1. X-Ray diffraction (XRD)

XRD measurements were carried out on bulk-rock powder with a SIEMENS D5000 X-ray diffractometer with Co Kα1+2 radiation (λ k_α = 0.1789 nm) operating at 40 kV and 100 mA. Intensities were recorded at a 0.02°(2θ)/s scanning rate from 4 to 84°. Qualitative identification was achieved by fitting peak positions and relative intensities. The abundant minerals discussed in this study, and their associated ICDD (International Center for Diffraction Data) records, are (in alphabetical order): ankerite (00-041-0586), anorthoclase (00-009-0478), calcite (00-005-0586), chlorite (clinochlore 00-029- 0701), dolomite (00-036-0426), kaolinite (01-075-0938), muscovite (01-086- 1385), pyrite (00-042-1340), quartz (00-046-1045), rutile (00-021-1276), and siderite (00-029-0696). Minerals identified by XRD under the term ‘‘mica + illite’’ include muscovite, biotite, illite and possibly glauconite.

The mineral semi-quantification was carried out according to a modified method from Calvert et al. [1]. This method is based on (a) the identification of mineral phases determined by X-ray diffraction, (b) the carbonate content, (c) the chemical composition of the whole rock and (d) a Cation Exchange Capacity (CEC) measurement. The associated algorithm consisted in minimizing a mathematical criterion obtained from (a) chemical mass balance principles similar to that used by Pearson [2] and (b) theoretical structural formula for each mineral species anticipated by the XRD (for micas, illite, glauconite and I/S ordered and disordered clay minerals: [3-5]; other minerals: [6]). The final mineral composition was estimated with an average precision of approximately 10 %. An extended description of this method can be found in Chen et al. [7].

2. Petrographic observations

Optical microscopy was carried out using an Olympus BH2 microscope in transmitted and reflected lights.

Scanning electron microscopy (SEM) was carried out at BRGM and at ERM. SEM at BRGM used a Low Vacuum-Field Emission Scanning Electron Microscope TESCAN Mira3XMU (TESCAN, Brno, Czech Republic) (LV-FE-SEM) coupled with an EDAX TEAM system equipped with a SDD detector APOLLO XPP. SEM at ERM used a Low Vacuum electron microscope (LV-SEM) JEOL 5600 equipped with an Everhart-Thornley detector that images secondary electrons and a Centaurus detector that images backscattered electrons. The system was coupled with a QUANTAX Energy Dispersive Spectrometer (EDS) (BRUKER) at 15 kV, 1 nA and a counting time of 50 seconds.

Spot analyses were carried out on polished thin sections of samples covered with a carbon coating, using a CAMECA SX Five electron microprobe with an acceleration voltage of 15 kV, a current beam of 12 nA and a 1–2 µm beam width. Peak and background counting times were 10 s for major elements.

3. Magnetic measurements

Magnetic measurements were used to identify magnetic iron minerals at a very low levels of concentration and to estimate goethite content when present.
Low temperature magnetic measurements were carried out by using SQUID cryogenic magnetometers called Magnetic Properties Measurement System (MPMS). For these measurements, aliquots of fine-grained bulk powder were inserted into gelatin capsules in the glove box under nitrogen atmosphere. Capsules were transferred in a vacuum cell to the Magnetism Laboratory. The samples were weighed before performing the magnetic measurements; therefore, mass-normalized curves were directly comparable. The complete cycle of measurement was composed of four steps. During the first step, the sample underwent a pre-treatment of cooling from 300 down to 10 K in a zero field (zero field cooled noted ZFC). At 10 K a field of 2.5 T is applied (LT-SIRM$_{2.5\ T}$). Then natural remanence was measured during warming from 10 K to 300 K under zero field. During the second step, the sample underwent a pre-treatment of cooling from 300 down to 10 K in a field of 2.5 T (field cooled noted FC). Then natural remanence was measured during warming from 10 K to 300 K under zero field. During the third step (RT-SIRM), a 2.5 T field was applied at 300 K and switched off. Natural remanence was measured during cooling from 300 to 10 K, and warming from 10 to 300 K in a zero field. The fourth step included a dedicated heating experiment to test the presence of high-coercivity components (specifically goethite). A pre-treatment was applied to acquire an enhanced RT-SIRM according to Guyodo et al. [8]. The sample underwent a heating/cooling cycle between 300 and 395 K under a 2.5 T field. Remanence was measured during two successive cycles of cooling-warming (cooling from 300 to 10 K, warming from 10 to 395 K, second cooling from 395 to 10 K, second warming from 10 to 300 K).

4. Bulk chemistry

The overall analyses of the major- and trace-elements were carried out by X-ray fluorescence spectrometry (XRF; Philips model 2400, Amsterdam, The Netherlands) and inductively coupled plasma-mass spectrometry (ICP-MS; Thermo seriX 2, Bremen, Germany). Total Fe content was assayed in the solid products through a modified 1,10-phenanthroline method [9]. This method proceeded in two steps, first measuring Fe^{2+} content by H_2SO_4-HF acid attack, and then measuring total Fe content by reducing all Fe present to Fe^{2+}. Total carbon and sulfur were analyzed using a Jobin Yvon EMIE 820V carbon/sulfur analyzer (Longjumeau, France). Organic carbon was determined by the same technique after acidic treatment of the sample to eliminate carbonates.

5. Petrophysical measurements

Petrophysical measurements were carried out on core samples as described below:

- Gravimetric water content at 150°C (*w*). Sample was dried and the water content determined by the mass before and after drying (*w* = mass of water/mass of dried sample). Water contents were determined on the drilling site after coring. .

- Densitometry. The grain density (ρ_g) was determined from helium pycnometry (Micromeritics 1305 pycnometer) on dried and crushed samples. The bulk density (ρ_w) was acquired using a hydrostatic weighting in kerosene of wet samples.
- Mercury intrusion/extrusion tests. These were carried out using a Micromeritics Autopore III 9410 V1.02 system. This method was used to determine the connected porosity accessible to mercury (ϕ_{Hg}) when applying a pressure of 414 MPa. In clay rocks, this method does not allow a quantification of pores smaller than 3 nm. Based on the assumption of cylindrical pores and the Washburn equation, the intrusion curve (intruded volume/pressure of mercury) was converted into a pore diameter distribution.
- Specific surface area. This was measured by the conventional BET method using nitrogen absorption (Micromeritics ASAP 2010 v4.00 on dried and degassed powder samples (~ 1g weight).

From the combination of water content and densities we determined the physical porosity of the rock samples. Two porosity values were defined based on the following relations:

Porosity 1: $\phi_1 = \frac{w \times \rho_g}{1 + w \times \rho_g}$ and ***Porosity 2***: $\phi_2 = \frac{\rho_w - \rho_g}{1 - \rho_g}$

For both equations, the density of water was assumed to be 1 g/cm^3. Porosity 1 can be calculated based on water content measured on the drilling site and assuming ρ_g = 2.7 g.cm^3. Uncertainties related to porosity 1 and porosity 2 are below 15 % and 10% respectively.

6. Squeezing

Pore waters were extracted from clay samples by squeezing according to Fernández et al. [10], but using a modified method for collecting the squeezed pore waters under anoxic conditions. The mass of core sample was measured before and after squeezing. The initial masses of core sample ranged between 300 and 500 g. Extractions were carried out at 20-25 MPa. Tests were run at 10 and 30 MPa, implying that pressures applied to tégulines clay samples between 10 and 30 MPa had low impact on the pore water chemistry. Squeezing duration varied with the samples and ranged between three and seven days.

7. Anion leaching

Anion concentrations in aqueous leachate ($C_{\text{leached,i}}$) allow estimating the anion concentrations in the clay porosity, when the anion concentration is not controlled by mineral–water reaction and sorption mechanisms. In that case, the anion concentration in the leachate is linearly proportional with the solid/water ratio, and the linear regression crosscuts zero [11, 12]. The anion concentration of the species *i* per mass of sample ($C_{\text{rock,i}}$) was calculated as $C_{\text{rock,i}} = \frac{C_{\text{leached,i}}}{m} V$ and the anion concentration of species *i* in the porosity as $C_{\text{poro,i}} = \frac{C_{\text{rock,i}}}{\omega}$, V being the volume (in L) of deionized water, m the mass (in

g) of dry powdered clay-rock and ω the water content of the rock at saturation (in $kg_{water}\, kg_{dry\ solid}^{-1}$). In clay-rich rocks, the pore water (PW) was assumed not to have a spatially homogeneous composition at the pore scale due to cation enrichment and anion depletion in the diffuse layer. Only a part of the porosity, corresponding to the bigger pores, contains electroneutral pore solution or "bulk" pore water. Consequently the $C_{\mathrm{poro,i}}$ is not the direct measurement of the anion concentrations in the bulk pore water ($C_{\mathrm{bulk,i}}$.). The $C_{\mathrm{poro,i}}/C_{\mathrm{bulk,i}}$ ratio, also called the anion accessibility porosity, can be estimated from leaching experiments and direct measurements of $C_{\mathrm{bulk,i}}$ by squeezing [10, 11].

We ran leaching experiments and cation exchange capacity measurements on rock reduced to a particle size <80 in a glove box under N_2 atmosphere. Bulk powders were leached with deionized water that was boiled and degassed under N_2. For each sample, a leaching test was carried out at three water/rock ratios (10 g/L, 20 g/L and 50 g/L) for a contact time of 24 h. After centrifugation for 10 min and filtration (0.1 µm) in the glove box, the leachates were analyzed for Cl, Br and SO_4 by ion chromatography, with a detection limit of 0.1 mg/L.

8. Cation exchange capacity and cation distribution on the clay exchanger

Cation exchange capacities (CEC) and cation selectivity coefficients were measured on bulk powders of claystone samples. CEC was measured by exchange of 1 g of powder with a solution of 4.458 g/L cobalt hexammine trichloride over 30 min at room temperature with a reagent/solid mass ratio of 20 [13]. The suspension was centrifuged and the supernatant filtered (0.1 µm). Major cation (Na^+, K^+, Ca^{2+}, Mg^{2+}) concentrations in the supernatant solution were determined by ion chromatography (KOH eluent, KOH suppressor at column exit), with a Dionex conductivity detector (detection limit of 0.5 mg/L). The total CEC was obtained from the cobalt hexammine concentration in the leachate determined by colorimetry (absorption band at 473 nm) on a Unicam UV visible spectrometer.

9. Stable Isotopes

9.1. Carbon and oxygen isotopes of carbonates

Carbon and oxygen isotopes of calcite, dolomite and siderite were analyzed in ~400 mg of bulk powder using the conventional Rosenbaum and Sheppard method (1986).The resulting CO_2 samples were analyzed for their isotopic compositions using a Delta S Finnigan-Mat gas-source mass spectrometer with a precision of 0.3‰ for $\delta^{18}O$ and 0.3‰ for $\delta^{13}C$.

9.2. Oxygen and hydrogen isotopes on extracted water by step heating

The sample, conditioned in a glass container under vacuum was heated during 30 minutes to 1 hour using a heating cable at 70°C to promote vaporization of the water and its recondensation on the walls and at the bottom of the container by cooling down to ambient temperature. This operation was repeated until almost total extraction of the water.

On one sample, the water extracted at each heating step was pipetted, weighted and isotopically measured.

$\delta^{18}O$ and δD values of water samples (per mil relative to V-SMOW) were determined following the gas-water equilibration techniques [14, 15]. All samples were analysed in duplicates. Analytical uncertainty, based on replicate analyses of international and laboratory standards, are ± 0.8 ‰ for δD and ± 0.1 ‰ for $\delta^{18}O$.

9.3. Strontium isotopes

Strontium in calcite was extracted with 0.2 N HCl solution for 30 minutes.

Siderite was cleaned with a 1 N HCl solution at 60°C for 2 hours to eliminate possible traces of calcite and strontium associated to traces of clay particles. Strontium in siderite was extracted at 60°C with 6 N HCl solution overnight.

Strontium in phosphate was extracted with 14 N HNO_3 solution overnight.

Strontium isotopic analyses were carried out according to the technique described in Lerouge et al. [16]. The reproducibility of the $^{87}Sr/^{86}Sr$ ratio measurements was tested through repeated analyses of the NBS987 standard for which we obtained, during the period of analysis, a mean value of 0.710249 ± 0.000012 (2σ, n = 23). Sample ratios were normalized to the certified value of the NBS987 (0.710240).

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