D$  calculations in  
 469 the case of high labile concentrations of elements present in the clay rock such as B.

### 470 5.3. *The role of natural abundance boron on its retention on Tégulines clay*

471 The  $R_D$  calculations for B were influenced by B abundance in the sediments, because of the low  
 472 natural  $R_D$  value. This  $R_D$  value reflects the high lability of this element *in situ*. However, B equilibration  
 473 concentrations ( $\sim 3 \cdot 10^{-6} \text{ mol L}^{-1}$  at  $R_{\text{SL}} = 10 \text{ g L}^{-1}$ , Fig. 8) were fifty times lower than the pore water  
 474 concentrations measured by squeezing (Table 2). With a water content of 0.15 and a  $R_{\text{SL}}$  of  $0.01 \text{ kg L}^{-1}$ ,  
 475 the contribution of pore water to the released B was  $2.3 \times 10^{-7} \text{ mol L}^{-1}$ , or 8 times less than the  
 476 equilibration concentration.

477 Consequently, B in solution originates mainly from desorption or from dissolution of a boron-bearing  
 478 phase such as carbonates (Hemming and Hanson, 1992; Hemming et al., 1998; Mavromatis et al.,  
 479 2015) or clay minerals (Muttik et al., 2011; Williams and Hervig, 2005). Because the squeezing  
 480 method provides us with the equilibrium concentration after long interaction times that cannot be  
 481 probed in laboratory experiments, the present observation indicates that B was mainly concentrated in  
 482 phases that have very slow kinetics of equilibration with water (Fig. 7), consistent with concentration in  
 483 the residual fraction. In addition, kinetic studies carried out on batch sorption experiments very  
 484 frequently show two stages of uptake: an initial rapid uptake (minutes to hours) of the sorbing species,  
 485 followed by a much slower uptake over the very long term. This behavior is generally interpreted as  
 486 being the result of a two-stage process wherein a rapid adsorption reaction (ion exchange or surface  
 487 complexation) is followed by a much slower process of sorbant incorporation into the solid matrix (by  
 488 diffusion in the solid, solid-solution formation or co-precipitation).  $R_D$  values determined in batch  
 489 systems on dispersed materials generally are based on the short-term sediment-solution partitioning  
 490 values, and do not take into consideration the long-term evolution of the B concentrations.

491 The concentration of B in solution increased with the  $R_{SL}$  ratio in the equilibration experiments (Fig. 8).  
 492 In all cases, B concentrations remained lower than the total B quantity in the sediments (from  $2 \cdot 10^{-6}$  to  
 493  $1 \cdot 10^{-5} \text{ mol L}^{-1}$ ). Those equilibration experiments enabled calculation of an initial distribution coefficient  
 494 from the initial B concentration in the sediments, according to the relationship between  $B_{\text{final}}$  and  $R_{SL}$ . It  
 495 is noteworthy that the Milli-Q® water and analytical grade salts contained B. Thus, an additional term  
 496 had to be considered in the calculations, and the balance equation for boron became:

$$497 \quad C_{\text{Swater}} + C_{\text{labile,ini}}R_{SL} + C_{\text{pore water}}w_{\text{water}}R_{SL} = C_{\text{final}} + C_{\text{sorb}}R_{SL} \quad (6)$$

498 where  $C_{\text{Swater}}$  is the element concentration in the synthetic solution once the analytical grade salts  
 499 were dissolved and  $w_{\text{water}}$  the water content. The relationship between the final concentration in the  
 500 experiment and the  $R_{D,\text{init}}$  is obtained from Equations 2 and 6:

$$501 \quad C_{\text{final}} = \frac{C_{\text{Swater}} + C_{\text{labile,ini}}R_{SL} + C_{\text{pore water}}w_{\text{water}}R_{SL}}{1 + R_{D,\text{ini}}R_{SL}} \quad (7)$$

502 Equation 7 and the equilibration experiments at several  $R_{SL}$  enabled  $C_{\text{labile,ini}}$  and  $R_{D,\text{ini}}$  for the two clay  
 503 samples to be determined (Fig. 8, Table 4).

504 **Table 4** Initial boron  $R_D$  ( $\text{L kg}^{-1}$ ) and initial boron labile concentrations ( $\text{mol L}^{-1}$ ) in the two Tégulines Clay samples.  
 505 The calculation is made considering the water content ( $w_{\text{water}}$ ), the boron concentration in the pore water ( $B_{\text{poral}}$ ),  
 506 the boron concentration brought in solution by the Milli-Q® water and the salt ( $C_{\text{Swater}}$ ) and the boron  
 507 concentration on the sediment ( $C_{\text{sediment}}$ ).

	Reduced sample (AUB00307)	Oxidized sample AUB00976
$w_{\text{water}}$ ( $\text{L kg}^{-1}$ )	$1.5 \cdot 10^{-1}$	$1.5 \cdot 10^{-1}$
$B_{\text{poral}}$ ( $\text{mol L}^{-1}$ )	$1.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$
$C_{\text{Swater}}$ ( $\text{mol L}^{-1}$ )	$2.1 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$
$C_{\text{sediment}}$ ( $\text{mol kg}^{-1}$ )	$8.9 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$
$R_{D,\text{ini}}$ ( $\text{L kg}^{-1}$ )	6.0	6.0
$C_{\text{labile,ini}}$ ( $\text{mol kg}^{-1}$ )	$1.3 \cdot 10^{-4}$	$7.5 \cdot 10^{-5}$

508  
 509 The labile concentration represents about 1 % of the total available boron in the sediments. In the  
 510 retention experiments on Tégulines Clay,  $R_{SL}$  was  $0.01 \text{ kg L}^{-1}$ . At this  $R_{SL}$ , the labile concentration  
 511 accounted for 40 % of the measured boron concentration in the reduced sample (AUB00307) and 28  
 512 % in the oxidized sample (AUB00976) in the equilibration experiments. Furthermore, the pore water

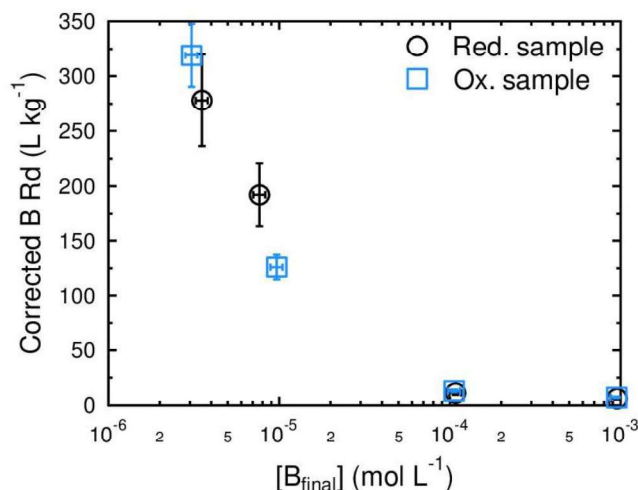
513 represented 18 % of this labile concentration in the reduced sample and 30 % in the oxidized sample.  
514 The remaining part is explained by boron derived from the Milli-Q® water and the analytical grade  
515 salts (Supplementary information D for detailed values).

516  $R_{D,ini}$  was then implemented in the Equation 4 to calculate the true  $R_D$  values, which considered the  
517 added concentration and the natural abundance in the sediments (Fig. 12).  $C_{added}$  represented the  
518 added B concentration plus the B concentration present in the synthetic solution. The  $R_D$  decrease  
519 with the equilibrium concentration of boron was observed, except for the highest concentration. In that  
520 case, the sorption was negligible compared to the added concentration. Those experiments showed  
521 an initial saturation of the B sorption sites that exist on the sediments. For this reason, if the B natural  
522 abundance was not considered, the  $R_D$  would have been lower than the calculated  $R_D$  or even  
523 negative, if the final concentration were lower than the added concentration. The  $R_D$  values of the two  
524 clay samples were similar, which indicates that the reducing capacity of the clay did not affect their  
525 ability to retain B. This behavior is in a good agreement with the work of Goldberg et al. (2004) and  
526 Hemming et al. (1998) which evidenced that B sorption capacity in rocks or soils mainly depends on  
527 the organic matter, carbonate and iron oxi/hydroxide contents.

528 In our experiments, B uptake in calcite as observed in literature (Hemming and Hanson, 1992;  
529 Hemming et al., 1998; Mavromatis et al., 2015) was rather limited because the solutions were initially  
530 close to equilibrium with the mineralogical assemblage, yet slightly undersaturated. Consequently, the  
531 carbonates were expected to dissolve slightly during the equilibration of the sediments with the  
532 solution and release natural B. This may explain the high value of B content observed at the end of  
533 some experiments. Finally, knowledge of the B natural background (abundance of an element) and its  
534 lability are required to understand and explain its fate in the experiments.

535

536



537

538 **Fig. 12.  $R_D$  (L kg<sup>-1</sup>) corrected from the natural B in the Tégulines clay samples ( $R_{D,ini} = 6$  L kg<sup>-1</sup>).**

539 **5.4. The role of redox on chromium retention on Tégulines Clay**

540 Under our measured conditions (pH = 7.4, pe = 6.8), Cr(III) was expected to be the predominant Cr  
 541 oxidation state, in the form of HCrO<sub>2</sub> or Cr(OH)<sub>3</sub>, despite the oxidized conditions (Supplementary  
 542 information E) according to the Thermoddem or Thermochimie database were considered in the  
 543 calculations. However, the experimental conditions were close to the domain where Cr(VI) is  
 544 predominant as CrO<sub>4</sub><sup>2-</sup>.

545 Cr speciation was strongly influenced by its interaction with the sediments. The reduced sample  
 546 efficiently reduced Cr(VI) to Cr(III) on the sediment, while the oxidized sample had a weaker influence  
 547 on Cr reduction. In any case, Cr(VI) was the only form of Cr detected in solution at the end of the  
 548 experiments.

549 EPMA analysis of the pristine rock revealed that Cr was closely associated to the glauconite.  
 550 However, Cr reduction can occur with Fe(II) derived from pyrite as well. This reduction operates even  
 551 in oxidizing conditions, because the Fe(II) oxidation by Cr(VI) is faster than by O<sub>2</sub> as demonstrated by  
 552 Eary and Rai (1989). Such reduction was previously demonstrated even under slight oxidizing  
 553 conditions, and with quantities 50 to 500 times greater than the amount of Cr(VI) introduced in our  
 554 reactors (Fendorf, 1995). This reduction caused Cr immobilization, leading to the formation of an  
 555 immobile coprecipitate with Cr(III), which stabilized the Cr (Markelova et al., 2018; Sass and Rai,  
 556 1987). Using geochemical calculations and the Cr concentration in squeezed pore water (2.9 10<sup>-8</sup> mol

557 L<sup>-1</sup>) in equilibrium with eskolaite (Cr<sub>2</sub>O<sub>3</sub>), chromite (FeCr<sub>2</sub>O<sub>4</sub>) or Cr hydroxide (Cr(OH)<sub>3</sub>) commonly  
 558 found in natural environments (Manning et al., 2007; Pantsar-Kallio et al., 2001), the redox potential  
 559 was found to be equal to -118 mV (pe = -2), which is consistent with a predominant +III oxidation state  
 560 for Cr.

## 561 5.5. The role of redox on arsenic retention on Tégulines Clay

### 562 5.5.1. As(III)

563 We carried out sensitivity tests on the calculation of R<sub>D</sub> for As(III) by varying the R<sub>D,ini</sub> value. Indeed As  
 564 concentration is independent of the solid/liquid ratio (section 4.4), therefore C<sub>labile,ini</sub> and R<sub>D,ini</sub> cannot be  
 565 determined according to the equation 7 as realized for B. In addition, As was poorly labile compared to  
 566 B, as demonstrated by the equilibration tests (Fig. 7) and the natural R<sub>D</sub> (Table 4). Therefore, there  
 567 were few differences between the R<sub>D</sub> calculated from Equation 1 and the R<sub>D</sub> calculated considering  
 568 the As labile fraction using Equation 5 (Table 5). In addition, no As(III) oxidation in As(V) were  
 569 observed in solution.

570 **Table 5** Influence of the R<sub>D,ini</sub> on the distribution coefficient (R<sub>D</sub>) calculated for As(III) sorption experiments. The  
 571 calculations with the R<sub>D,ini</sub> correction were done with the equation 5 while the calculation without correction were  
 572 done with the equation 1.

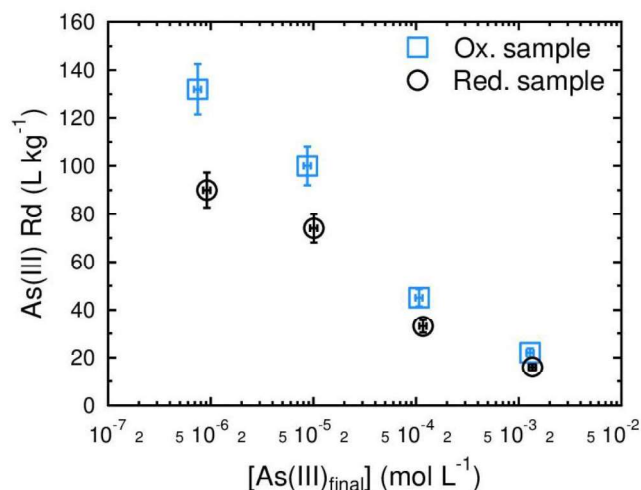
	C <sub>final</sub> (mol L <sup>-1</sup> )	R <sub>D</sub> without correction (L kg <sup>-1</sup> )	R <sub>D,ini</sub> (L kg <sup>-1</sup> )		
			200	500	1000
Reduced (AUB00307)	9.18·10 <sup>-7</sup>	90	93	96	101
	1.01·10 <sup>-5</sup>	74	74	74	75
	1.17·10 <sup>-4</sup>	33	33	33	33
	1.36·10 <sup>-3</sup>	16	16	16	16
Oxidized (AUB00976)	7.46·10 <sup>-7</sup>	132	135	139	145
	8.73·10 <sup>-6</sup>	100	100	100	101
	1.07·10 <sup>-4</sup>	45	45	45	45
	1.29·10 <sup>-3</sup>	22	22	22	22

573

574 The R<sub>D,ini</sub> value was constrained by the equilibration tests and the squeezing results. In contrast to B,  
 575 the two values were similar (~10<sup>-8</sup> mol L<sup>-1</sup>), and thus by considering an R<sub>D,ini</sub> equal to 100 L kg<sup>-1</sup>,



576  $C_{labile,ini}$  was  $10^{-6}$  mol kg<sup>-1</sup>. This As(III) quantity was diluted in the equilibration experiments ( $10^{-8}$  mol L<sup>-1</sup>) and was allocated equally between the measured concentration in solution ( $\sim 0.5 \times 10^{-8}$  mol L<sup>-1</sup>) and the sediments. That quantity on the sediments is consistent with the assumed  $R_{D,ini}$ , according to the Equation 1 ( $0.5 \times 10^{-8} \times 100 \times 0.01 = 0.5 \times 10^{-8}$  mol L<sup>-1</sup>). Finally, As(III) retention and the natural concentrations measured by squeezing and equilibration were explained by a reversible adsorption mechanism.



582  
583 **Fig. 13. Comparison of the retention values obtained for As(III) on the oxidized sample (AUB00976) and on the reduced sample (AUB00307), based on the squeezed pore water concentration ( $1 \times 10^{-8}$  mol L<sup>-1</sup>).**

#### 586 5.5.2. As(V) case

587 Significant As(III) concentrations were measured in solution during the As(V) retention experiments  
588 (see Section 4.5). The distribution coefficient previously calculated for As(III) (see Section 5.5.1) for  
589 each Tégulines Clay enabled calculation of the As(III) labile concentration on the sediments according  
590 to Equation 2. The total concentration of As(V) reduced to As(III) was then calculated with this labile  
591 concentration on the sediments and the concentration in solution (Equation 8). Finally, the sorbed  
592 concentration of the As(V) can be corrected from the contribution of As(III) (see Supplementary  
593 information F for details). This concentration permitted calculation of the distribution coefficient of  
594 As(V) (Equation 9) on the two samples of Tégulines Clay (Fig. 14).

$$595 \quad [As(V)]_{reduced} = [As(III)]_{labile} + [As(III)]_{final} \quad (8)$$

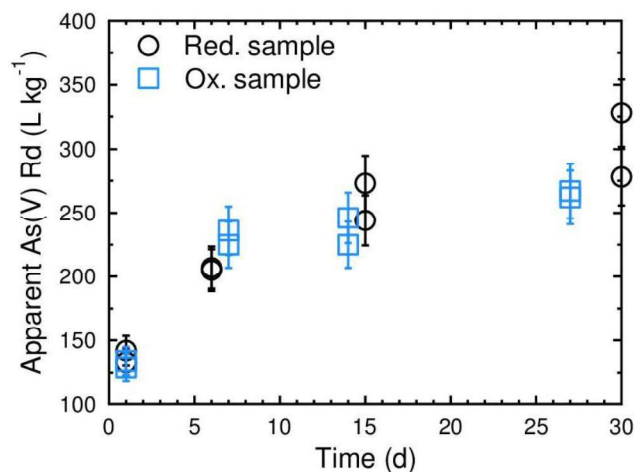
$$R_{D,As(V)} = \frac{[As(V)]_{ini} - [As(V)]_{final} - [As(V)]_{reduced}}{[As(V)]_{final}} \quad (9)$$

597 In contrast to Cr(VI), the  $R_D$  for As(V) were almost identical for the reduced and oxidized samples.  
 598 Thus, by analogy with Cr(VI), As(V) was reduced to As(III) by the sediments, albeit the degree of  
 599 reduction was much lower. It is noteworthy that the hypothesis of As(V) reduction on the sediments is  
 600 consistent with the As(III) release in solution observed in the equilibration tests (see Section 4.4).

601 As(III)  $R_D$  can be compared to the As(V)  $R_D$  obtained after 7 days of equilibration. From this  
 602 comparison, it appears that the As(V)  $R_D$  was higher than that of As(III) (Fig. 14), consistent with  
 603 previous studies (Goldberg and Johnston, 2001; Liu et al., 2001; Verbeeck et al., 2017) and its high  
 604 affinity for Fe and Mn oxyhydroxides (Wu et al., 2018). In addition, the  $R_D$  of As(III) was higher on the  
 605 oxidized sample than on the reduced sample, consistent with the observed presence of Fe  
 606 oxyhydroxides in the sample collected near the surface, which have high affinity for As(III) (Daus et al.,  
 607 1998; Frommer et al., 2011; Giménez et al., 2007).

608 The reduction of As(V) into As (III) on the sediments made impossible the determination of an  
 609 adsorption coefficient for As(V). However, the retention experiments involving As(III) enabled the  
 610 deconvolution of the mechanisms involved in the As retention in the Tégulines Clay. Without this  
 611 information, it would have been impossible to distinguish the sorbed As(V) from the As(V) that was  
 612 reduced and then sorbed as As(III). The redox potential processes make the  $R_D$  of As dependent on  
 613 the mineralogy of the sample and on the solid/liquid ratio.

614 As shown by the EPMA analyses of pristine rock, As was essentially carried by pyrite in the reduced  
 615 sample (Fig. 4). Furthermore, electron microprobe analyses made on pristine samples revealed an  
 616 enrichment of the iron oxide formed by the oxidation of pyrite compared to the iron hydroxides in the  
 617 clay matrix. Thus, the presence of Fe oxyhydroxides enhanced the retention of the added As on the  
 618 samples (Goldberg, 2002; Goldberg and Johnston, 2001).



619

620 **Fig. 14. Apparent As(V)  $R_D$  values corrected from the As(III) reduced on the sediments in**  
 621 **contact with the reduced sample (AUB00307) and the oxidized sample (AUB00976). The two**  
 622 **dots for a same time are replicates.**

## 623 6. Conclusions

624 The behavior of As, Cr, and B retention has been investigated in Tégulines Clay, an outcropping clay-  
 625 rich rock formation. The retention of the studied oxyanions was affected by the clay mineralogy (As, Cr  
 626 and B), their natural abundance (B), and the reducing capacity of the samples (As and Cr). Cr(VI)  
 627 oxyanion ( $\text{CrO}_4^{2-}$ ) was immobilized by its reduction on the sediments. The reduction was more  
 628 effective in the reduced sample than in the oxidized sample. Such reduction also occurs to a lesser  
 629 extent for As(V).  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_2^-$ , which are As(V) and As(III) oxyanions, were retained by their  
 630 sorption on the positively charged mineral surfaces. As(III) was retained slightly more in the oxidized  
 631 sample (AUB00976) than in the reduced sample (AUB00307), due to presence of Fe oxyhydroxides  
 632 on which is preferably sorbed. The sorption sites of the samples were initially saturated with B and  
 633 could not retain additional  $\text{B}(\text{OH})_4^-$ . Any analysis of B lability needs to consider its natural occupancy to  
 634 avoid an underestimation of the sorption capacities of B on the samples. This abundance is usually  
 635 excluded from the distribution coefficient calculations, mostly on the basis of the low initial B contents.  
 636 This study demonstrates that B natural abundance can strongly influence the distribution calculations.  
 637 We proposed a methodology for the estimation of the retention properties of weakly adsorbed species  
 638 on natural sediment. This methodology makes it possible to obtain accurate distribution coefficients  
 639 that are useful for the prediction of the mobility of toxic chemicals in order to support the assessment  
 640 of the environmental impact of a LL-LL radioactive waste repository.

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- 788



789

790 **Supplementary files**791 **Supplementary information A. Sequential extraction steps and mineralogical targets**

792

793 **Table A-1. Chemical extraction scheme for As, Cr and B fractionation.**

Step	Extractant	Mineralogical target
1	MgCl <sub>2</sub> 1 M	Interfoliar exchange in clay minerals
2	Sodium acetate / Acetic acid (pH 5)	Calcite and clay edge sites
3	NH <sub>2</sub> OH	Iron and manganese oxyhydroxides
4	H <sub>2</sub> O <sub>2</sub> 30 % + ammonium acetate (pH 2 at 85°C)	Organic matter

794

795

796

797 **Supplementary information B. Synthetic water composition and analytical grade salts**

798

799 **Table B-1. Synthetic water composition in mol L<sup>-1</sup> given in element.**

Element	Ca	Na	Mg	K	Sr	HCO <sub>3</sub> <sup>-</sup>	Cl	SO <sub>4</sub>
Concentration (mol L <sup>-1</sup> )	3.09 10 <sup>-3</sup>	2.43 10 <sup>-3</sup>	1.94 10 <sup>-3</sup>	6.70 10 <sup>-4</sup>	2.50 10 <sup>-4</sup>	3.16 10 <sup>-3</sup>	1.56 10 <sup>-3</sup>	4.44 10 <sup>-3</sup>

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802 **Table B-2. Analytical grade salt used to prepare synthetic water and their weight (mg L<sup>-1</sup>) and molar (mol L<sup>-1</sup>) concentrations.**

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Salt	Molar mass (g mol <sup>-1</sup> )	Weight concentration (mg L <sup>-1</sup> )	Molar concentration (mol L <sup>-1</sup> )
CaCO <sub>3</sub> ·2 H <sub>2</sub> O	118.1	7.1	6.01 10 <sup>-5</sup>
SrCl <sub>2</sub> ·6 H <sub>2</sub> O	266.6	66.7	2.50 10 <sup>-4</sup>
MgCl <sub>2</sub>	95.2	50.5	5.30 10 <sup>-4</sup>
MgSO <sub>4</sub>	120.4	169.7	1.41 10 <sup>-3</sup>
CaSO <sub>4</sub>	136.1	412.5	3.03 10 <sup>-3</sup>
NaHCO <sub>3</sub>	84	204.1	2.43 10 <sup>-3</sup>
KHCO <sub>3</sub>	100.1	67.1	6.70 10 <sup>-4</sup>

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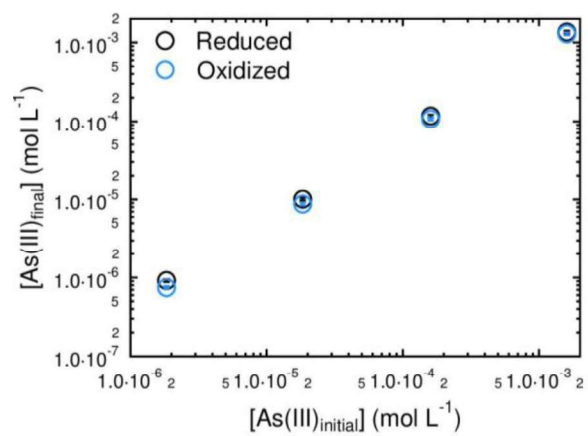
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807 **Supplementary information C. Results of As(III) sorption on the Tegulines Clay**

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809 **Figure C-1. Initial and final As(III) concentrations in sorption tests with the oxidized sample**  
810 **(AUB00976) and the reduced sample (AUB009307) of Tégulines Clay.**



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814 **Supplementary information D. Parameters for the determination of the boron  $R_{D,ini}$ ,  $C_{labile,ini}$  and**  
 815 **concentrations repartition (labile, sediment, poral, salt, Milli-Q® water).**

816

817 **Table D-1. Initial boron  $R_D$ , initial boron labile concentrations, percentage of each end member**  
 818 **in the boron concentrations of the two samples of Tégulines Clay**

	Reduced sample (AUB00307)	Oxidized sample (AUB00976)
$w_{water}$ (L kg <sup>-1</sup> )	$1.5 \cdot 10^{-1}$	$1.5 \cdot 10^{-1}$
$B_{poral}$ (mol L <sup>-1</sup> )	$1.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$
$C_{Swater}$ (mol L <sup>-1</sup> )	$2.1 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$
$C_{sediment}$ (mol kg <sup>-1</sup> )	$8.9 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$
$R_{D,ini}$ (L kg <sup>-1</sup> )	6.0	6.0
$C_{labile,ini}$ (mol kg <sup>-1</sup> )	$1.3 \cdot 10^{-4}$	$7.5 \cdot 10^{-5}$
$C_{labile,ini}$ (mol L <sup>-1</sup> )	$1.3 \cdot 10^{-6}$	$7.5 \cdot 10^{-7}$
$C_{final}$ (mol L <sup>-1</sup> )	$3.1 \cdot 10^{-6}$	$2.7 \cdot 10^{-6}$
$C_{labille} / C_{sediment}$ (%)	1.4	0.7
$C_{labille} / C_{final}$ (%)	40.1	27.7
$B_{poral} / C_{labille}$ (%)	17.8	29.6

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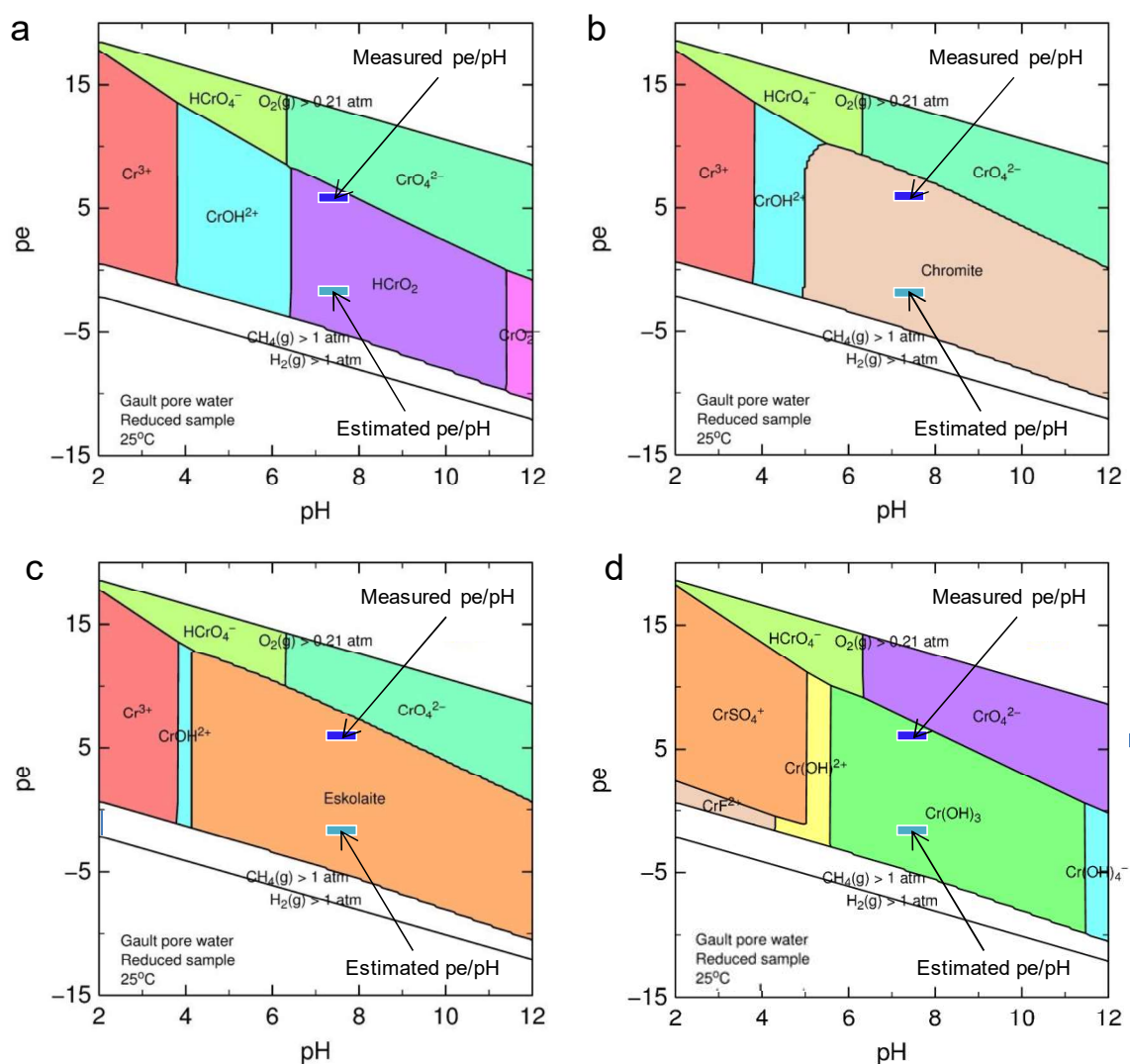
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822 **Supplementary information E. Chromium stability diagrams**

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824 **Figure E-1. Cr stability diagram calculated using the Tégulines pore water chemistry**  
 825 **determined by squeezing (Lerouge et al., 2018) and the Thermoddem database (Blanc et al.,**  
 826 **2012): (a) aqueous species; (b) chromite; (c) eskolaite; (d) aqueous species with ThermoChimie**  
 827 **database (Giffaut et al., 2014).  $\text{Cr}(\text{OH})_3$  was undersaturated in those conditions. Measured and**  
 828 **estimated pe/pH domains (see section 5.4) are highlighted on the diagrams.**



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832 **Supplementary information**Supplementary information F. Determination of the total reduced  
 833 **As(III) on the sediment in the sorption experiments**

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835 **Table F-1. Case of the reduced sample (AUB00307)**

$\text{As(III)}_{\text{final}}$ (mol L <sup>-1</sup> )	$R_D$ (L·kg <sup>-1</sup> )	$\text{As(III)}_{\text{labijle}}$ (mol·kg <sup>-1</sup> )	$\text{As(V)}_{\text{reduced}}$ (mol·L <sup>-1</sup> )	$\text{As(V)}_{\text{final}}$ (mol·L <sup>-1</sup> )	$\text{As(V)}_{\text{sorp}}$ (mol·kg <sup>-1</sup> )
$1.45 \cdot 10^{-6}$	$9.04 \cdot 10^1$	$1.32 \cdot 10^{-4}$	$2.78 \cdot 10^{-6}$	$9.33 \cdot 10^{-6}$	$1.32 \cdot 10^{-3}$
$7.31 \cdot 10^{-7}$	$9.04 \cdot 10^1$	$6.61 \cdot 10^{-5}$	$1.42 \cdot 10^{-6}$	$7.60 \cdot 10^{-6}$	$1.58 \cdot 10^{-3}$
$1.42 \cdot 10^{-6}$	$9.04 \cdot 10^1$	$1.29 \cdot 10^{-4}$	$2.71 \cdot 10^{-6}$	$6.08 \cdot 10^{-6}$	$1.66 \cdot 10^{-3}$
$6.38 \cdot 10^{-7}$	$9.04 \cdot 10^1$	$5.77 \cdot 10^{-5}$	$1.23 \cdot 10^{-6}$	$6.25 \cdot 10^{-6}$	$1.74 \cdot 10^{-3}$
$1.00 \cdot 10^{-6}$	$9.04 \cdot 10^1$	$9.05 \cdot 10^{-5}$	$1.94 \cdot 10^{-6}$	$9.86 \cdot 10^{-6}$	$1.31 \cdot 10^{-3}$
$8.41 \cdot 10^{-7}$	$9.04 \cdot 10^1$	$7.60 \cdot 10^{-5}$	$1.64 \cdot 10^{-6}$	$7.54 \cdot 10^{-6}$	$1.55 \cdot 10^{-3}$
$4.83 \cdot 10^{-7}$	$9.04 \cdot 10^1$	$4.37 \cdot 10^{-5}$	$9.35 \cdot 10^{-7}$	$6.92 \cdot 10^{-6}$	$1.69 \cdot 10^{-3}$
$6.22 \cdot 10^{-7}$	$9.04 \cdot 10^1$	$5.62 \cdot 10^{-5}$	$1.21 \cdot 10^{-6}$	$5.48 \cdot 10^{-6}$	$1.80 \cdot 10^{-3}$

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838 **Table F-2. Case of the oxidized sample (AUB00976)**

$\text{As(III)}_{\text{final}}$ (mol L <sup>-1</sup> )	$R_D$ (L·kg <sup>-1</sup> )	$\text{As(III)}_{\text{labijle}}$ (mol·kg <sup>-1</sup> )	$\text{As(V)}_{\text{reduced}}$ (mol·L <sup>-1</sup> )	$\text{As(V)}_{\text{final}}$ (mol·L <sup>-1</sup> )	$\text{As(V)}_{\text{sorp}}$ (mol·kg <sup>-1</sup> )
$2.00 \cdot 10^{-6}$	$1.32 \cdot 10^2$	$2.64 \cdot 10^{-4}$	$4.69 \cdot 10^{-6}$	$8.84 \cdot 10^{-6}$	$1.16 \cdot 10^{-3}$
$1.43 \cdot 10^{-6}$	$1.32 \cdot 10^2$	$1.89 \cdot 10^{-4}$	$3.33 \cdot 10^{-6}$	$6.57 \cdot 10^{-6}$	$1.54 \cdot 10^{-3}$
$5.39 \cdot 10^{-7}$	$1.32 \cdot 10^2$	$7.12 \cdot 10^{-5}$	$1.26 \cdot 10^{-6}$	$6.90 \cdot 10^{-6}$	$1.70 \cdot 10^{-3}$
$1.55 \cdot 10^{-6}$	$1.32 \cdot 10^2$	$2.04 \cdot 10^{-4}$	$3.59 \cdot 10^{-6}$	$6.05 \cdot 10^{-6}$	$1.58 \cdot 10^{-3}$
$2.13 \cdot 10^{-6}$	$1.32 \cdot 10^2$	$2.81 \cdot 10^{-4}$	$4.98 \cdot 10^{-6}$	$8.96 \cdot 10^{-6}$	$1.13 \cdot 10^{-3}$
$9.88 \cdot 10^{-7}$	$1.32 \cdot 10^2$	$1.30 \cdot 10^{-4}$	$2.30 \cdot 10^{-6}$	$7.05 \cdot 10^{-6}$	$1.59 \cdot 10^{-3}$
$9.32 \cdot 10^{-7}$	$1.32 \cdot 10^2$	$1.23 \cdot 10^{-4}$	$2.18 \cdot 10^{-6}$	$7.08 \cdot 10^{-6}$	$1.59 \cdot 10^{-3}$
$1.76 \cdot 10^{-6}$	$1.32 \cdot 10^2$	$2.32 \cdot 10^{-4}$	$4.10 \cdot 10^{-6}$	$5.81 \cdot 10^{-6}$	$1.53 \cdot 10^{-3}$

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