



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

Mathieu Debure, Christophe Tournassat, Catherine Lerouge, Benoît Made, Jean-Charles Robinet, Ana María Fernández, Sylvain Grangeon

### ► To cite this version:

Mathieu Debure, Christophe Tournassat, Catherine Lerouge, Benoît Made, Jean-Charles Robinet, et al.. Retention of arsenic, chromium and boron on an outcropping clay-rich rock formation (the Tégulines Clay, eastern France). *Science of the Total Environment*, 2018, 642, pp.216-229. 10.1016/j.scitotenv.2018.06.037 . insu-01817676

**HAL Id: insu-01817676**

**<https://insu.hal.science/insu-01817676>**

Submitted on 30 Sep 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Mathieu Debure<sup>1,\*</sup>, Christophe Tournassat<sup>1,2,3</sup>, Catherine Lerouge<sup>1</sup>, Benoît Madé<sup>4</sup>,  
Jean-Charles Robinet<sup>4</sup>, Ana María Fernández<sup>5</sup>, Sylvain Grangeon<sup>1</sup>

<sup>1</sup> BRGM – French Geological Survey - 45060 Orléans - France.

<sup>2</sup> UMR 7327 Institut des Sciences de la Terre d'Orléans (ISTO), Université  
d'Orléans-CNRS/INSU-BRGM, Orléans, France

<sup>3</sup> Energy Geoscience Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, CA  
94720, USA

<sup>4</sup> Andra, R&D Division, Transfer Migration Group, 92298 Châtenay-Malabry, France

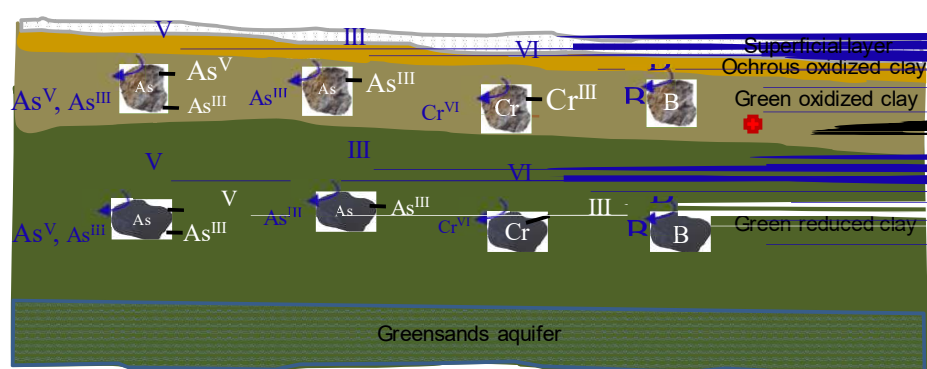
<sup>5</sup> CIEMAT, Dpto. Medio Ambiente, Avda./Complutense 40, 28040, Madrid, Spain

**Abstract**

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

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

\* Corresponding author. E-mail address: [m.debure@brgm.fr](mailto:m.debure@brgm.fr) (M. Debure).

29 **Graphical abstract**

30

31

32

## 1. Introduction

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

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

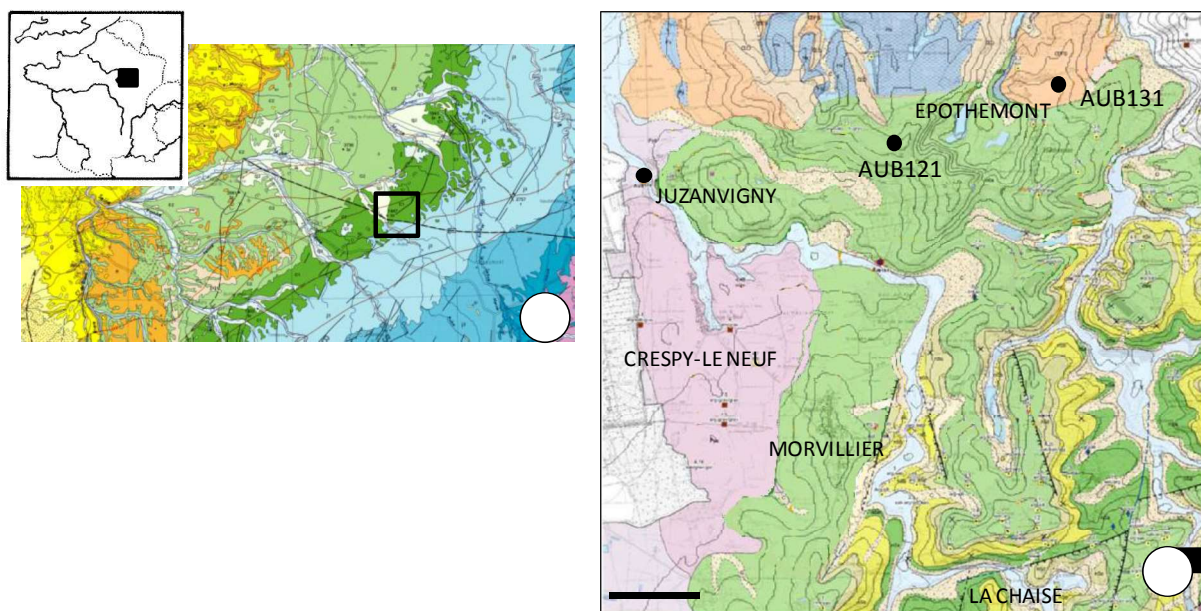
identified toxic elements from the industrial facilities toward the biosphere necessitate a good parametrization of their retention behavior. Long live low activity level (LL-LL) wastes include radium bearing wastes as well as toxic chemicals such as As, Cr and B not only from the nuclear power sector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

## 2. Context of the study and samples

### 2.1. Geological setting

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

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



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

## 2.2. Sampling

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

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

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

### 3. Materials and methods

#### 3.1. Mineral characterization

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

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

##### 3.1.2. Electron microprobe

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

Fully quantitative compositional spot analyses of silicates (clay minerals, feldspar), carbonates, pyrite, sulfates (gypsum and celestite), phosphates, and iron-hydroxides were carried out at BRGM using a Cameca SXFive electron microprobe with an accelerating voltage of 20 kV and a beam current of 100 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,  $\text{SK}\alpha$ ,  $\text{CaK}\alpha$ ,  $\text{KK}\alpha$  on PET,  $\text{CrK}\alpha$  and  $\text{MnK}\alpha$  on LPET, and  $\text{FeK}\alpha$  on LiF. Counting times on peaks and backgrounds were 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 calibrated with a variety of natural minerals (albite for Na, andradite for Si and Ca, pyrite for Fe and S, 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



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

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

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

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

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

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

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

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

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

The synthetic pore water was prepared with boiled and outgassed Millipore Milli-Q® 18 MΩ water and 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 (Supplementary information B). The preparation was done in a glove box with an atmosphere closed to the field, and equilibrated with carbonates (99 %  $\text{N}_2$  / 1 %  $\text{CO}_2$ ). The synthetic pore water chemistry was based on pore water chemistry modeled in Tégulines Clay from the drilling campaigns described in Lerouge et al. (2018), following the procedure given by Gaucher et al. (2009) for the Callovian-Oxfordian clay rock. *In situ* pore water measured by squeezing (Lerouge et al., 2018) was consistent with the model and validated it. Synthetic pore water was used in this study for the equilibration and “batch” sorption tests in order to reach the steady state concentrations of major elements faster than by addition of Milli-Q® 18 MΩ water and avoid mineral dissolution.

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

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

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

To determine the natural release of As, Cr, and B from the Tégulines Clay, and thus the equilibrium concentrations, kinetic experiments were completed over 49 days at a solid to liquid ratio ( $R_{SL}$ ) of 1 g  $L^{-1}$ . Measurements were performed on independent experiment samples at 8, 9, 26, 42, and 49 days. For each contact time, three replicates were analyzed. In addition, equilibration experiments were 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 constrain the natural source.

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

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

## 4. Results

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

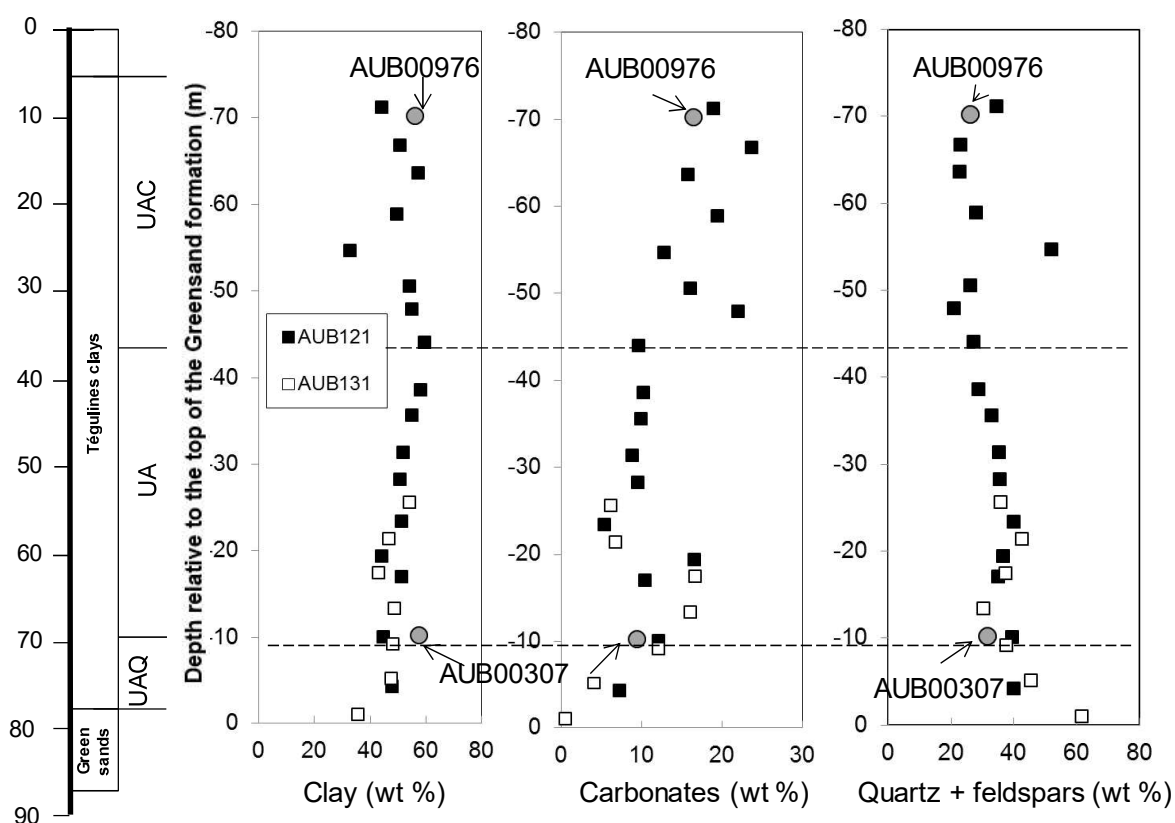
The AUB00307 sample of Tégulines Clay consisted of ~57 wt.% clay minerals, ~9 wt.% carbonates, and 32 wt.% quartz-feldspar (Table 1). The AUB00976 sample consisted of ~56 wt.% clay minerals, ~16.5 wt.% carbonates, and 26 wt.% quartz-feldspar (Table 1). Variation in carbonate content and quartz-feldspar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

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

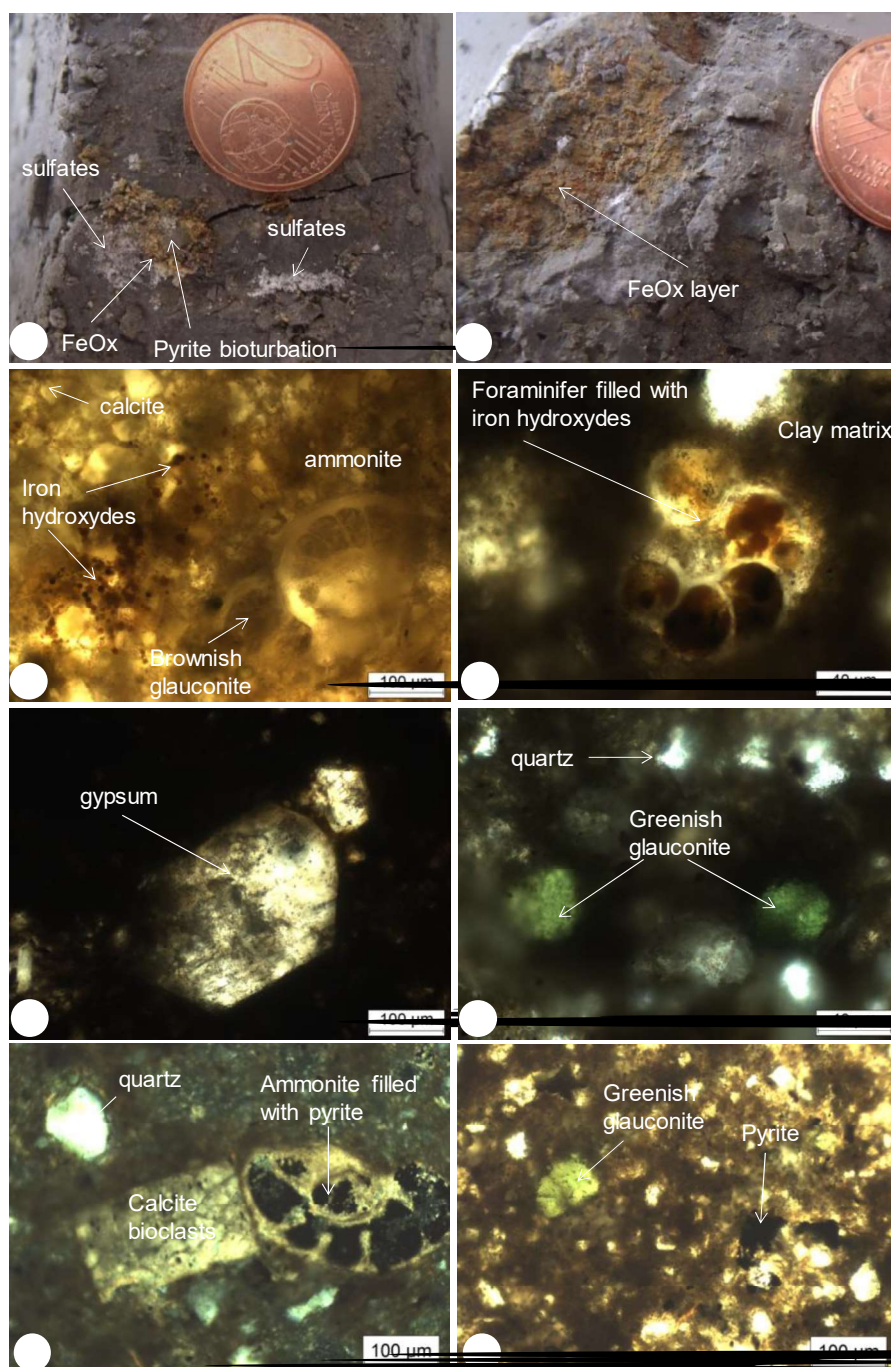
270  
 271 **Table 1** Quantification of the mineralogical composition of the oxidized sample (AUB00976) and  
 272 reduced sample (AUB00307) by XRD (data in wt.%). Names in italics refer to the drilling described in  
 273 Fig. 1 and in Lerouge et al. (2018).

|                        |                                 | <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



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



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

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

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

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

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

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

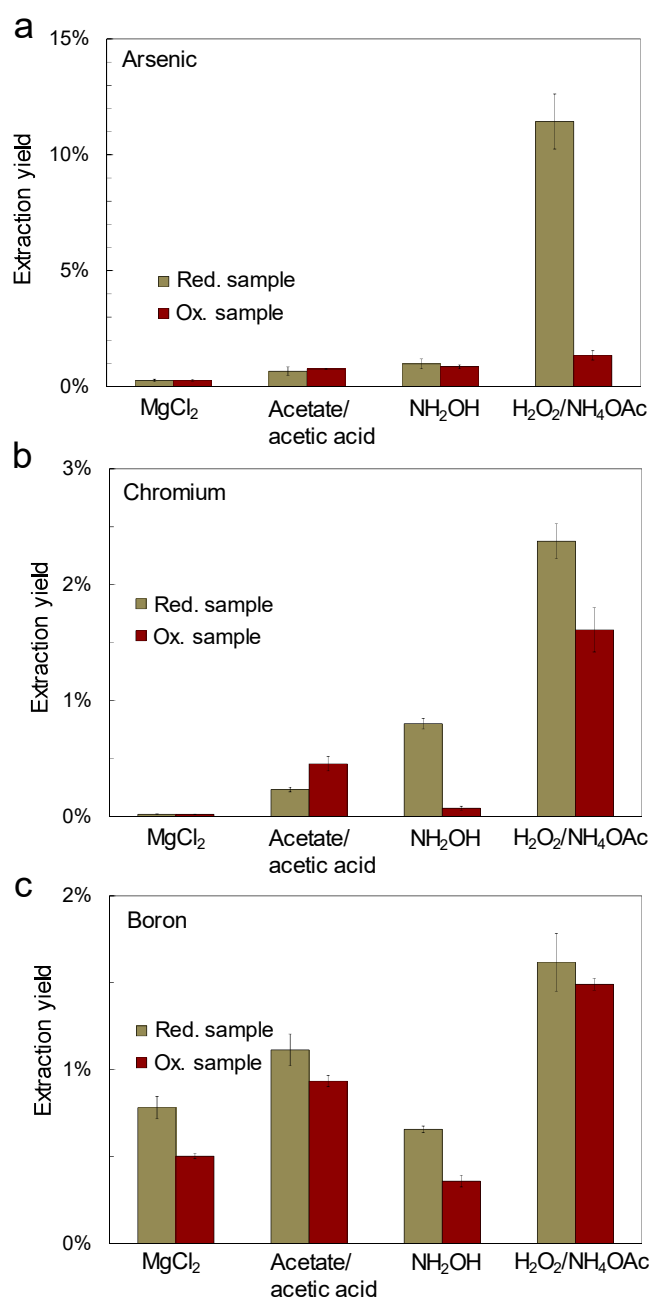
Electron microprobe analyses of pyrite, iron hydroxides, gypsum, celestite, calcite, glauconite, and clay matrix indicated that As was essentially detected in pyrite ( $628 \pm 240 \mu\text{g g}^{-1}$ ,  $n = 27$ ), iron-



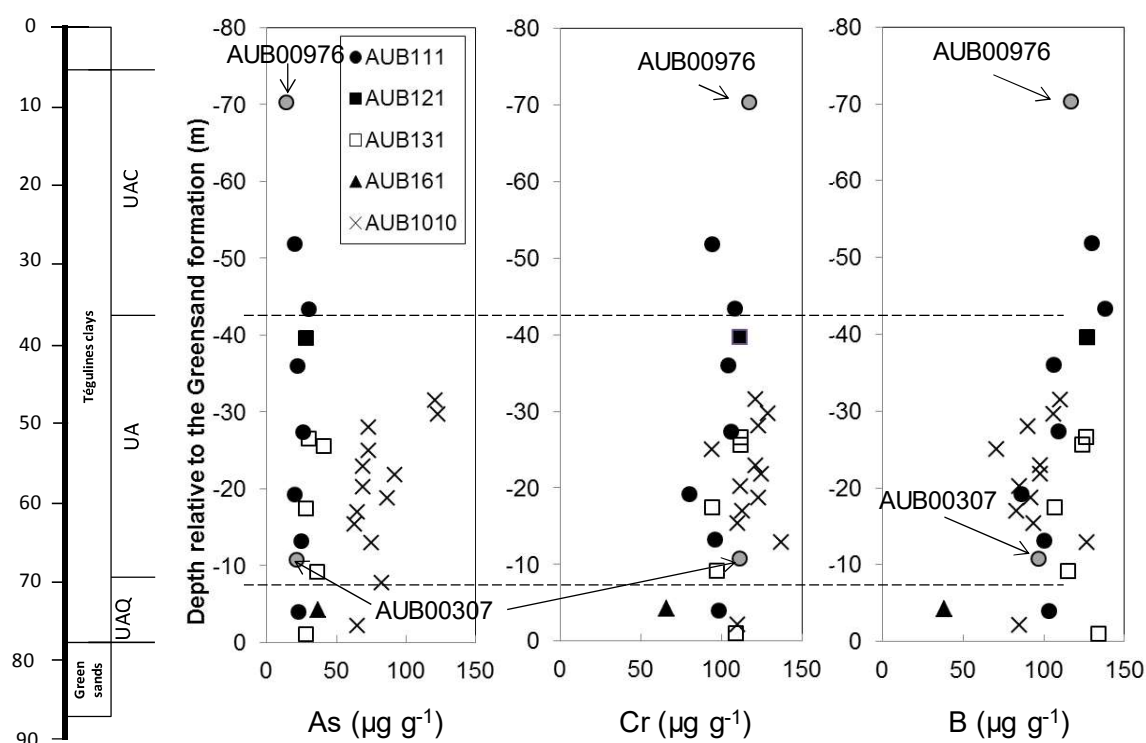
321 hydroxides ( $211 \pm 307 \mu\text{g g}^{-1}$ ,  $n = 20$ ), and gypsum ( $170 \mu\text{g g}^{-1}$ ), whereas Cr was detected essentially  
322 in glauconite ( $564 \pm 288 \mu\text{g g}^{-1}$ ,  $n = 30$ ), clay matrix ( $188 \pm 33 \mu\text{g g}^{-1}$ ,  $n = 20$ ), and also in phosphates  
323 ( $114 \pm 106 \mu\text{g g}^{-1}$ ,  $n = 5$ ). 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).

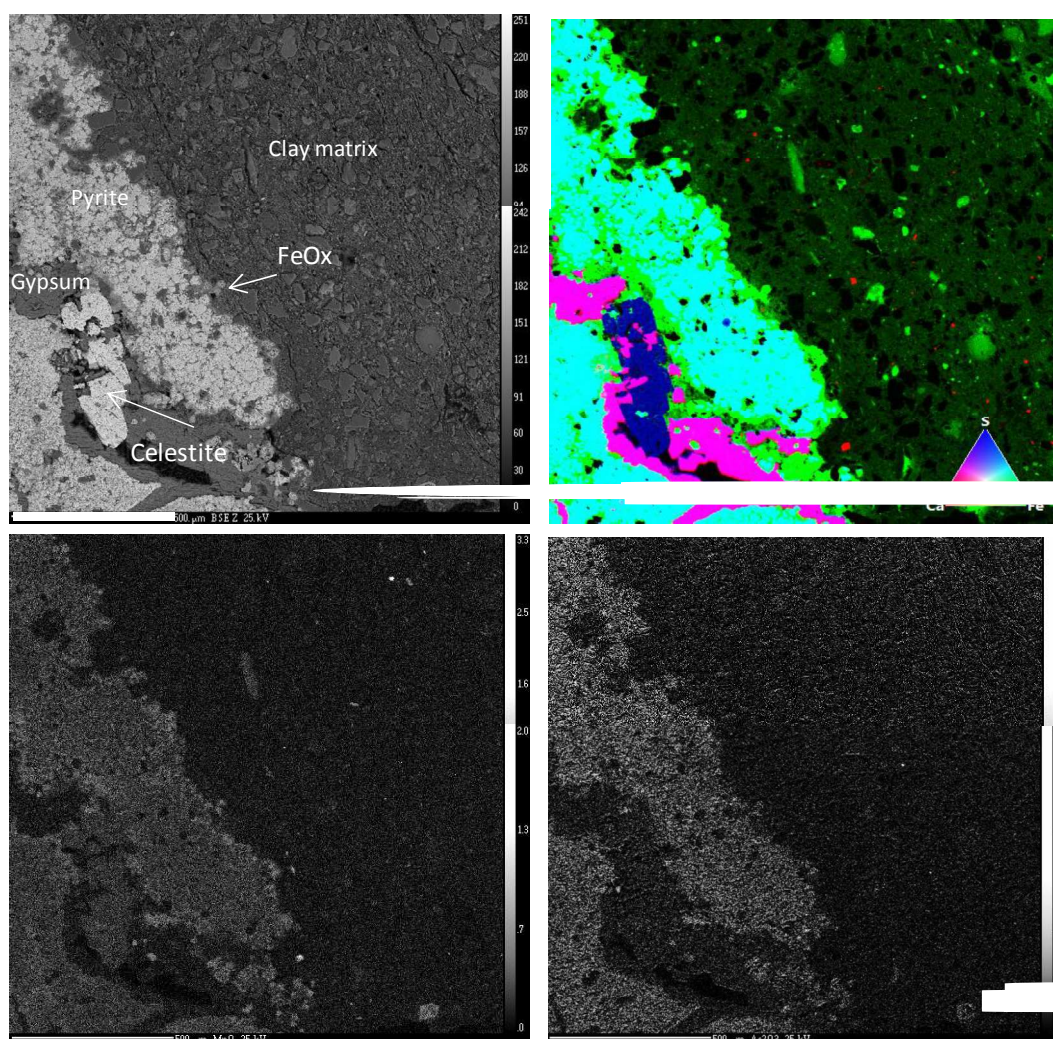
329



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



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



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

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

Pore waters were extracted by squeezing technique from the reduced sample (Table 2). The pH value of the extracted pore waters was measured at 7.7, and a carbonate alkalinity value at 3.7 meq L<sup>-1</sup>. The calculated ionic strength was 0.1. The concentrations of Ca, Mg and sulfate were the greatest in the 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 sample. Both Fe and Al were systematically below the detection limit (0.01 mmol L<sup>-1</sup>).

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

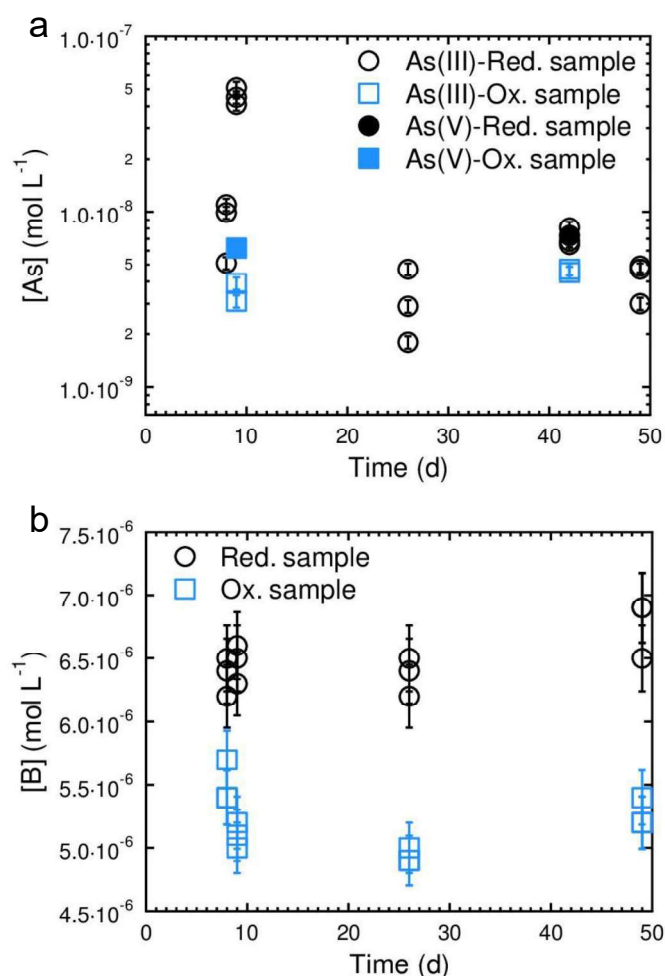
|                         |                 |                               |   |                 |                              |                               |                |         |
|-------------------------|-----------------|-------------------------------|---|-----------------|------------------------------|-------------------------------|----------------|---------|
| 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      |

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

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

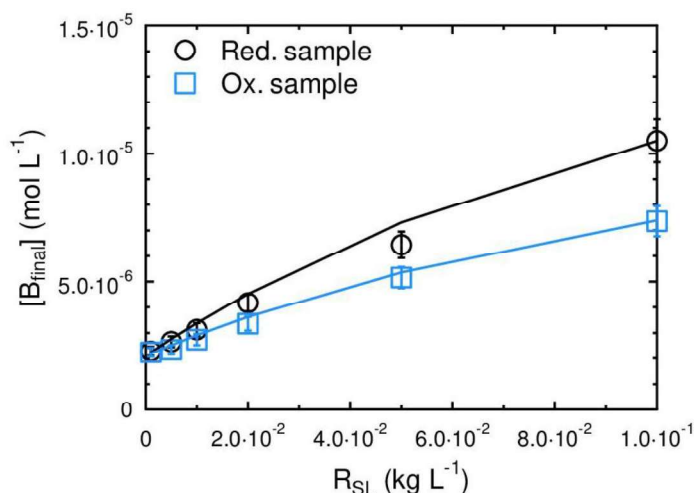
The measured Cr concentrations in solution (i.e. Cr<sub>total</sub> and Cr(VI)) remained negligible in the time scale investigated here ( $< 1.9 \cdot 10^{-9}$  mol L<sup>-1</sup>), and therefore, they were lower than those found in the squeezed pore water ( $2.9 \cdot 10^{-8}$  mol L<sup>-1</sup>, see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

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



**Fig. 7. As (a) and B (b) concentrations during the kinetic equilibration of the oxidized sample (AUB00976) and reduced sample (AUB00307) of Tégulines Clay. Analytical uncertainties are 4 %, 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. For a same time, the different circles and squares were replicates.**

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



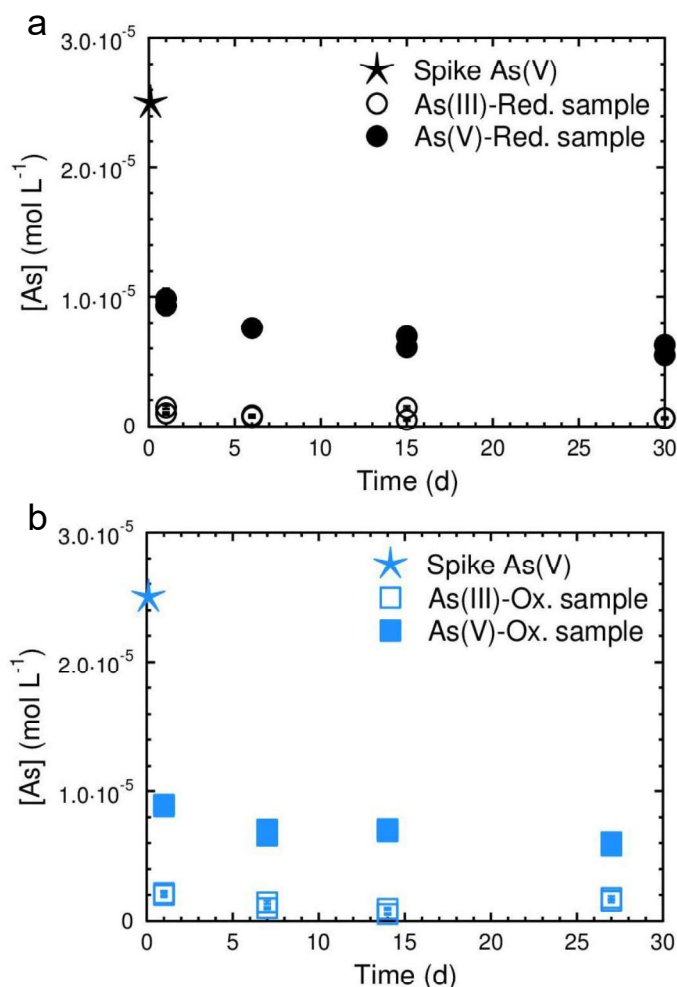
**Fig. 8. B concentrations in solution (mol L<sup>-1</sup>) are a function of the solid to liquid ratio ( $R_{SL}$  in kg L<sup>-1</sup>). The solid lines represent the fits obtained according to Equation 7 (see section 5.3).**

#### 4.5. Sorption experiments on Tégulines Clay

##### 4.5.1. Arsenic

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

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

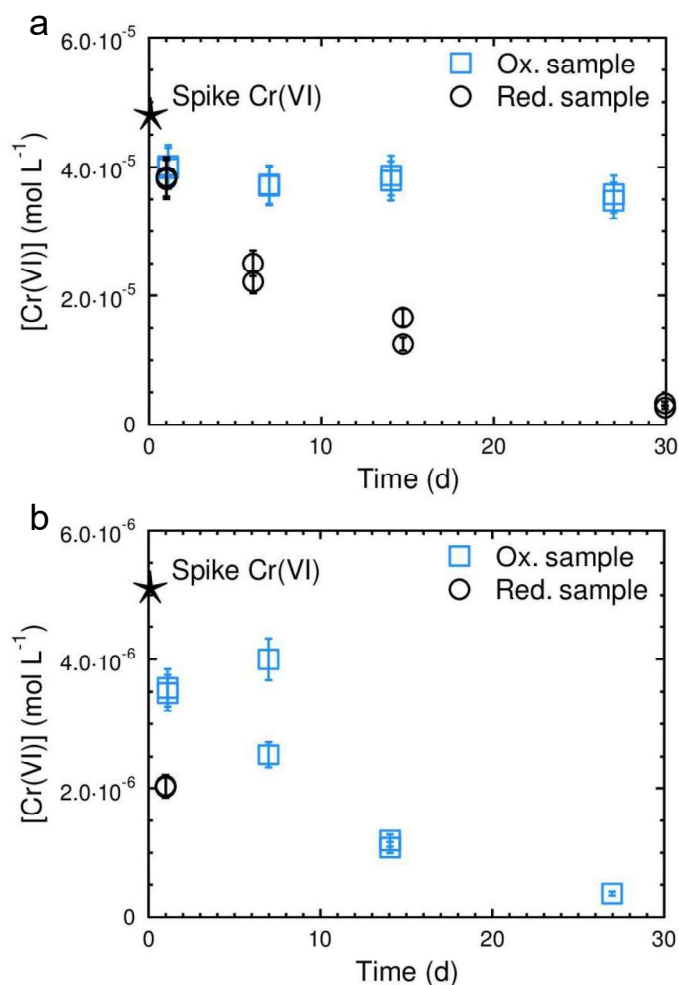


**Fig. 9. As speciation (As(V) and As(III)) in the kinetic experiment of sorption with an initial concentration of  $2.5 \times 10^{-5}$  mol L<sup>-1</sup> in contact with: (a) the reduced sample (AUB00307); (b) the oxidized sample (AUB00976).**

#### 4.5.2. Chromium

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

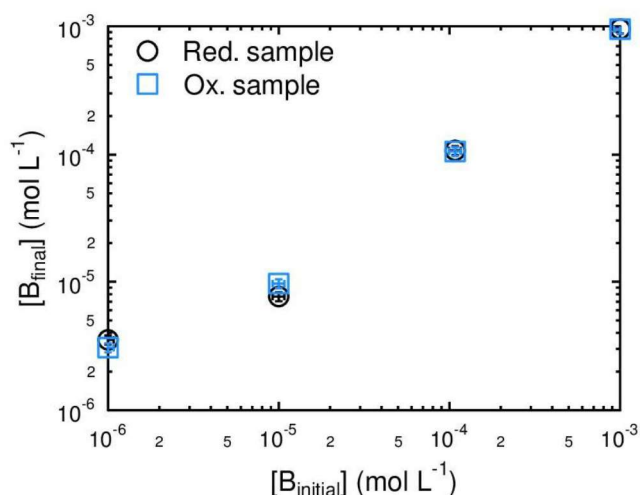




**Fig. 10. Comparison of Cr(VI) concentrations in the kinetic experiments of sorption with an initial concentration of: (a)  $4.8 \times 10^{-5} \text{ mol L}^{-1}$ ; (b)  $5.1 \times 10^{-6} \text{ mol L}^{-1}$  in contact with the reduced sample (AUB00307) and the oxidized sample (AUB00976) of Tégulines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

#### 4.5.3. Boron

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



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

## 5. Discussion

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

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

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

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  $C_{sediment,Nat}$  is the concentration of this toxic element in the sediments in mol kg<sup>-1</sup> determined with the sequential extractions (section 4.2).

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> L kg<sup>-1</sup> for Cr), which confirm the affinity of those elements for the sediment phases in Tégulines Clay (Table 3). In the meantime, the natural  $R_D$  of boron is three orders of magnitude lower (~60 L kg<sup>-1</sup>), and indicates the high lability of this element.

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

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

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

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

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

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

where  $C_{added}$  is the added concentration in the retention experiments in  $mol\ L^{-1}$ ,  $C_{final}$  is the element 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 relationship modifies the distribution coefficient calculation, and is given by the relation 4:

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

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 natural labile abundance of an element on the sediments. In the case of equilibration,  $C_{\text{added}}$  is equal to zero, so Equation 4 becomes:

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

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

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

The  $R_D$  calculations for B were influenced by B abundance in the sediments, because of the low natural  $R_D$  value. This  $R_D$  value reflects the high lability of this element *in situ*. However, B equilibration 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 concentrations measured by squeezing (Table 2). With a water content of 0.15 and a  $R_{\text{SL}}$  of  $0.01 \text{ kg L}^{-1}$ , 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 equilibration concentration.

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

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

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

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

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

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

**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. The calculation is made considering the water content ( $w_{\text{water}}$ ), the boron concentration in the pore water ( $B_{\text{poral}}$ ), the boron concentration brought in solution by the Milli-Q® water and the salt ( $C_{\text{Swater}}$ ) and the boron concentration on the sediment ( $C_{\text{sediment}}$ ).

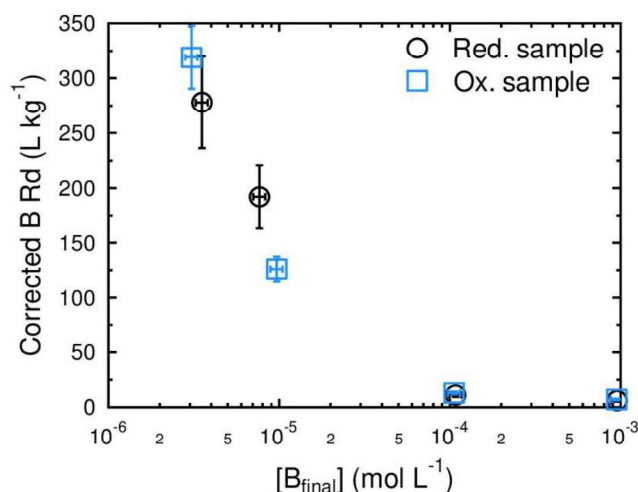
|  | Reduced sample (AUB00307) | Oxidized sample AUB00976 |
|--|---------------------------|--------------------------|
| $w_{\text{water}}$ ( $\text{L kg}^{-1}$ )        | $1.5 \cdot 10^{-1}$       | $1.5 \cdot 10^{-1}$      |
| $B_{\text{poral}}$ ( $\text{mol L}^{-1}$ )       | $1.5 \cdot 10^{-4}$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

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

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

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

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



**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>).**

#### 5.4. The role of redox on chromium retention on Tégulines Clay

Under our measured conditions (pH = 7.4,  $p_e = 6.8$ ), Cr(III) was expected to be the predominant Cr oxidation state, in the form of  $HCrO_2$  or  $Cr(OH)_3$ , despite the oxidized conditions (Supplementary information E) according to the Thermoddem or Thermochimie database were considered in the calculations. However, the experimental conditions were close to the domain where Cr(VI) is predominant as  $CrO_4^{2-}$ .

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

EPMA analysis of the pristine rock revealed that Cr was closely associated to the glauconite. However, Cr reduction can occur with Fe(II) derived from pyrite as well. This reduction operates even in oxidizing conditions, because the Fe(II) oxidation by Cr(VI) is faster than by  $O_2$  as demonstrated by Eary and Rai (1989). Such reduction was previously demonstrated even under slight oxidizing conditions, and with quantities 50 to 500 times greater than the amount of Cr(VI) introduced in our reactors (Fendorf, 1995). This reduction caused Cr immobilization, leading to the formation of an immobile coprecipitate with Cr(III), which stabilized the Cr (Markelova et al., 2018; Sass and Rai, 1987). Using geochemical calculations and the Cr concentration in squeezed pore water ( $2.9 \cdot 10^{-8}$  mol

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 found in natural environments (Manning et al., 2007; Pantesar-Kallio et al., 2001), the redox potential was found to be equal to -118 mV (pe = -2), which is consistent with a predominant +III oxidation state for Cr.

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

### 5.5.1. As(III)

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

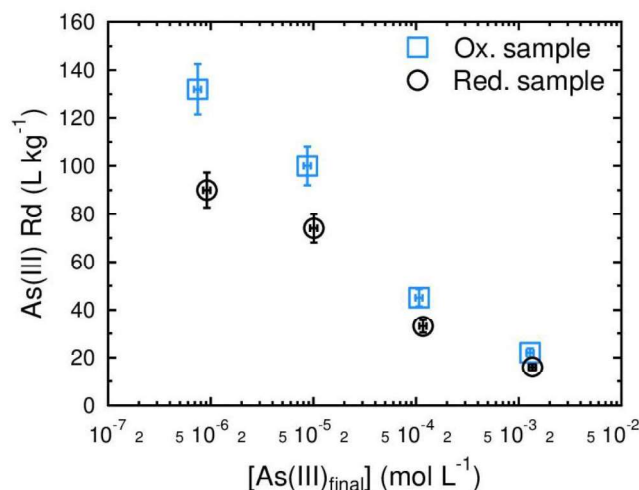
**Table 5** Influence of the  $R_{D,ini}$  on the distribution coefficient ( $R_D$ ) calculated for As(III) sorption experiments. The calculations with the  $R_{D,ini}$  correction were done with the equation 5 while the calculation without correction were done with the equation 1.

|                        |                                    | $R_{D,ini}$ (L kg <sup>-1</sup> )              |                       |      |     |
|------------------------|------------------------------------|--|-----------------------|------|-----|
|                        |                                    | 200  | 500                   | 1000 |     |
|                        | $C_{final}$ (mol L <sup>-1</sup> ) | $R_D$ without correction (L kg <sup>-1</sup> ) | $R_D$ with correction |      |     |
| Reduced<br>(AUB00307)  | $9.18 \cdot 10^{-7}$               | 90   | 93                    | 96   | 101 |
|                        | $1.01 \cdot 10^{-5}$               | 74   | 74                    | 74   | 75  |
|                        | $1.17 \cdot 10^{-4}$               | 33   | 33                    | 33   | 33  |
|                        | $1.36 \cdot 10^{-3}$               | 16   | 16                    | 16   | 16  |
| Oxidized<br>(AUB00976) | $7.46 \cdot 10^{-7}$               | 132  | 135                   | 139  | 145 |
|                        | $8.73 \cdot 10^{-6}$               | 100  | 100                   | 100  | 101 |
|                        | $1.07 \cdot 10^{-4}$               | 45   | 45                    | 45   | 45  |
|                        | $1.29 \cdot 10^{-3}$               | 22   | 22                    | 22   | 22  |

The  $R_{D,ini}$  value was constrained by the equilibration tests and the squeezing results. In contrast to B, the two values were similar ( $\sim 10^{-8}$  mol L<sup>-1</sup>), and thus by considering an  $R_{D,ini}$  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  
 577 <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  
 578 the sediments. That quantity on the sediments is consistent with the assumed  $R_{D,ini}$ , according to the  
 579 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  
 580 concentrations measured by squeezing and equilibration were explained by a reversible adsorption  
 581 mechanism.



582  
 583 **Fig. 13. Comparison of the retention values obtained for As(III) on the oxidized sample**  
 584 **(AUB00976) and on the reduced sample (AUB00307), based on the squeezed pore water**  
 585 **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).

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

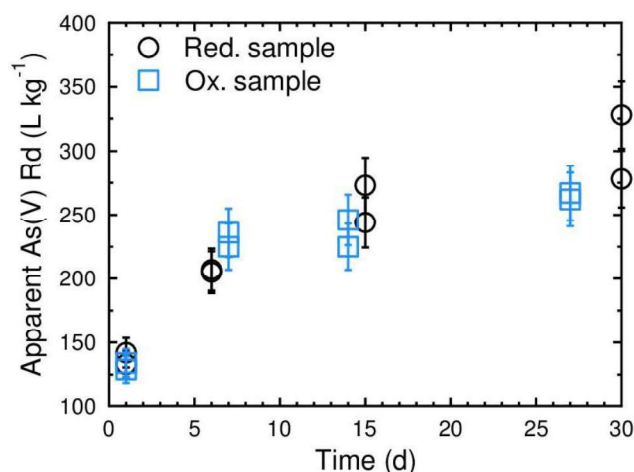
$$R_{D,As(V)} = \frac{[As(V)]_{ini} - [As(V)]_{final} - [As(V)]_{reduced}}{[As(V)]_{final}} \quad (9)$$

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

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

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

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



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

## 6. Conclusions

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

641 **Acknowledgements**

642       This research was financially supported by the BRGM–Andra scientific partnership (TOGAULT  
643 project). Thank you to Michel Fialin (IPGP, Camparis) for his support with the electron microprobe  
644 mapping. We would like to thank Editage ([www.editage.com](http://www.editage.com)) for English language editing.

645

646

647 **References**

- 648 Adriano DC. Trace elements in the terrestrial environment. New York: Springer-Verlag, 1986.
- 649 Alloway B. Soil processes and the behavior of metals. *Heavy metals in soils* 1995; 2: 11-37.
- 650 Amédéo F, Matrimon B, Deconinck J-F, Huret E, Landrein P. Les forages de Juzanvigny (Aube, France):  
651 litho-biostratigraphie des formations du Barrémien à l'Albien moyen dans l'est du bassin de  
652 Paris et datations par les ammonites. *Geodiversitas* 2017; 39: 185-212.
- 653 Arai Y. Arsenic and Antimony. In: Hooda P, S., editor. *Trace Elements in Soils*. Wiley, London, 2010,  
654 pp. 618.
- 655 Bartlett R, James B. Behavior of Chromium in Soils: III. Oxidation<sup>1</sup>. *Journal of Environmental Quality*  
656 1979; 8: 31-35.
- 657 Blanc P, Lassin A, Piantone P, Azaroual M, Jacquemet N, Fabbri A, et al. Thermoddem: A  
658 geochemical database focused on low temperature water/rock interactions and waste  
659 materials. *Applied Geochemistry* 2012; 27: 2107-2116.
- 660 Claret F, Lerouge C, Laurieux T, Bizi M, Conte T, Ghestem JP, et al. Natural iodine in a clay formation:  
661 Implications for iodine fate in geological disposals. *Geochimica et Cosmochimica Acta* 2010;  
662 74: 16-29.
- 663 Couch EL, Grim RE. Boron fixation by illites. *Clays Clay Miner* 1968; 16.
- 664 Daus B, Weiß H, Wennrich R. Arsenic speciation in iron hydroxide precipitates. *Talanta* 1998; 46: 867-  
665 873.
- 666 Eary LE, Rai D. Kinetics of chromate reduction by ferrous ions derived from hematite and biotite at  
667 25°C. *Am. J. Sci.* 1989; 289: 180-213.
- 668 Evans LJ. Chemistry of metal retention by soils. *Environmental Science & Technology* 1989; 23: 1046-  
669 1056.
- 670 Fendorf S, Eick MJ, Grossl P, Sparks DL. Arsenate and Chromate Retention Mechanisms on  
671 Goethite. 1. Surface Structure. *Environmental Science & Technology* 1997; 31: 315-320.
- 672 Fendorf SE. Surface reactions of chromium in soils and waters. *Geoderma* 1995; 67: 55-71.
- 673 Fernández AM, Sánchez-Ledesma DM, Tournassat C, Melón A, Gaucher EC, Astudillo J, et al.  
674 Applying the squeezing technique to highly consolidated clayrocks for pore water  
675 characterisation: Lessons learned from experiments at the Mont Terri Rock Laboratory.  
676 *Applied Geochemistry* 2014; 49: 2-21.
- 677 Fleet M. Preliminary investigations into the sorption of boron by clay minerals. *Clay Miner* 1965; 6: 3-  
678 16.
- 679 Frommer J, Voegelin A, Dittmar J, Marcus MA, Kretzschmar R. Biogeochemical processes and  
680 arsenic enrichment around rice roots in paddy soil: results from micro-focused X-ray  
681 spectroscopy. *European Journal of Soil Science* 2011; 62: 305 - 317.
- 682 Gaucher EC, Tournassat C, Pearson FJ, Blanc P, Crouzet C, Lerouge C, et al. A robust model for  
683 pore-water chemistry of clayrock. *Geochimica et Cosmochimica Acta* 2009; 73: 6470-6487.

- 684 Giffaut E, Grivé M, Blanc P, Vieillard P, Colàs E, Gailhanou H, et al. Andra thermodynamic database  
685 for performance assessment: ThermoChimie. *Applied Geochemistry* 2014; 49: 225-236.
- 686 Giménez J, Martínez M, de Pablo J, Rovira M, Duro L. Arsenic sorption onto natural hematite,  
687 magnetite, and goethite. *Journal of Hazardous Materials* 2007; 141: 575-580.
- 688 Goldberg S. Reactions of boron with soils. *Plant and Soil* 1997; 193: 35-48.
- 689 Goldberg S. Competitive adsorption of arsenate and arsenite on oxides and clay minerals. *Soil Sci.*  
690 *Soc. Am. J.* 2002; 66: 413–421.
- 691 Goldberg S, Johnston CT. Mechanisms of Arsenic Adsorption on Amorphous Oxides Evaluated Using  
692 Macroscopic Measurements, Vibrational Spectroscopy, and Surface Complexation Modeling.  
693 *Journal of Colloid and Interface Science* 2001; 234: 204-216.
- 694 Goldberg S, Suarez DL. Role of Organic Matter on Boron Adsorption-Desorption Hysteresis of Soils.  
695 *Soil Science* 2012; 177: 417-423.
- 696 Goldberg S, Suarez DL, Basta NT, Lesch SM. Predicting Boron Adsorption Isotherms by Midwestern  
697 Soils using the Constant Capacitance Model. *Soil Science Society of America Journal* 2004;  
698 68: 795-801.
- 699 Gorny J, Billon G, Lesven L, Dumoulin D, Madé B, Noiriél C. Arsenic behavior in river sediments under  
700 redox gradient: A review. *Science of The Total Environment* 2015; 505: 423-434.
- 701 Gorny J, Billon G, Noiriél C, Dumoulin D, Lesven L, Madé B. Chromium behavior in aquatic  
702 environments: a review. *Environmental Reviews* 2016; 24: 503-516.
- 703 Gran G. Determination of the equivalence point in potentiometric titrations. Part II. *Analyst* 1952; 77:  
704 661-671.
- 705 Gulens J, Champ DR, Jackson RE. Influence of redox environments on the mobility of arsenic in  
706 ground water. *Am. Chem. Soc. Symp. Ser.* 1979; 93: 81-95.
- 707 Hemming NG, Hanson GN. Boron isotopic composition and concentration in modern marine  
708 carbonates. *Geochimica et Cosmochimica Acta* 1992; 56: 537-543.
- 709 Hemming NG, Reeder RJ, Hart SR. Growth-step-selective incorporation of boron on the calcite  
710 surface. *Geochimica et Cosmochimica Acta* 1998; 62: 2915-2922.
- 711 Jain A, Loeppert RH. Effect of competing anions on the adsorption of arsenate and arsenite by  
712 ferrihydrite. *J. Environ. Qual.* 2000; 29: 1422–1430.
- 713 James BR, Bartlett RJ. Behavior of Chromium in Soils. VI. Interactions Between Oxidation-Reduction  
714 and Organic Complexation1. *Journal of Environmental Quality* 1983a; 12: 173-176.
- 715 James BR, Bartlett RJ. Behavior of Chromium in Soils: V. Fate of Organically Complexed Cr(III) Added  
716 to Soil1. *Journal of Environmental Quality* 1983b; 12: 169-172.
- 717 Lerouge C, Robinet J-C, Debure M, Tournassat C, Bouchet A, Fernández AM, et al. A Deep Alteration  
718 and Oxidation Profile in a Shallow Clay Aquitard: Example of the Tégulines Clay, East Paris  
719 Basin, France. *Geofluids* 2018: 20.
- 720 Li Z. Oxyanion Sorption and Surface Anion Exchange by Surfactant-Modified Clay Minerals. *Journal of*  
721 *Environmental Quality* 1999; 28: 1457-1463.
- 722 Li Z, Bowman RS. Retention of inorganic oxyanions by organo-kaolinite. *Water Research* 2001; 35:  
723 3771-3776.

- 724 Liu SX, Athar M, Lippai I, Waldren C, Hei TK. Induction of oxyradicals by arsenic: Implication for  
725 mechanism of genotoxicity. *Proceedings of the National Academy of Sciences* 2001; 98:  
726 1643-1648.
- 727 Lynch S, Batty L, Byrne P. Environmental Risk of Metal Mining Contaminated River Bank Sediment at  
728 Redox-Transitional Zones. *Minerals* 2014; 4: 52-73.
- 729 Ma Y, Hooda PS. Chromium, Nickel and Cobalt. In: Hooda PS, editor. *Trace Elements in Soils*. Wiley,  
730 London, 2010, pp. 618.
- 731 Manning BA, Kiser JR, Kwon H, Kanel SR. Spectroscopic Investigation of Cr(III)- and Cr(VI)-Treated  
732 Nanoscale Zerovalent Iron. *Environmental Science & Technology* 2007; 41: 586-592.
- 733 Markelova E, Couture R-M, Parsons CT, Markelov I, Madé B, Van Cappellen P, et al. Speciation  
734 dynamics of oxyanion contaminants (As, Sb, Cr) in argillaceous suspensions during oxic-  
735 anoxic cycles. *Applied Geochemistry* 2018.
- 736 Masscheleyn PH, Delaune RD, Patrick WH. Effect of redox potential and pH on arsenic speciation and  
737 solubility in a contaminated soil. *Environmental Science & Technology* 1991; 25: 1414-1419.
- 738 Mavromatis V, Montouillout V, Noireaux J, Gaillardet J, Schott J. Characterization of boron  
739 incorporation and speciation in calcite and aragonite from co-precipitation experiments under  
740 controlled pH, temperature and precipitation rate. *Geochimica et Cosmochimica Acta* 2015;  
741 150: 299-313.
- 742 Muttik N, Kirsimäe K, Newsom HE, Williams LB. Boron isotope composition of secondary smectite in  
743 suevites at the Ries crater, Germany: boron fractionation in weathering and hydrothermal  
744 processes. *Earth and Planetary Science Letters* 2011; 310: 244-251.
- 745 Nagajyoti PC, Lee KD, Sreekanth TVM. Heavy metals, occurrence and toxicity for plants: a review.  
746 *Environ Chem Lett* 2010; 8: 199-216.
- 747 Nakayama E, Tokoro H, Kuwamoto T, Fujinaga T. Dissolved state of chromium in seawater. *Nature*  
748 1981; 290: 768-770.
- 749 Pansar-Kallio M, Reinikainen S-P, Oksanen M. Interactions of soil components and their effects on  
750 speciation of chromium in soils. *Analytica Chimica Acta* 2001; 439: 9-17.
- 751 Parkhurst DL, Appelo CAJ. Description of Input and Examples for PHREEQC Version 3—a Computer  
752 Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse  
753 Geochemical Calculations., 2013.
- 754 Penrose WR. Arsenic in the marine and aquatic environments: Analysis, occurrence, and significance.  
755 *CRC Crit. Rev. Environ. Control* 1974; 4: 465–482.
- 756 Poggio L, Vrščaj B, Schulin R, Hepperle E, Ajmone Marsan F. Metals pollution and human  
757 bioaccessibility of topsoils in Grugliasco (Italy). *Environmental Pollution* 2009; 157: 680-689.
- 758 Pouchou JL, Pichoir F. New model for quantitative x-ray microanalysis. Part I: Application to the  
759 analysis of homogeneous samples [English Ed.]. Vol 3, 1984.
- 760 Sass BM, Rai D. Solubility of amorphous chromium(III)-iron(III) hydroxide solid solutions. *Inorganic*  
761 *Chemistry* 1987; 26: 2228-2232.
- 762 Smedley PL, Kinniburgh DG. A review of the source, behaviour and distribution of arsenic in natural  
763 waters. *Applied Geochemistry* 2002; 17: 517-568.
- 764 Sparks DL. Metal and Oxyanion Sorption on Naturally Occurring Oxide and Clay Mineral Surfaces. In:  
765 Grassian V, H., editor. *Environmental Catalysis*, 2005, pp. 3–36.

- 766 Taghipour M, Jalali M. Effect of clay minerals and nanoparticles on chromium fractionation in soil  
767 contaminated with leather factory waste. *Journal of Hazardous Materials* 2015; 297: 127-133.
- 768 Tallman DE, Shaikh AU. Redox stability of inorganic arsenic(III) and arsenic(V) in aqueous solution.  
769 *Analytical Chemistry* 1980; 52: 196-199.
- 770 Tessier A, Campbell PGC, Bisson M. Sequential extraction procedure for the speciation of particulate  
771 trace metals. *Analytical Chemistry* 1979; 51: 844-851.
- 772 Verbeeck M, Hiemstra T, Thiry Y, Smolders E. Soil organic matter reduces the sorption of arsenate  
773 and phosphate: a soil profile study and geochemical modelling. *European Journal of Soil*  
774 *Science* 2017; 68: 678-688.
- 775 Walsh LM, Keeney DR. Behavior and Phototoxicity of Inorganic Arsenicals in Soils. *Arsenical*  
776 *Pesticides*. 7. AMERICAN CHEMICAL SOCIETY, 1975, pp. 35-52.
- 777 Wauchope RD, McDowell. LL. Adsorption of phosphate, arsenate, methanearsonate, and cacodylate  
778 by lake and stream sediments: Comparisons with soils. *J. Environ. Qual.* 1984; 13: 499–504.
- 779 Williams LB, Hervig RL. Lithium and boron isotopes in illite-smectite: The importance of crystal size.  
780 *Geochimica et Cosmochimica Acta* 2005; 69: 5705-5716.
- 781 Wu Y, Kukkadapu RK, Livi KJT, Xu W, Li W, Sparks DL. Iron and Arsenic Speciation During As(III)  
782 Oxidation by Manganese Oxides in the Presence of Fe(II): Molecular-Level Characterization  
783 Using XAFS, Mössbauer, and TEM Analysis. *ACS Earth and Space Chemistry* 2018.
- 784 Wuana RA, Okieimen FE. Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry,  
785 Risks and Best Available Strategies for Remediation. *ISRN Ecology* 2011; 2011: 20.
- 786 Zhang G, Germaine JT, Martin RT, Whittle AJ. A simple sample-mounting method for random  
787 powder X-ray diffraction. *Clays and Clay Minerals* 2003; 51: 218-225.

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> |

800

801

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

| 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>                      |

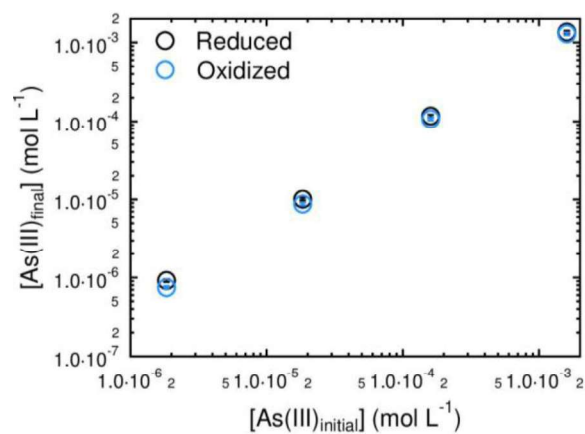
804

805

806

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

808

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.**

811

812

813

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**

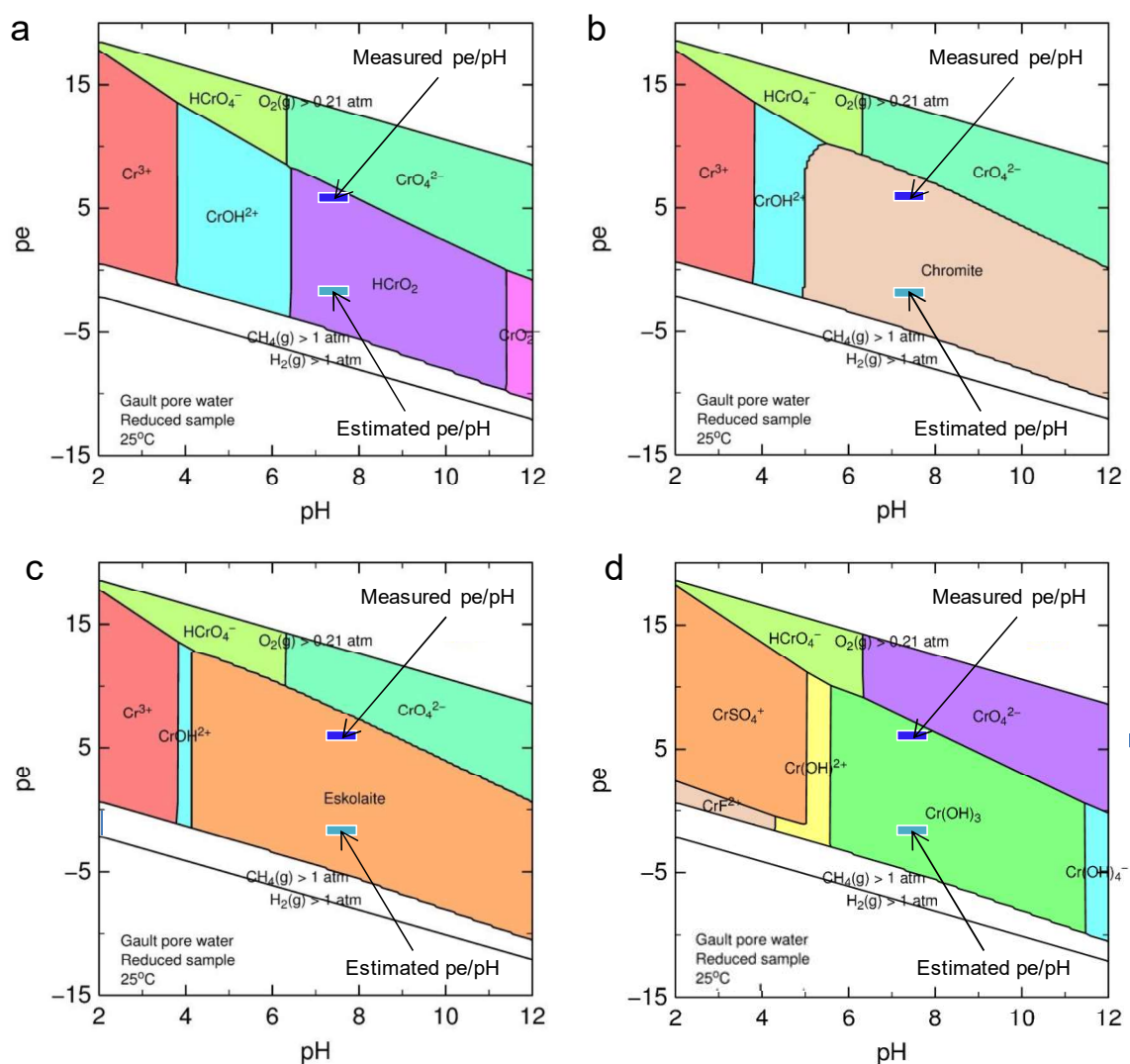
|  | Reduced sample<br>(AUB00307) | Oxidized sample<br>(AUB00976) |
|--|------------------------------|-------------------------------|
| $w_{water}$ (L kg <sup>-1</sup> )        | $1.5 \cdot 10^{-1}$          | $1.5 \cdot 10^{-1}$           |
| $B_{poral}$ (mol L <sup>-1</sup> )       | $1.5 \cdot 10^{-4}$          | $1.5 \cdot 10^{-4}$           |
| $C_{Swater}$ (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                          |

819

820

# Supplementary information E. Chromium stability diagrams

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



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

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

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

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

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