



**HAL**  
open science

## **Strontium distribution and origins in a natural clayey formation (Callovian-Oxfordian, Paris Basin, France): A new sequential extraction procedure**

Catherine Lerouge, Eric C. Gaucher, Christophe Tournassat, Philippe Négrel, Catherine Crouzet, Catherine Guerrot, Anne Gautier, Pascale Michel, Agnès Vinsot, Stéphane Buschaert

### ► To cite this version:

Catherine Lerouge, Eric C. Gaucher, Christophe Tournassat, Philippe Négrel, Catherine Crouzet, et al.. Strontium distribution and origins in a natural clayey formation (Callovian-Oxfordian, Paris Basin, France): A new sequential extraction procedure. *Geochimica et Cosmochimica Acta*, 2010, 74 (10), p. 2926-2942. 10.1016/j.gca.2010.02.013 . hal-00552939

**HAL Id: hal-00552939**

**<https://brgm.hal.science/hal-00552939>**

Submitted on 6 Jan 2011

**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.

Strontium distribution and origins in a natural clayey formation (Callovian-Oxfordian, Paris Basin, France): a new sequential extraction procedure

C. Lerouge <sup>a,\*</sup>, E.C. Gaucher <sup>a</sup>, C. Tournassat <sup>a</sup>, P. Negrel <sup>a</sup>, C. Cruzet <sup>a</sup>, C. Guerrot <sup>a</sup>, A. Gautier <sup>a</sup>, P. Michel<sup>a</sup>, A. Vinsot <sup>b</sup>, S. Buschaert <sup>c</sup>

<sup>a</sup> BRGM, BP36009, 45060 Orléans Cédex 2, France

<sup>b</sup> ANDRA, Meuse/Haute-Marne Underground Research Laboratory (URL), RD 960, 55290 Bure, France

<sup>c</sup> ANDRA, Scientific Management, 1-7 Rue Jean-Monnet, 92298 Châtenay-Malabry Cedex, France

\* Corresponding author.

*E-mail address:* [c.lerouge@brgm.fr](mailto:c.lerouge@brgm.fr) (C. Lerouge)

**Final version January 2010**

Strontium distribution and origins in a natural clayey formation (Callovian-Oxfordian, Paris Basin, France): a new sequential extraction procedure

C. Lerouge <sup>a,\*</sup>, E.C. Gaucher <sup>a</sup>, C. Tournassat <sup>a</sup>, P. Negrel <sup>a</sup>, C. Cruzet <sup>a</sup>, C. Guerrot <sup>a</sup>, A. Gautier <sup>a</sup>, P. Michel, A. Vinsot <sup>b</sup>, S. Buschaert <sup>c</sup>

<sup>a</sup> BRGM, BP36009, 45060 Orléans Cédex 2, France

<sup>b</sup> ANDRA, Meuse/Haute-Marne Underground Research Laboratory (URL), RD 960, 55290 Bure, France

<sup>c</sup> ANDRA, Scientific Management, 1-7 Rue Jean-Monnet, 92298 Châtenay-Malabry Cedex, France

\* Corresponding author.

*E-mail address:* [c.lerouge@brgm.fr](mailto:c.lerouge@brgm.fr) (C. Lerouge)

Abstract - Strontium is a good monitor of geochemical processes in natural clayey formations. In the Callovian-Oxfordian formation of Bure in France, strontium is sorbed on clay minerals and carried by carbonates, detrital minerals and accessory celestite. In order to determine the strontium distribution among these different phases, four-step sequential extractions (1. cobalt hexamine trichloride, 2. acetic acid, 3. EDTA and 4. tri-acid) were performed on samples from different levels of the clayey formation. The leachates were also analyzed for strontium isotopes, in order to determine the strontium origins. This sequential procedure is well suited to determining strontium distribution in claystones, although it is less efficient in clay-rich limestones and in celestite-rich samples. The carbonates (38-47 % of the total strontium) show  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.7070-0.7071) that have recorded the isotopic composition of the Callovian-Oxfordian seawater. Diagenetic carbonates (dolomite, ankerite and siderite) have almost not incorporated any strontium, which has been trapped by celestite during the late diagenesis. The major part of the celestite shows  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.7069-0.7070) quite close to the primary carbonates. However, a second generation of celestite (0.7074) shows a slight  $^{87}\text{Sr}$ -enrichment and is isotopically in equilibrium with the exchangeable strontium (27 to 48 % of the total strontium with a mean  $^{87}\text{Sr}/^{86}\text{Sr}$  value of 0.70745) and the present-day porewater (0.7074). This very low  $^{87}\text{Sr}$ -enrichment could be explained by the partial destabilisation of detrital minerals (feldspars, micas, clays) which exhibit  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios consistent with their pristine Hercynian origin (0.7229-0.7350). Diffusion of strontium from the subjacent Dogger aquifers (0.7076-0.7082) could also be invoked to explain the slight  $^{87}\text{Sr}$ -enrichment.

Keywords: Clay, sequential extraction, strontium isotopes, Sr, URL Bure, ANDRA

## 1. Introduction

Strontium is an alkali earth metal present as divalent cation that readily substitutes for calcium in carbonates, sulphates, feldspars, mica, clays and other minerals, and weakly sorbs on clay minerals. Strontium is also present as a trace element in major fluid reservoirs (seawater, groundwaters). Strontium has four natural stable isotopes:  $^{84}\text{Sr}$  (0.56 %),  $^{86}\text{Sr}$  (9.87 %),  $^{87}\text{Sr}$  (7.04 %) and  $^{88}\text{Sr}$  (82.53 %).  $^{87}\text{Sr}$  results from the decay of  $^{87}\text{Rb}$ , which substitutes for potassium in feldspars, micas, K-bearing clays and other minerals. Like  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  actively participates in fluid-rock interactions. As a result of these characteristics, strontium isotopes are good tracers of strontium sources (solid and fluid) and a powerful tool for fluid-rock interactions and hydrogeological investigations (PACE et al., 2007).

Strontium isotopes were particularly developed in the study of marine carbonate sediments (BATHURST, 1975). The strontium is accumulated in biogenic carbonates (2000-10000 ppm: MORSE and MACKENZIE, 1990) and not fractionated by biological processes from  $^{87}\text{Sr}/^{86}\text{Sr}$  seawater values (MORSE and MACKENZIE, 1990). Consequently, strontium isotopes of well-preserved biogenic carbonates measured in marine carbonates of various ages were used to trace the strontium isotopic variations of seawater throughout the Phanerozoic, reflecting the relative contributions of continental weathering and hydrothermal activity associated with mid-oceanic ridges (JONES and JENKYN, 2001; JONES et al., 1994; KOEPNICK et al., 1990; VEIZER et al., 1989). Since the residence time of strontium is significantly longer than the mixing of the oceans, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is quite homogeneous in all oceans at the same time (HODELL et al., 1990). During normal burial diagenesis, the strontium concentration in carbonate minerals decreases as they recrystallize, resulting in low strontium contents of most ancient limestones (200-600 ppm: BATHURST, 1975). The strontium lost by biocarbonates undergoing recrystallization is transferred to the porewaters (BRAND, 1991). Thus, carbonate diagenesis is one mechanism for raising the strontium content of porewaters above the ~8 ppm strontium content of contemporaneous seawater. The isotopic composition of the strontium added to porewater by carbonate recrystallization remains the same as the biogenic carbonate from which it formed, when there is no external strontium support. Consequently, isotope studies on diagenetic carbonates can provide important constraints on the timing of diagenetic events, but also on the estimation of radiogenic strontium support in the system by measuring differences between the  $^{87}\text{Sr}/^{86}\text{Sr}$  values in porewaters and their host carbonates of known age (BAKER et al., 1981; ELDERFIELD et al., 1982).

Comparatively few other types of sediments have been investigated for strontium. In carbonate-bearing sediments, diluted hydrochloric acid leaching is currently used to extract the carbonate cement and trace its origin (NEGREL et al., 2000). The leachate classically displays a strontium ratio above coeval seawater, suggesting partial equilibration between seawater strontium fixed by diagenetic carbonates and strontium derived from terrigenous fraction (HODELL et al., 1990), or a partial mobilization of strontium from residual fraction by weak acid (HODELL et al., 1990; NÉGREL et al., 2001a). Celestite [SrSO<sub>4</sub>] and barite [BaSO<sub>4</sub>] present as accessory diagenetic minerals in marine sediments and sediments undergoing Ba-Sr-sulphate-rich hydrothermal alteration were also analyzed for strontium to constrain the origins and the timing of late diagenetic fluids.

Over the last few decades, part of the available data concerning strontium behaviour in sediments has come from the environmental field. Strontium has at least sixteen artificial radioactive isotopes; strontium 90 is one of the major radionuclides contained by high-level radioactive nuclear waste studied for its high toxicity and its long lifetime. The radionuclide sorption potential of the mineral constituents is one of the main aspects that needs to be evaluated in contaminated sediments and also in claystones that are considered as potential geological repositories of nuclear wastes. In the safety assessment of future disposals, <sup>85</sup>Sr and accessorially <sup>90</sup>Sr are currently used as tracers in experiments to study processes of retardation of radionuclides by clays: sorption/desorption, diffusion, isotopic exchange (VAN LOON et al., 2005). Experimental data has provided evidence of the weak sorption property of strontium on clay minerals (VAN LOON et al., 2005). In contaminated sediments, sequential extraction procedures have been developed to constrain the behaviour of toxic metals by determining their main carriers and their distribution (MESTER et al., 1998; PACE et al., 2007; TESSIER et al., 1979), but none is specifically dedicated to strontium in claystones (RAO et al., 2008). The protocols for sequential extraction of radiostrontium in soils were too specific to organic rich soils (RIGOL et al., 1999; VIDAL and RAURET, 1995).

In order to contribute to constraining the retardation processes controlling strontium migration in clayey sediments better, we propose to study the behaviour of natural strontium in a marine clayey formation over geological times. This paper describes a specific sequential extraction procedure to extract strontium in the Callovian-Oxfordian (noted COx) carbonate-cemented clayey formation of the Bure site in the Eastern part of the Paris Basin, in order 1) to determine the strontium distribution among the main mineral fractions in a natural clayey formation, and 2) to constrain the strontium origin of the main Sr-carriers, taking into account the existing data available on strontium isotopes in marine carbonates and new isotopic approaches regarding contaminated sediments. The Bure site was selected by ANDRA (French National Radioactive Waste Management Agency) to build an Underground Research Laboratory (URL) and test the feasibility of deep nuclear disposal in a clay formation. We took advantage of this well-studied field to adapt the procedure to the mineralogy of the claystone. The mineralogy, the proportions of the major phases and the diagenetic sequence have been extensively described in (ANDRA, 2005; CLAUER et al., 2007;

GAUCHER et al., 2004b). The strontium-carrier phases of the claystone have already been determined in (TOURNASSAT et al., 2008). Preliminary tests of the selected reagents were carried out on claystone samples and pure phases to determine the optimal time and reagent/solid ratio of reaction for each extraction stage, but also to minimize artefacts due to unexpected dissolution of phases. Previous strontium isotopic work has already been performed on carbonates from the clayey formation and the limestones surrounding it using dilute hydrochloric acid leaching (CASANOVA et al., 1999; NÉGREL et al., 2001b). Otherwise, strontium isotopes have already been studied on porewaters of the clayey formation (VINSOT et al., 2008) and on groundwaters in surrounding limestones of the eastern part of the Paris Basin (FONTES and MATRAY, 1993a; FONTES and MATRAY, 1993b). Isotopic data are compared with previous data acquired on claystones and surrounding limestones, discussing the origin of the radiogenic enrichment of the carbonate fraction relative to coeval seawater obtained by conventional weak hydrochloric acid leaching. The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope geochemistry of all the strontium-carrier minerals replaced in the diagenetic sequence can significantly contribute to a better understanding of strontium behaviour in clay formation in terms of 1) adsorption/desorption on clays, 2) isotopic exchange between porewaters and the strontium-carrier phases, and 3) retention by formation of Sr-bearing minerals. The comparison of CO<sub>x</sub> data with the strontium signatures of groundwaters in Dogger and Oxfordian limestones provides evidence of restricted diffusion of strontium between the clay formation and the surrounding carbonate platforms acting as aquifers, thus complementing previous hydrogeological works (BUSCHAERT et al., 2007a).

## 2. Geological setting

The Underground Research Laboratory is located in the eastern part of the Paris Basin. The sedimentation of the Paris Basin was initiated after the Variscan Orogeny at the northern part of the belt. Infilling of the basin consists of Mesozoic and Cenozoic sediments (*Fig. 1a*). In the eastern part of the basin, the formations dip slightly 1-2° to the west within a monocline related to the subsidence of the centre of the basin. The investigated area around the URL is located in the synclinal of Savonnières limited by two major regional fault systems: in the western part the Bray, Vittel and Metz faults (LAMIRAUX and MASCLE, 1998) and in the eastern part the faults of Gondrecourt and Marne. Low seismicity and slight vertical movements suggest that the area is quite devoid of tectonic activity. On the site, the studied Callovian-Oxfordian claystone is a 130 m-thick clay formation accessible at 400 metres depth, which is surrounded by the Dogger carbonate platform at the bottom and the Oxfordian carbonate platform (oolitic shelf limestone and bioherms) at the top (*Fig. 1*). The Dogger limestones overlie Liassic marls and claystones. The Oxfordian limestones are 300 m thick and are covered by 100 m thick Kimmeridgian marls and Barrois limestones on the outcrops (Table 1).

### 3. Materials

Sixteen samples from several drill-cores performed in the ANDRA URL, which have been previously studied for their mineralogical, chemical and physical properties (Blanc et al., 2007; Gaucher et al., 2004b), were selected for the strontium isotopes in the four main units of the Callovian-Oxfordian clayey formation (Table 2). The main mineralogy and the distribution of the principal fractions (clay, siltite and carbonates) are summarized in *Fig. 2*. The claystones contain a dominant detrital fraction represented by detrital minerals and bioclasts. Detrital minerals are dominantly clays (illite, illite/smectite mixed layers, chlorite and kaolinite) and micas (muscovite and biotite), associated with a variable siltite fraction, consisting of dominant quartz with minor K-feldspar and plagioclase. Bioclasts are essentially shells and otoliths formed by calcium carbonate polymorphs (fibrous calcite, aragonite) and calcium phosphates, and organic matter (< 1.4 wt % C) (GAUCHER et al., 2004b). This does not exclude the possibility that a minor part of the illite (CLARET et al., 2004) and smectite (ROUSSET and CLAUER, 2003) could be authigenic. A textural and mineralogical study of the claystones has enabled their diagenetic mineral sequence to be established as follows:

1. Early diagenetic cement of micritic calcite with pyrite
2. Glauconite, euhedral carbonates (dolomite/ankerite, siderite)
3. Vugs and veinlets infilling by celestite with more or less dolomite
4. Chalcedony in vugs and in veinlets penetrating celestite and dolomite
5. Quartz in rare vugs only observed in carbonate-rich layers of the upper sequence of the clayey formation. Vugs are small cavities in the claystones corresponding to primary porosity due to the presence of shells that created protected micro-zones or secondary dissolution porosity.

#### *Strontium content in phases of the Callovian-Oxfordian clay formation of Bure*

Strontium is a trace element in the Callovian-Oxfordian clayey formation. Its content varies between 225 and 470 ppm with a peak at 1000 ppm (EST05485) in the EST205 drill hole, and does not depend on the lithology (*Fig. 1c*) (GAUCHER et al., 2004b; LEROUGE et al., 2006). The strontium is carried by detrital clays, micas and rare feldspar, diagenetic carbonates and diagenetic celestite (strontium sulphate [SrSO<sub>4</sub>]) when present, and by detrital carbonate and phosphate bioclasts (TOURNASSAT et al., 2008). In clays, strontium is assumed to be in exchangeable position. Strontium in detrital feldspar and micas occupies the same site as potassium or calcium. In these

two minerals,  $\text{Sr}^{2+}$  replaces  $\text{Ca}^{2+}$  while  $^{87}\text{Sr}$ , stemming from the disintegration of rubidium ( $^{87}\text{Rb}$ ), replaces potassium. The strontium content in carbonate phases is significant in inherited biocarbonates (up to 1850 ppm) and lower in diagenetic carbonates represented by micritic cement and euhedral carbonates (760 ppm Sr, (TOURNASSAT et al., 2008). Celestite is observed through all the clay formation as disseminated microcrystalline grains up to centimetre-sized euhedral crystals infilling late vugs.

#### *Previous isotopic strontium data on the Callovian-Oxfordian clay formation of Bure*

The labile fraction was separated in different samples of the claystones from the Callovian-Oxfordian clay formation and Oxfordian limestones, using a simple method of leaching with cold HCl (CASANOVA et al., 1999). Following the investigations of (NEGREL et al., 2000), HCl digestion enables the extraction of elements that are bound to Fe–Mn oxides, adsorbed on clays, and occurring in carbonates and sulphides as well as in natural organic matter. HCl digestion neither further disturbs the clay-mineral lattice nor dissolves silicates. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the leaching are mostly in agreement with that of contemporaneous Jurassic seawater (Late Callovian–Early Oxfordian–Kimmeridgian), even in the clay-rich sections (Fig. 2) (CASANOVA et al., 1999).

## **4. Analytical methods**

### **4.1. Celestite separates**

100  $\mu\text{m}$  to 2 cm crystals of celestite were separated by hand picking on thin sections (EST05433) and sample chips. Crushed celestite was cleaned with a 0.2N HCl solution to eliminate possible traces of calcite. Strontium extraction used 112  $\mu\text{g}$  in the sample EST05433 and 7 to 47 mg in other samples added to 10 ml of 2N HCl solution (extra-pure quality grade concentrated HCl and deionised water) in covered Teflon beakers at 100°C for two weeks. The extraction yield was low however and only 125 ng of strontium was loaded onto the tungsten filament for the strontium isotopic analyses.

### **4.2. Development of the sequential extraction procedure**

In order to estimate the strontium distribution and isotopes in the claystones from Bure, a four-step sequential extraction procedure was adapted to the mineralogy of the samples in order to separate: 1) exchangeable Sr, 2) Sr in calcite, 3) Sr associated with late diagenetic dolomite, siderite and celestite, and 4) Sr in detrital minerals. The procedure was applied to 1 g of bulk rock reduced to a less than 50  $\mu\text{m}$  sized powder. Successive sequential leaching of each sample was



processed in the same tube, except for the last extraction, for which the sample was transferred to a Teflon vial for strong acid and high temperature processing.

#### **4.2.1. Sr exchangeable fraction**

The exchangeable strontium was extracted at the first step by exchanging the cations with cobalt hexamine trichloride using the method adapted from (RÉMY and ORSINI, 1976) and (CIESIELSKI and STERCKEMAN, 1997). As a consequence, the cobalt blocks the sites of the exchangeable cations in clays and avoids any re-adsorption (or minimizes the adsorption) of strontium extracted at a subsequent step. 20 ml or 40 ml of cobalt hexamine trichloride (4.458 g/l) was added to 1 g of sample, centrifuged at room temperature for different times and filtrated immediately. Strontium and major cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) were determined in the exchange solution by ion chromatography with a conductivity detector (DIONEX). Concurrently, the equilibrium concentration of the leachate was determined colorimetrically (Co absorption band at 473 nm) on a UNICAM UV visible spectrometer that gives the CEC (cation exchange capacity).

#### **4.2.2. Sr in the calcite fraction**

The acetic acid buffered by sodium acetate method was used to extract strontium in the calcite fraction. 20 g of  $\text{CH}_3\text{COONa}$  (1M), adjusted to pH 5.0 with  $\text{CH}_3\text{COOH}$ , was added to the first residue of the first step then left to stand for 4 h, centrifuged and immediately filtrated.

#### **4.2.3. Residual carbonate fraction (dolomite, siderite)**

The residual carbonate fraction (dolomite, ankerite, siderite) was treated using EDTA, a reagent used to extract metals and divalent cations such as strontium from sediments (PACE et al., 2007). 20 ml of EDTA was added to the second residue then left to stand for 1 h, centrifuged and filtrated.

#### **4.2.4. Residual fraction containing essentially detrital minerals, pyrite and possibly remaining carbonates and celestite**

$\text{HNO}_3$  (2 ml) + HF (10 ml) +  $\text{HClO}_4$  (5 drops) were added to the residual solid and heated on a hot plate at 120°C in a closed Savillex container for one week, the HF was evaporated and the residue was dissolved in 10 ml of 6N HCl at 100°C again for one week.

For the ten samples that underwent the entire sequential extraction procedure, the strontium and rubidium concentrations were measured at each step using an element inductively coupled plasma mass spectrometer. Rubidium contents are used in the following part to correct present-day strontium isotope ratios of the  $^{87}\text{Rb}$  disintegration into  $^{87}\text{Sr}$  with geological times. The blanks were measured for each sequential extraction step, in order to correct of reagent impurities:

Cobalt hexamine trichloride:	Sr = 10 µg/l	$^{86}\text{Sr}/^{88}\text{Sr} = 0.715600$
Acetic acid:	Sr = 19.9 µg/l	$^{86}\text{Sr}/^{88}\text{Sr} = 0.708635$
EDTA:	Sr = 168.3 µg/l	$^{86}\text{Sr}/^{88}\text{Sr} = 0.707104$

In the first two extraction steps, the blank represents respectively less than 0.2 % and 0.4 % of the extracted strontium in the samples and can be considered as negligible. For the EDTA extraction, the blank is high and the strontium extracted from the samples is rather low; consequently, the strontium content and the  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of the EDTA fraction were corrected for EDTA contribution.

#### 4.3. Separation of the labile fraction by leaching with 0.2N HCl

This separation was performed in order to provide additional results to compare with the previous strontium data of (CASANOVA et al., 1999). Extractions used 300 mg of bulk rock powder added to 20 ml HCl solution (extra-pure quality grade concentrated HCl and deionised water) in covered Teflon beakers, following the procedure described in (NEGREL et al., 2006; NEGREL et al., 2000). An ultrasound treatment was performed at room temperature over the 30 minutes of the extraction. After sonication and checking the total acid-solid reaction, the solid residue was separated by centrifugation. The quantity of acid-extractable matter or the labile fraction was determined by the weight difference between the dried powder before and after acid extraction, expressed as a percentage of the total matter content. The HCl solution was evaporated, the residual product was weighed and aliquots were analyzed for Rb and Sr contents and for Sr isotope composition.

#### 4.4. Strontium isotopes

For the isotopic analyses, Sr was purified using an ion-exchange resin (Sr-Spec) before mass analysis according to a method adapted from (PIN and BASSIN, 1992), with total blank <1 ng for the entire chemical procedure. After chemical separation, around 150 ng of Sr was loaded onto a tungsten filament with tantalum activator and analyzed with a Finnigan MAT262 multi-collector solid source mass spectrometer. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were normalized to an  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.1194. An average internal precision of  $\pm 10$  ppm ( $2\sigma_m$ ) was obtained and reproducibility of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio measurements was tested through repeated analyses of the NBS987 standard for which we obtained, during the period of analysis, a mean value of  $0.710227 \pm 0.000017$  ( $2\sigma$ ,  $n = 70$ ). Sample ratios were normalized to the certified value of the NBS987 (0.710240).

## 5. Results

### 5.1. Refinement of the sequential extraction procedure

CEC measurements using the cobalt hexamine chloride method have previously been performed on samples of Callovian-Oxfordian claystones from the Bure site, with a reagent/solid ratio of 20 and a reaction time of 24 hours (GAUCHER et al., 2004a; GAUCHER et al., 2004b; GAUCHER et al., 2007). In order to reduce the reaction time, so as to complete the entire sequential extraction procedure in only one day and improve the reagent/solid ratio, tests of CEC measurements were performed with various reaction times (15 min, 30 min, 4 h, 24 h) and two reagent/solid ratios (20 and 40), in a clay-rich limestone (EST05485) and a calcite-poor claystone (EST25687) (Electronic annex 1). In the sample EST05485, the CEC calculated by the sum of the exchanged cations  $CEC_{\Sigma}$  is higher than the CEC measured by colorimetry, indicating the partial dissolution of a mineral. The increase in  $CEC_{\Sigma}$  with increasing reagent/solid ratio is related to the increase in the extracted calcium, suggesting a partial dissolution of calcite. In the sample EST25687, the  $CEC_{\Sigma}$  is reproducible for the same reagent/solid ratio at different times of reaction. On the other hand, the CEC measured by colorimetry slightly increases with time, suggesting a possible degradation of the cobalt hexamine trichloride. According to these tests, the reagent/solid ratio was adjusted to 20 to reduce the partial extraction of carbonates and the time of reaction to 30 minutes to avoid the degradation of the reagent for the routine analyses.

In order to quantify the partial dissolution of carbonates and celestite, the main Sr-carrier minerals, by the cobalt hexamine chloride, the method was applied to pure calcite, dolomite and celestite crushed to below a 50  $\mu\text{m}$  sized powder. The CEC measured by colorimetry was close to the detection limit in all cases. On the other hand, the CEC calculated by the sum of the cations measured in the leachates from the three experiments was higher than the CEC measured by colorimetry, providing evidence of the partial dissolution of the minerals (Electronic annex 2). This dissolution was estimated to be around 0.1 % for calcite, 0.4 % for dolomite and 0.9 % for celestite. The value obtained for celestite is quite close to its saturation index (RUSHDI et al., 2000). For a reagent/solid ratio of 20, it corresponds to  $\sim 4000$  ppm Sr in the solid. The main consequence of this result is that a little celestite present in the Callovian-Oxfordian claystone (generally  $<0.5$  %) will be dissolved during this extraction step and will contaminate the Sr exchangeable fraction.

In order to control the efficiency of the Na-acetate + acetic acid method to extract the calcite, tests were performed on dolomite (Electronic annex 3) and celestite (Electronic annex 4). They clearly show that around 15 % of dolomite and 1.1 % of celestite ( $\sim 1.1$  %) are also extracted. The slight dissolution of celestite in the Na-acetate + acetic acid solution does not constitute a real problem, because the little amount of celestite present in the sample will be entirely dissolved at the first

step of the sequential extraction procedure. Even though a significant percentage of dolomite is dissolved by this method, the low content of dolomite (<7 %) compared to the calcite abundance in Callovian-Oxfordian claystones, and the low strontium content of dolomite, indicate that the strontium content attributed to dolomite dissolution will represent a very small part of the strontium extracted at this step.

In order to control the efficiency of EDTA to extract diagenetic iron-bearing carbonates, tests were performed on dolomite/ankerite and siderite. They show that dolomite/ankerite and siderite are only partially extracted by EDTA with this reagent/solid ratio. However, the use of larger amounts of EDTA remains difficult for strontium isotopes because of the significant Sr content of the blank. The EDTA step does not allow the total extraction of dolomite and siderite, however the strontium isotope ratio of the EDTA leachate is representative of both of these diagenetic carbonates.

A summary of the sequential extraction procedure, the extracted strontium fractions and the associated mineral dissolution is given in the *Fig. 3*.

## **5.2. Sr extraction on Callovian-Oxfordian claystones**

The complete extraction procedure was performed on ten samples. The first two extraction steps were performed on six other samples (Table 2).

The Sr extracted by cobalt hexamine trichloride at step 1 (designated the 'exchangeable fraction') corresponds essentially to exchangeable Sr adsorbed on clay minerals and to strontium stemming from the dissolution of celestite. The Sr content of all the leachates 1 varied between 10 and 210 ppm in rock and was significantly lower than the 4000 ppm corresponding to celestite saturation. This confirms that celestite, when it is present, is present as traces in all the samples and is entirely dissolved during this first extraction step. The highest Sr contents were measured in two samples EST05485 and EST20714, in which celestite is observed as veinlets. The Sr content is correlated with the clay content of the rock except for these two samples (*Fig. 4*), indicating that strontium extracted by cobalt hexamine trichloride is dominantly exchangeable strontium in all cases, with a significant contribution of celestite in the two celestite-bearing samples.

The Sr extracted by sodium acetate + acetic acid at step 2 (designated the 'calcite fraction') essentially corresponds to strontium carried by calcite and its polymorph (aragonite). Its content varied between 100 and 180 ppm of rock independently of the calcite content of the sample, except in the sample EST05485, in which the extracted strontium attained 290 ppm (*Fig. 5*). Measurements of the calcium concentration in leachate 2 allowed the percentage of extracted calcite to be calculated, corresponding to an extraction yield of between 64 and 94 %; the lowest yields were obtained in limestones, probably due to a lack of reagent or an increasing pH of reagent by calcite buffering (*Electronic annex 5*).

EDTA reagent allows a partial extraction of residual carbonates (designated the 'EDTA fraction'), i.e. calcite unextracted by acetic acid, dolomite (s.l.) and possibly siderite. The strontium concentration of leachate 3 was significantly lower than the leachates of the first two steps. The highest values were measured in the samples that gave the lowest calcite extraction yields at step 2.

The tri-acid attack conducted on the last residue (designated the 'residual fraction') also enabled the extraction of strontium present in carbonates not extracted in the first steps (limestone samples) and strontium carried by detrital feldspars, micas and illite. The amounts of strontium extracted in the residue were quite constant and low (50 ppm) in the claystone samples and significantly higher in the limestone samples.

The strontium contents extracted at each step were relatively homogeneous in the claystone samples but were different in the limestone samples and especially in limestones crosscut by a veinlet of celestite (EST05485, EST20714). Precautions were taken to avoid the celestite veinlets when sampling the bulk rock; however celestite may also be present as rare fine-grained crystals disseminated in the matrix of the rock.

### **5.3. Sr isotopes on celestite separates**

$^{87}\text{Sr}/^{86}\text{Sr}$  ratios were determined in celestite from three core samples (EST05485, EST 20714 and EST 5433) of the EST205 and three samples from the experimental gallery (-490 m) (Table 3). For five of these samples, the strontium isotopic signature of celestite separates ranges between 0.70687 and 0.70704, suggesting that celestite was formed from Callovian-Oxfordian seawater (0.7068-0.7072, (JONES et al., 1994). Celestite in the sample EST05485 clearly occurs as a post-compaction mineral. Its  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.70737 is slightly higher than Callovian-Oxfordian seawater, providing evidence for a second generation of celestite.

### **5.4. Sr isotopic results of the sequential extraction procedure**

Each leachate was isotopically analyzed (Table 4). In the ten samples that underwent the entire sequential extraction procedure, the Rb contents were measured in the leachates and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were corrected from the age of the sediments, i.e. 160 Ma according to (ODIN, 1994) ( Table 5). The measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were not significantly higher than the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios calculated at 160 Ma, except for the EDTA extraction. The strontium content of the EDTA fraction was generally low, whereas the blank contribution was high. The corrections were significant due to the measurement precision of the Rb and Sr contents and only one blank measurement. However, they have no strong influence on the interpretation of the data.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the exchangeable fraction ranged between 0.7073 and 0.7075. Even after age correction, the values are slightly higher than Callovian-Oxfordian seawater (0.7068-0.7072, (JONES et al., 1994)). The strontium attributed to the dissolution of celestite potentially present in the sample should tend to decrease the strontium isotopic signature of the exchangeable fraction, considering the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of previous analyzed celestite (average value  $\sim 0.7070$ ).

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the calcite fraction ranged between 0.7070 and 0.7072. This range is in accordance with the Callovian-Oxfordian seawater value.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the EDTA fraction ranged between 0.70715 and 0.70735 and between 0.7067 and 0.7071 after blank and age corrections. These values after age correction are also consistent with the Callovian-Oxfordian seawater values.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the residual fraction, i.e. dominantly the detrital minerals, ranged between 0.7083 and 0.7350. These values are significantly higher than values measured on the other fractions. The lowest values (0.7083-0.7125) were measured in the limestone samples; these values correspond to a mixing of detrital minerals with residual carbonates, which were not extracted in the previous extraction steps.

#### **5.5. Sr isotopic results of leaching with dilute 0.2N HCl**

Leaching using the cold dilute HCl method was applied to the four samples that underwent the sequential extraction procedure in order to compare the data obtained by sequential extraction with previous data acquired with the leaching method (CASANOVA et al., 1999) (Table 6).

The dissolved fraction of rock was quite comparable with the calcite content of the rock, except for sample EST05485. The extracted strontium content was higher than the strontium carried by the calcite fraction of the sequential extraction and is comparable with the cumulated strontium of the exchangeable fraction and the calcite fraction, except for sample EST5485. The low extraction yield and corresponding strontium are probably due to the high carbonate content of the sample and also to the significant presence of celestite.

The measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios corrected from age are comparable and relatively homogeneous. The values are intermediate between the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the exchangeable fraction ( $\pm$  celestite) and those of the calcite fraction. They are totally consistent with the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio calculated by mixing the strontium of the exchangeable and calcite fractions obtained by sequential extraction.

## 6. Discussion

### 6.1. Sr distribution in the clay formation – efficiency of the sequential extraction procedure

The total sequential extraction procedure applied to ten samples from the Callovian-Oxfordian clay formation enabled the distribution of strontium among the four fractions to be quantified. In the claystone samples, overall 31-48 % of Sr was recovered in the exchangeable fraction, 33-41 % in the calcite fraction, 0-6 % in the EDTA fraction and 11-27 % in the residual fraction. In the calcite-rich and limestone samples, strontium was differently distributed. The exchangeable fraction was logically very low (< 8 %) in celestite-free limestones (EST21400, K108), due to the low content of clay minerals, and overestimated in the celestite-bearing calcite-rich samples (EST05485, EST20714), due to celestite dissolution. The residual fraction was abnormally high, due to the extraction of residual carbonates. The partial extractions applied to the other six claystone samples showed a homogeneous distribution of the exchangeable and calcite fractions, comparable to the other claystone samples (*Fig. 6*).

The strontium of the exchangeable fraction corresponding to strontium in exchangeable positions in illite and illite/smectite mixed layer surfaces was clearly dominant as compared to the strontium of the detrital fraction carried by micas, feldspars and also structural K-sites of illite.

The calcite fraction includes strontium carried by diagenetic micritic calcite, but also and mainly strontium that was preferentially incorporated by detrital calcite and aragonite of biological origin (shells, tests from benthic microfauna). The low Sr content in the dolomite (*sensus lato*) and siderite extracted by EDTA is consistent with previous EPMA analyses (TOURNASSAT et al., 2009). This could indicate that the recrystallization of detrital Sr-rich biogenic carbonates during the diagenesis released the Sr in the porewater leading to the formation of Sr-poor carbonates and celestite, in agreement with (BATHURST, 1975).

According to these results, the strontium is distributed in a first approximation as follows:

In claystones, Sr adsorbed on clays ± celestite > Sr in carbonates > Sr in detrital minerals.

In clay-poor limestone, Sr in carbonates > Sr adsorbed on clays ± celestite, Sr in detrital minerals.

This rule does not apply when celestite is abundant in the sample.

The strontium distribution evaluated with the sequential procedure proposed in this paper needs to be considered with caution in limestone and celestite-bearing samples. The dissolution of celestite at the first step of the sequential extraction involves an overestimation of the exchangeable fraction. A simple correction of the strontium provided by the celestite dissolution cannot be done

because its content is unknown in the samples. It is clearly lower than 4000 ppm, corresponding to celestite saturation in the leachates.

The development of the sequential extraction procedure for the Callovian-Oxfordian formation shows the importance of the first cobalt hexamine trichloride step to extract the exchangeable strontium adsorbed on clay minerals and block the exchangeable sites with cobalt for the following steps. This procedure clearly made it possible to separate strontium adsorbed on clay minerals and strontium incorporated in carbonates and in that way was more efficient for this type of rock to characterize marine fluids at equilibrium with diagenetic carbonates than the conventional technique of weak leaching with dilute HCl, which is well adapted to limestones (NEGREL et al., 2000). The EDTA step was not totally efficient in extracting late diagenetic iron-bearing carbonates and estimating the associated strontium. However, it was efficient enough to provide a representative strontium isotopic signature of them. This procedure is limited to the extraction of the main strontium-carrier fractions in the Callovian-Oxfordian clay formation, which evolved in reduced conditions.

## **6.2. Factors controlling strontium isotope distribution in the Callovian-Oxfordian clay formation**

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the Callovian-Oxfordian claystones from Bure are controlled by the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the main strontium carrier fractions, which are in decreasing order:

- 1) Sr adsorbed on clay minerals  $\pm$  Sr due to partial dissolution of celestite ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7073-0.7075)
- 2) Sr carried by celestite ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7069-0.7074)
- 3) Sr carried by carbonates ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7070-0.7072)
- 4) Residual strontium incorporated by detrital minerals excluding residual carbonate phases ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7246-0.7350).

### *Carbonate fraction*

The strontium of the carbonate fraction that corresponds to micritic calcite, diagenetic carbonates (calcite, dolomite and siderite) and calcium carbonate polymorphs from the bioclasts of the Callovian-Oxfordian benthic microfauna showed lower values than (CASANOVA et al., 1999) and a narrower range of  $^{87}\text{Sr}/^{86}\text{Sr}$  values than the Callovian-Oxfordian seawater defined by (JONES et al., 1994). This range of values can be considered as the regional strontium isotope reference of the Callovian-Oxfordian seawater. Consequently detrital biocarbonates and diagenetic carbonates,



and celestite formed at different stages of the geological evolution of the Paris Basin, have preserved their pristine signature of the Callovian-Oxfordian marine signature.

### *Celestite*

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of celestite provide evidence of two generations at least. A first generation directly precipitated from the Callovian-Oxfordian porewaters or remobilizing the Sr released by the re-crystallization of the primary carbonate bioclasts, and consequently recorded chemical conditions of sedimentation and early diagenesis. A later generation of celestite infillings (sample EST05485) exhibits a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio close to present-day pore waters and is clearly in equilibrium with the exchangeable ions and with present-day porewaters.

### *Detrital fraction*

The detrital fraction showed the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. These high values are in agreement with the origin of the illite, micas and feldspars reformed from the Hercynian basement (PELLENARD and DECONINCK, 2006). The preservation of the pristine signature of the detrital fraction in contrast with the Callovian-Oxfordian marine signature of the carbonate and exchangeable fractions indicates that no re-equilibration of the detrital fraction has occurred since the deposition of the formation. This is consistent with the modelling of the present porewater chemistry proposed by (GAUCHER et al., 2009) .

### *The exchangeable strontium fraction. Comparison with the different strontium reservoirs in the Paris Basin*

The exchangeable fraction represents the dominant strontium fraction. It has recorded an isotopic signature still belonging to the large range of values of the Jurassic seawater (JONES and JENKYNS, 2001; JONES et al., 1994). Calcite, celestite and exchangeable Sr have very similar values that lie within Jurassic seawater values. However, slight  $^{87}\text{Sr}$  enrichment can be noticed for the exchangeable fraction compared to the calcite and celestite. As is discussed in the analytical and strontium distribution sections, the strontium extracted by the cobalt hexamine trichloride method ( $\text{Sr}_{\text{CEC}}$ ) corresponds dominantly to exchangeable strontium ( $\text{Sr}_{\text{exch}}$ ) mixed with strontium due to partial celestite dissolution ( $\text{Sr}_{\text{cel}}$ ) and strontium in porewater ( $\text{Sr}_{\text{porewater}}$ ).

$$\text{Sr}_{\text{CEC}} = \text{Sr}_{\text{exch}} + \text{Sr}_{\text{cel}} + \text{Sr}_{\text{porewater}}$$

The strontium in porewater is considered as negligible relative to the strontium supported by celestite and adsorbed on clays. Furthermore, it can be noticed that present-day waters in the Callovian-Oxfordian formations (VINSOT et al., 2008) have the same signature as  $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{CEC}}$ , indicating that the strontium in present-day waters is at equilibrium with and is controlled by the exchangeable fraction. A diagram of  $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{CEC}}$  as a function of  $1/\text{Sr}$  shows that most of the

samples have a ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) ratio between 0.7074 and 0.7075, whereas the celestite bearing samples (EST5485, EST20714) plot along a line defined between them and the celestite pole (*Fig. 7*). Consequently, the range of ( $^{87}\text{Sr}/^{86}\text{Sr}$ )<sub>CEC</sub> can be considered as representative of the ( $^{87}\text{Sr}/^{86}\text{Sr}$ )<sub>exch</sub>, whereas the local presence of celestite in the samples tends to decrease it. In *Fig. 8*, two causes of the slight  $^{87}\text{Sr}$  enrichment of the exchangeable fraction are proposed: (i) an internal  $^{87}\text{Sr}$  support from the detrital fraction and/or (ii) external  $^{87}\text{Sr}$  diffusion from subjacent aquifers: the Dogger, Rhaetian and Keuper aquifers (FONTES and MATRAY, 1993a; FONTES and MATRAY, 1993b; BUSCHAERT et al., 2007a).

(i) A low support (<1 %) of radiogenic strontium derived from the detrital fraction ( $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.734$ ) added to a Callovian-Oxfordian marine value is enough to explain a ( $^{87}\text{Sr}/^{86}\text{Sr}$ )<sub>exch</sub> value of 0.7074. Taking account of the long lifetime of the basin and given that  $^{87}\text{Sr}$  enrichment of porewaters and brines from Dogger and Triassic aquifers in the Paris Basin are partly explained by diagenetic dissolution of Rb-rich detrital minerals (K-micas, K-feldspar), a partial contribution of the detrital fraction may also be invoked in the clay formation. GAUCHER et al. (2004b) have shown that the biotite grains of the COx are altered and they can be a good candidate in order to provide the  $^{87}\text{Sr}$  that is needed.

(ii) The groundwater from the Oxfordian limestones ( $0.70715 \pm 0.000018$ : BUSCHAERT et al., 2007b) has a strontium isotopic signature fairly comparable with Callovian-Oxfordian seawater (0.7068-0.7072: JONES et al., 1994), and lower than the present-day COx porewaters. Consequently strontium diffusion from the Oxfordian aquifer reservoir through the clay formation cannot be invoked to explain the  $^{87}\text{Sr}$  enrichment of the present-day COx porewaters (cf. *Fig. 9*). This confirms the disconnection between the Oxfordian aquifers and the Callovian-Oxfordian clay formation demonstrated by oxygen and hydrogen isotope data for the water of both formations (GIANNESINI, 2006) and indicates that the Sr does not diffuse significantly into the COx from the Oxfordian. Quite the reverse, the oxygen and hydrogen isotopic data and the profile of the chloride content of the COx porewater argue in favour of a water diffusion from the Dogger aquifers into the Callovian-Oxfordian clay formation (BUSCHAERT et al., 2007a; GAUCHER et al., 2006). The strontium isotopic signature of the Dogger aquifers (0.7076-0.7082: FONTES and MATRAY, 1993a) compared to the signature of the exchangeable fraction of the Callovian-Oxfordian claystones allows a possible diffusion of Sr from the Dogger.

However, the homogeneous exchangeable strontium isotope composition across the clayey formation has not shown a diffusion profile of strontium between the overlying Oxfordian and the subjacent Dogger aquifers (*Fig. 9*). On this basis, the authors consider that the first hypothesis is more likely.

### 6.3. Broader implications

Strontium is present as a trace element in major fluid reservoirs: seawater and groundwaters. Its long residence time in seawater involves homogeneity of the seawater strontium isotopic composition at the earth scale for a geological period and consequently is favourable to hydrogeological investigations in ancient marine sedimentary rocks (BANNER, 2004). Moreover, strontium does not fractionate during mineral precipitation from fluid and the strontium isotopic ratio of a phase is directly representative of the fluid from which it precipitates. Thus, the strontium isotopic characterisation of different minerals of a well-established diagenetic sequence makes it possible to determine the different fluid supports in the basin and to build up the fluid migration in sediments over the lifetime of a sedimentary basin.

In the sedimentary domain, strontium isotopes have been particularly developed on carbonates to trace seawater during Phanerozoic times (JONES and JENKYN, 2001), but also to constrain the timing of diagenetic events in sedimentary rocks (ARMSTRONG-ALTRIN et al., 2009; BRIGAUD et al.). This topic is currently of major interest in the exploitation of gas and oil reservoirs (CHAUDHURI et al., 1987; NEILSON et al., 1998) and aquifers. The classical technique of weak leaching with dilute HCl, well adapted to limestones, has been widely used to extract the carbonate cement in carbonate-bearing sedimentary rocks and trace its origin (NEGREL et al., 2000). In this study, strontium ratios of leachates obtained by weak leaching with dilute HCl on the bulk rock are systematically slightly higher than strontium ratios of the carbonate fractions obtained by sequential extraction. As discussed in paragraph §6.1., the first extraction step with cobalt hexamine trichloride clearly made it possible to eliminate strontium adsorbed on clay minerals, which contaminated strontium associated with the carbonate fraction, and in that way was more efficient for carbonate-bearing sedimentary rocks to characterize fluids at equilibrium with carbonates.

Fluid migration is an important factor when considering the feasibility of nuclear disposal in a clay formation. Strontium 90 is one of the major radionuclides contained by high-level radioactive nuclear waste studied for its long lifetime. Understanding the behaviour of natural strontium in clayey formations is an alternative way of constraining retardation processes by clay that control strontium migration in the long term. The sequential extraction procedure developed and applied in this study has clearly shown that strontium sorption on clays is a major factor in controlling migration in the COx clayey formation. These data are in agreement with previous experimental sorption and diffusion data of strontium and geochemical calculations in Opalinus Clay (Van Loon et al., 2005; Wersin et al., 2008). Strontium isotopes provide evidence of diagenetic minerals from an early diagenesis phase in equilibrium with Callovian-Oxfordian seawater and a late generation in equilibrium with present-day porewaters.

The homogeneity of the exchangeable strontium isotope composition, its similarity with present-day porewaters and the preservation of the pristine signature of the detrital fraction indicates no re-

equilibration of the detrital fraction since the deposition of the formation. These data validate the modelling of the porewater chemistry in the COx clayey formation by (GAUCHER et al., 2009), assuming an equilibrium between the adsorbed cations and some diagenetic minerals providing constraints on the evolution of fluids. At the scale of a sedimentary formation, the homogeneity of the exchangeable strontium isotope composition along the vertical profile and its significant difference from the present-day groundwaters of the surrounding aquifers may indicate or not the existence of a strontium diffusion profile. Consequently, this demonstrates that the clay formation is a strong buffer considering the diffusion of alkaline-earth cations and that the ion exchange processes limit the diffusion of Sr for very long periods. This provides evidence of the interest of investigating the behaviour of natural strontium in sediments contaminated by strontium radionuclide and clayey formations considered as potential geological repositories of high-level radioactive nuclear wastes.

The sequential extraction procedure combined with strontium isotopes in sedimentary series can be used as a systematic approach at the scale of a carbonate-bearing sedimentary formation to consolidate the modelling of pore water geochemistry, to determine the timing of diagenetic events and to define fluid migration within the formation. This approach is efficient when combined with petrological work identifying strontium carrier minerals and defining the diagenetic mineral sequence. A limiting factor of this approach is the natural strontium content of the sediment or the clayey formation. This approach may be completed by the study of other radiogenic elements such as Nd or Pb, which do not fractionate with the fluid but are more sensitive to crustal support, or by the study of classic stable isotopes which fractionate with temperature, when strontium data are not decisive. Oxygen and hydrogen isotopes are suitable as tracers of major water migrations, whereas carbon, sulphur and nitrogen are more sensitive to microbial processes.

## **7. Conclusions**

The sequential extraction developed and applied to the Callovian-Oxfordian claystones provided evidence of two main fractions carrying the strontium: the exchangeable fraction and the carbonate fraction, the detrital fraction being secondary. Celestite is a major strontium mineral that can perturb the results of the sequential extraction but not significantly modify the distribution of strontium at the scale of the formation. The development of this sequential extraction procedure for the Callovian-Oxfordian formation shows the importance of the first cobalt hexamine trichloride step to extract the exchangeable strontium adsorbed on clay minerals and block the exchangeable sites with cobalt for the following steps, allowing a good separation of exchangeable fraction and carbonates. However, the reagent/solid ratio of 20 seems to be less adapted to carbonate-rich samples. The good separation between exchangeable strontium and strontium incorporated by

carbonates made it possible to obtain a strontium isotopic composition representative of each one. The isotopic signature of exchangeable Sr (0.70745) is in equilibrium with the present-day porewaters (0.7074-0.7076) and is significantly different from the strontium isotopic signatures of the carbonate fraction (0.7070-0.7072) and celestite, which are quite similar to Callovian-Oxfordian seawater (JONES et al., 1994). The small detrital fraction (K-micas and feldspars) shows high strontium isotope values, in agreement with their Hercynian continental origin, providing evidence of low exchange with other main strontium fractions. This demonstrates the low contribution of the detrital minerals in the establishment of the present porewater chemistry of this formation, as has been demonstrated by (GAUCHER et al., 2009) using thermodynamic and kinetic arguments.

### **Acknowledgements**

The results presented in this article were collected during the ISODIAR Project granted by ANDRA in the framework of the ANDRA/BRGM scientific partnership. We are grateful to Dr. Gregory Connelly (Scientific Translations Limited) for proofreading and editing the English text. The Associate Editor, Dr Sydney Hemming, and three anonymous referees are thanked for their constructive comments and their significant improvements to the manuscript.

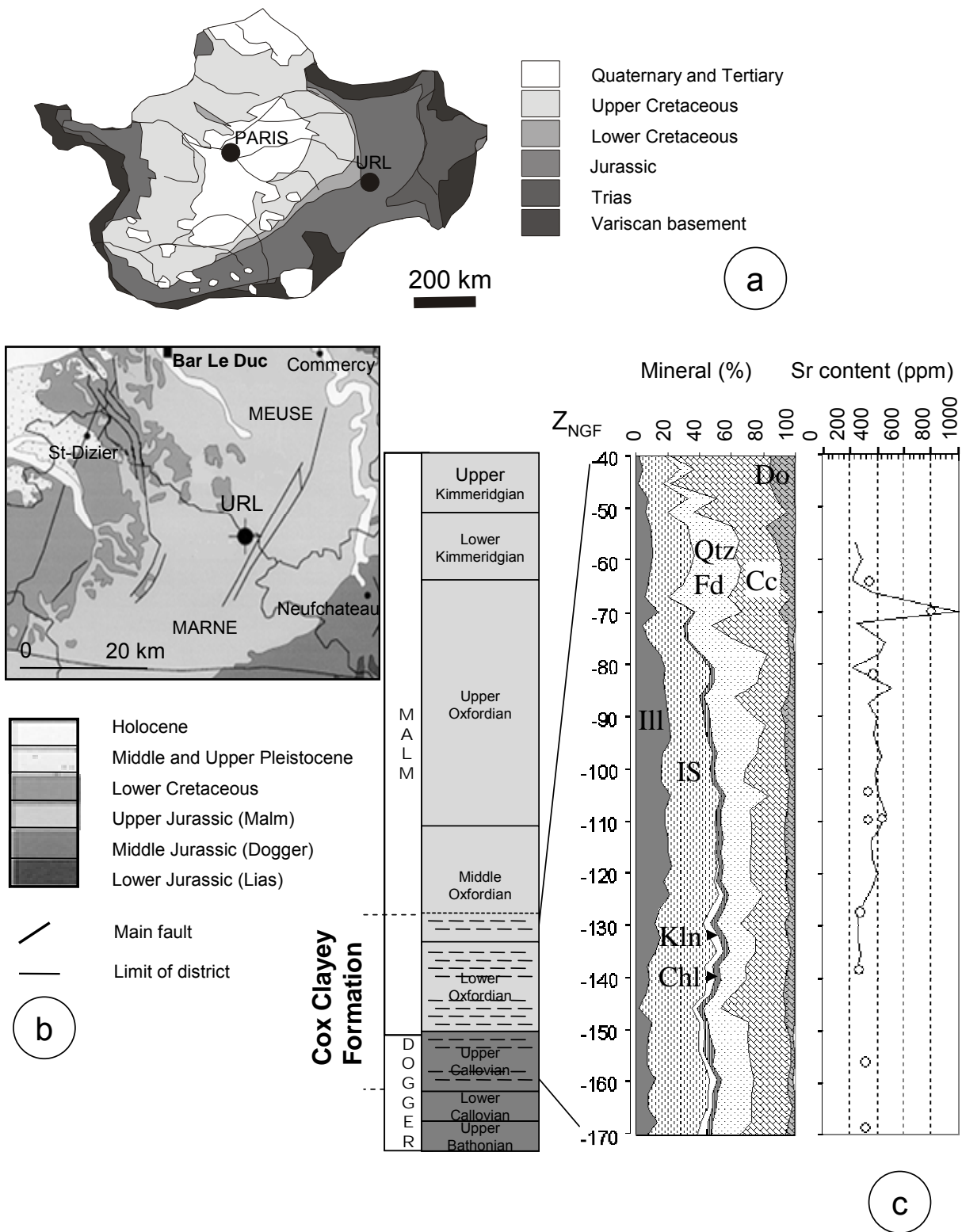


Fig. 1. Geological setting of the ANDRA Underground research Laboratory (URL). a. Geological map of the Paris Basin, location of the Bure URL, b. Geological and structural map of the eastern part of the Paris Basin, c. Lithostratigraphic column with the mineralogical detail of the Callovian-Oxfordian clayey formation and its strontium content.

Abbreviations : Cc = calcite, chl = chlorite, Do = dolomite, Fd = feldspar, III = illite, IS = illite smectite mixed layers, Kln = kaolinite, Qtz = quartz.

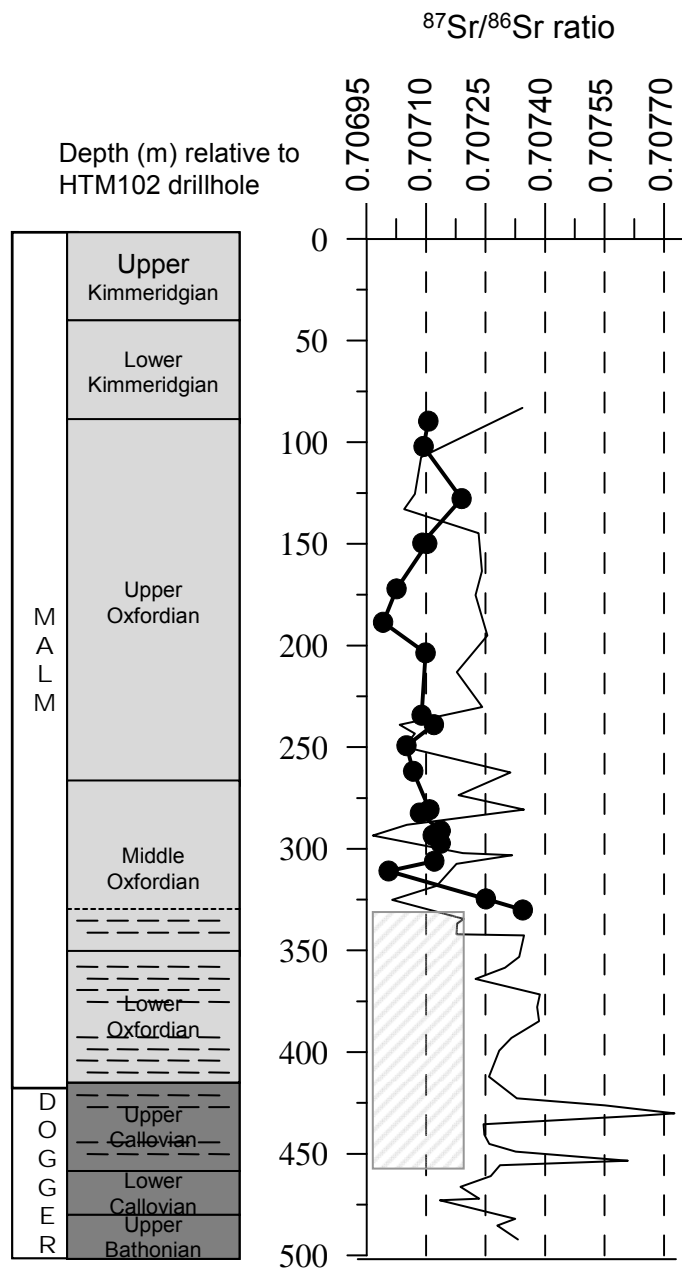


Fig. 2. Previous strontium isotopic data on the Callovian-Oxfordian clayey formation and surrounding limestones (overlying Oxfordian carbonate platform and overlaid Dogger carbonate platform). The line indicates the strontium isotope profile of the labile carbonate fraction obtained on bulk rock by weak HCl leaching. The points are strontium isotopic ratios obtained on separates of late diagenetic carbonates in vugs (Negrel et al. 2001). The shaded area shows the range of strontium isotope values of the Callovian-Oxfordian seawater, according to Jones et al. (1994).

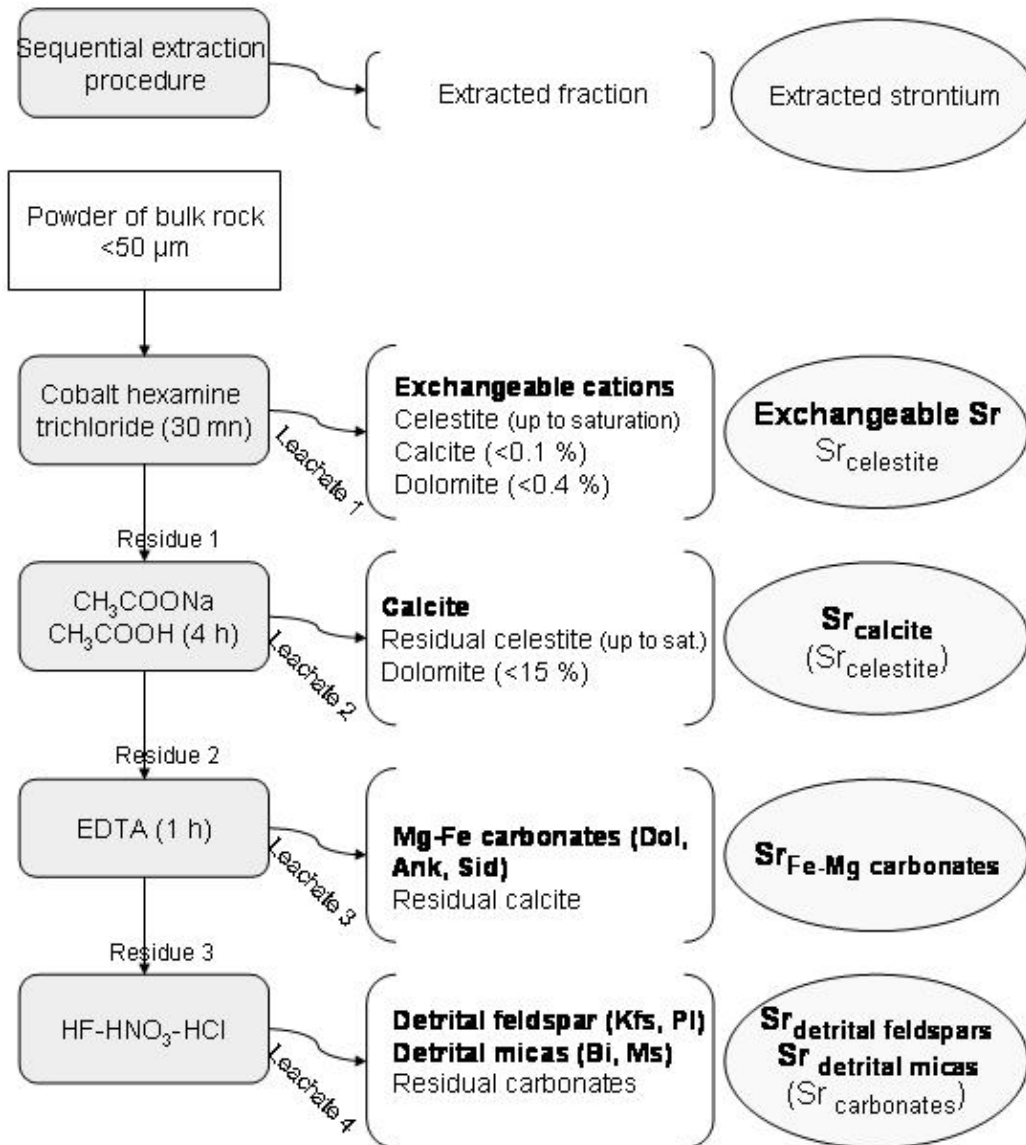


Fig. 3. Sequential extraction protocol. Main phases or fractions extracted at each step and main corresponding strontium carriers.



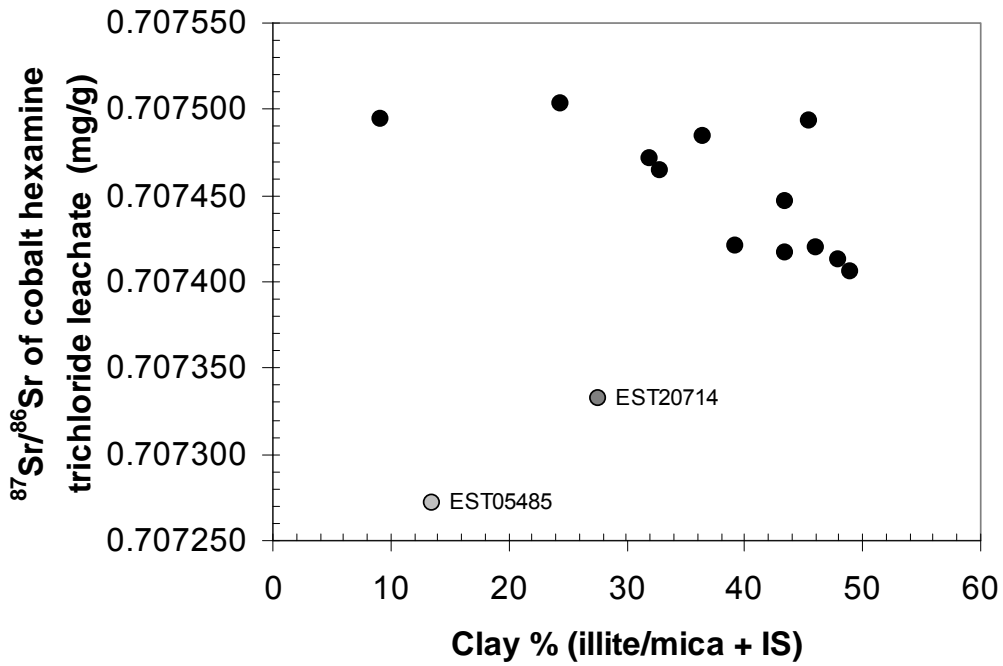


Fig. 4. Diagram showing the relationship between the strontium isotope ratio of cobalt hexamine trichloride leachate and the clay content of the samples.

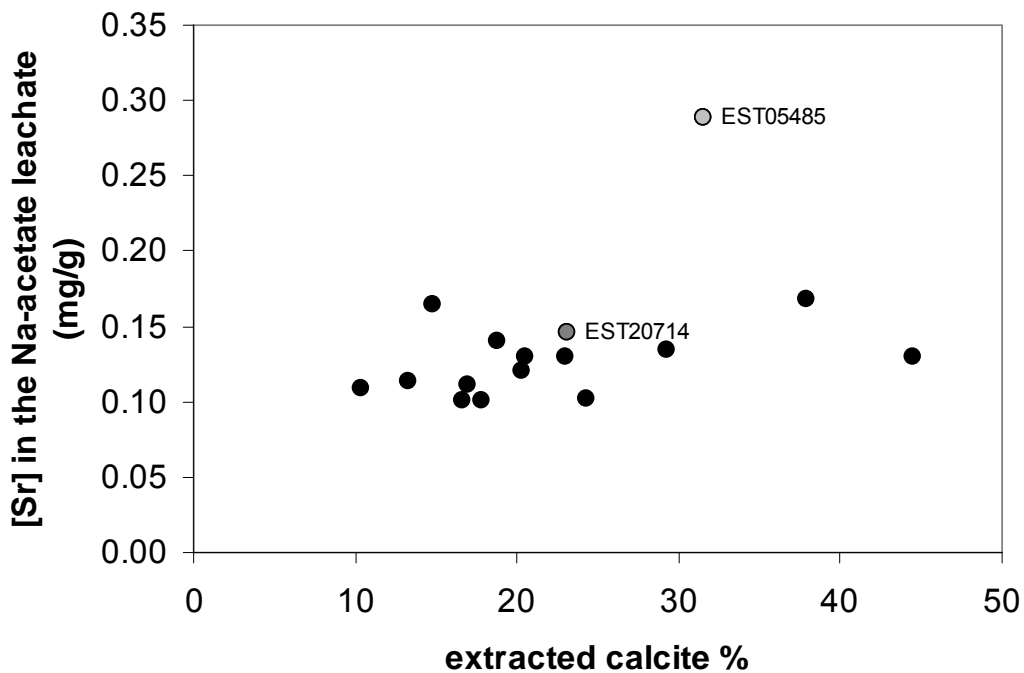


Fig. 5. Diagram showing the relationship between the Sr content of the Na-acetate leachate and the calcite content of the samples.

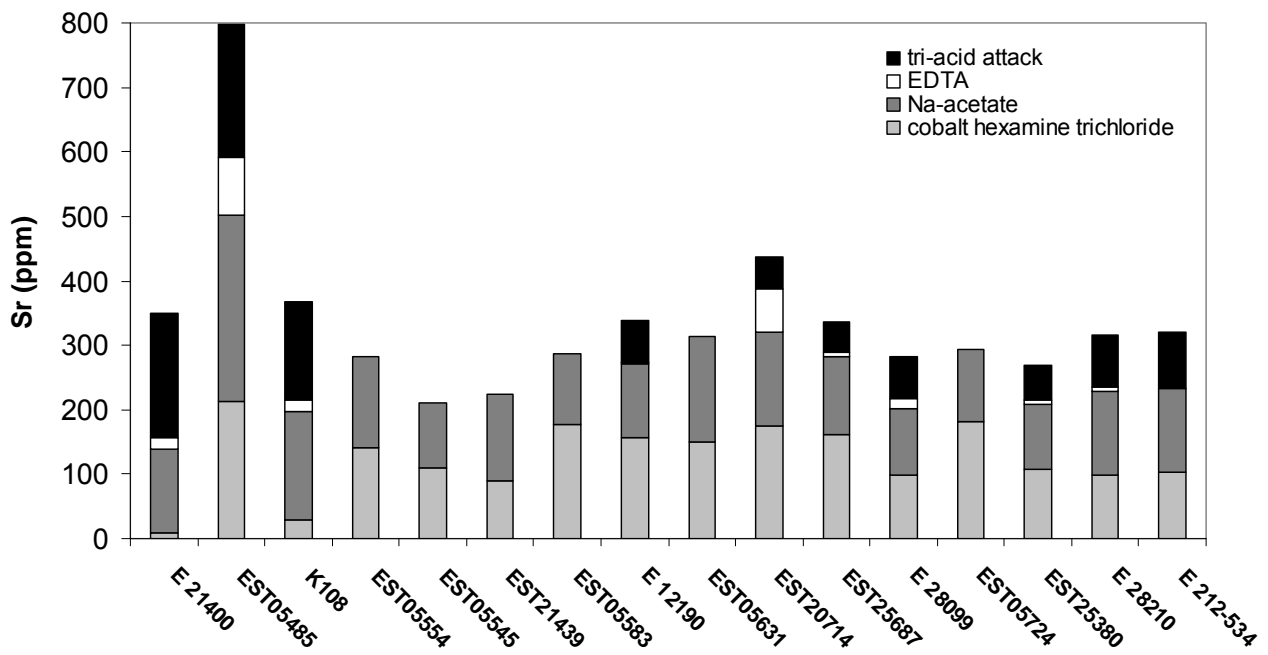


Fig. 6. Distribution of strontium among the main fractions in all the samples (x-axis).

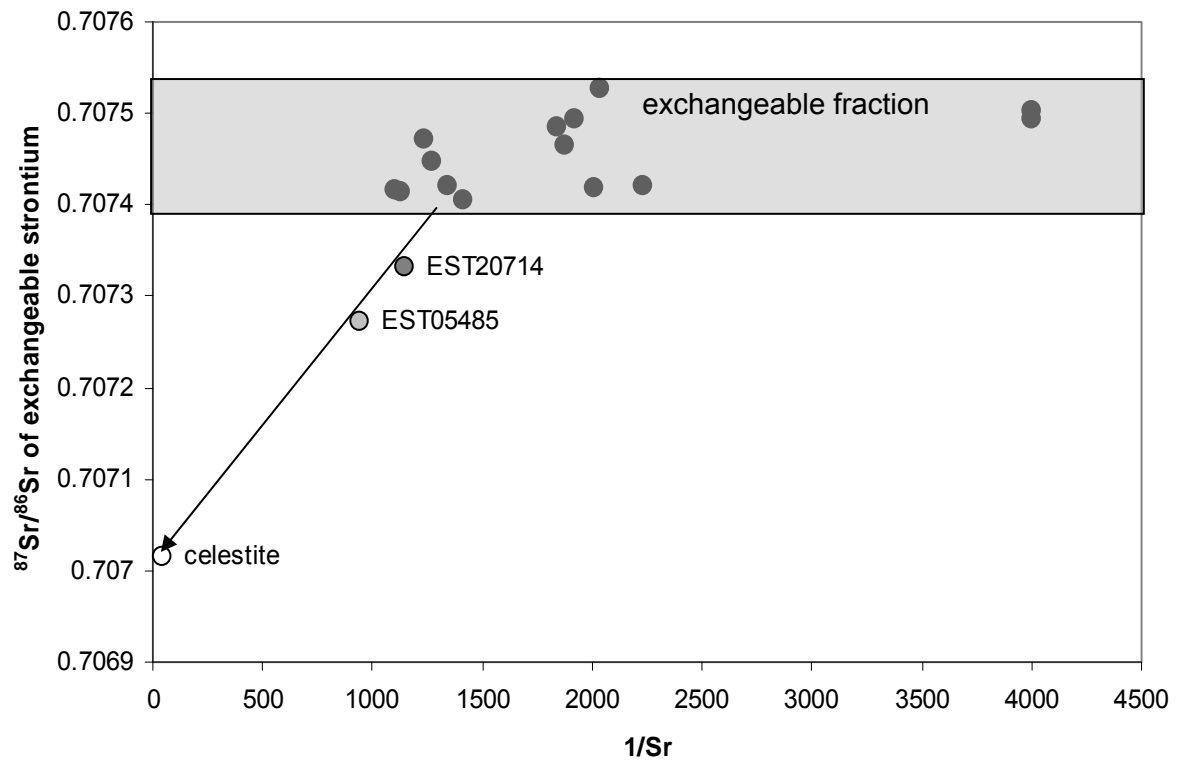


Fig. 7. Strontium isotope ratio and content of the cobalt hexamine trichloride leachate reported in a diagram of  $^{87}\text{Sr}/^{86}\text{Sr}$  as a function of  $1/\text{Sr}$ , providing evidence of mixing between exchangeable strontium and strontium due to celestite dissolution.

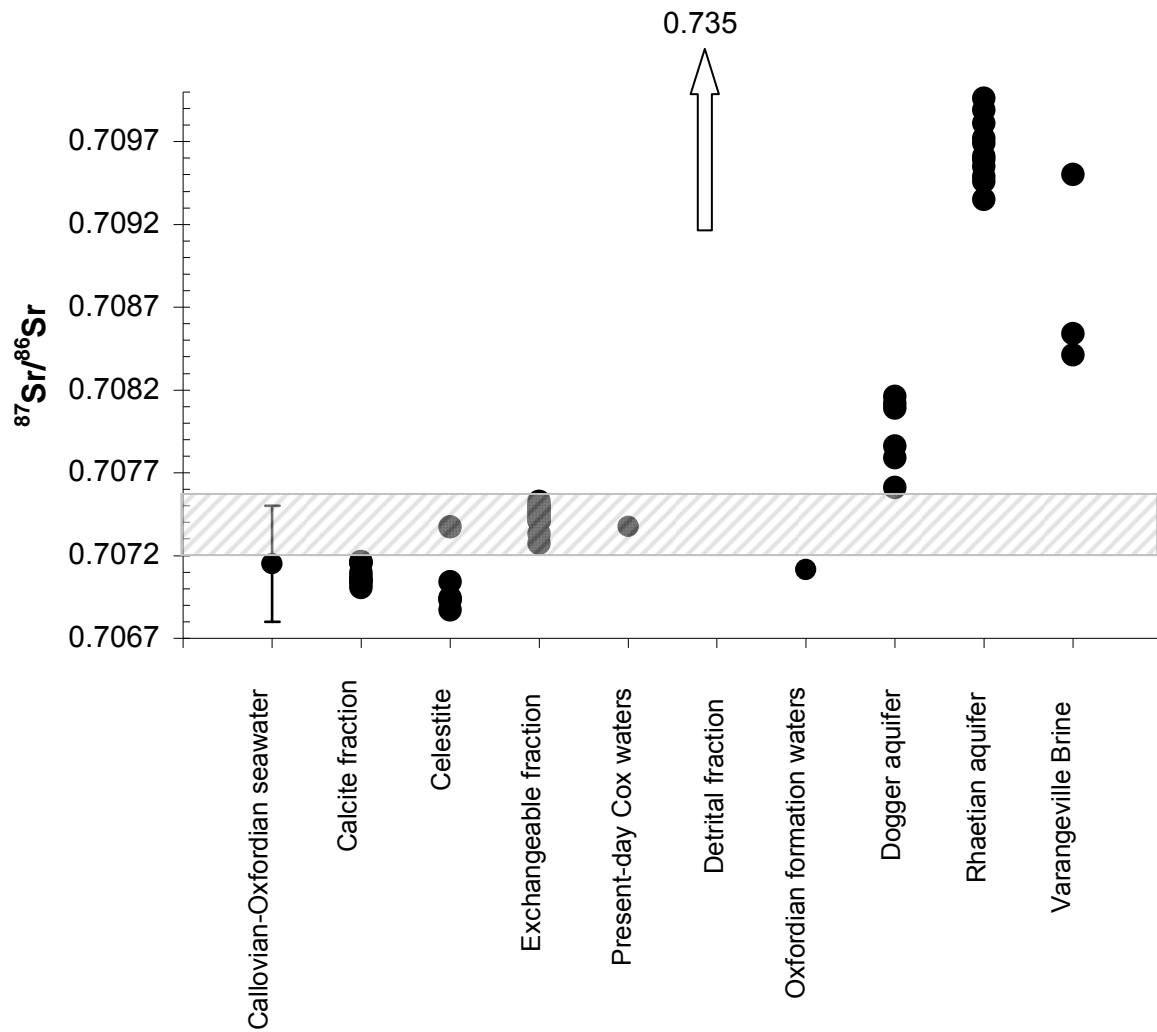


Fig. 8. Strontium isotopic signatures of the different fractions in claystones, compared with the local reservoirs: Callovian-Oxfordian seawater (JONES et al., 1994), natural and forced percolating COx waters (VINSOT et al., 2008), Oxfordian formation waters (BUSCHAERT et al., 2007a), the Dogger, Rhaetian and Keuper aquifers (FONTES and MATRAY, 1993a; FONTES and MATRAY, 1993b);(BUSCHAERT et al., 2007b) and the Varangeville brines (FONTES and MATRAY, 1993b). The shaded region represents the range of strontium isotope values of the exchangeable strontium.

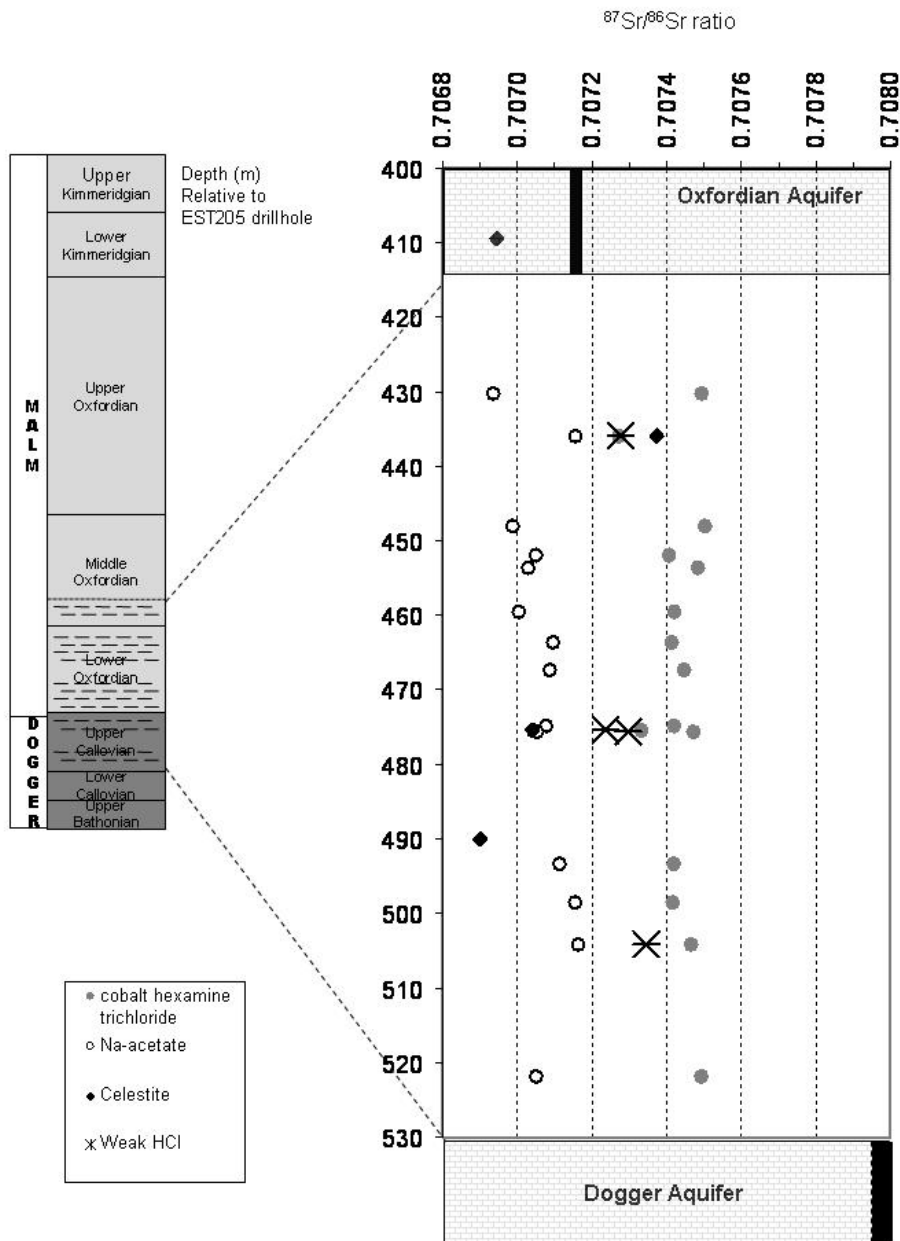


Fig. 9. Strontium isotopic ratios of exchangeable strontium (cobalt hexamine trichloride) at equilibrium with present day porewaters, strontium in carbonates (Na-acetate) and separated celestite in the Callovian-Oxfordian clayey formation, reported as a function of the depth of the sample. Strontium isotopic ratios of the labile fraction after weak HCl leaching are reported for comparison. The black lines in the surrounding limestones (Dogger and Oxfordian aquifers) indicate the average strontium isotope ratio of the present-day groundwaters. The depth is relative to the surface and is given relative to the EST205 borehole. The equivalent  $Z_{\text{NGF}}$  (depth relative to the present-day sea level) can be calculated by 368 minus the depth for the EST205 borehole.

Sample	Borehole	Zngf	Lithology	Clay fraction	Siltite fraction	Carbonate fraction	
						Cc	Dol
EST05433	EST205	-43.5	C3a			91.0	9.0
E 21400	PAC2002	-64.2	C2d	9.2	9.1	79.3	1.7
EST05485	EST205	-69.9	C2d	15.0	36.5	45.5	6.5
K108	EST205	-82.0	C2c	25.3	32.4	24.4	4.6
EST05554	EST205	-85.9	C2c	50.5	25.5	20.0	4.0
EST05545	EST205	-87.6	C2c	40.5	25.5	28.5	8.5
EST21439	PAC2001	-93.5	C2b2	39.2	14.5	40.2	2.6
EST5583	EST205	-97.6	C2b2	52.0	37.5	12.0	3.0
EST12190	EST212	-101.3	C2b2	47	25	32.5	2.0
EST05632	EST205	-108.8	C2b1	49.5	30.0	17.5	2.0
EST20714	PPA1191	-109.4	C2b1	29.0	28.8	35.9	3.4
EST25687	PAC1002	-109.6	C2b1	39.9	27.7	22.2	5.5
EST28099	EST423	-266.0	C2b1				
EST05724	EST205	-132.5	C2b1	50.0	19.5	21.0	2.5
EST25380	PAC1001	-138.1	C2b1	47.8	19.4	21.9	6.8
EST28210	EST423	-294.5	C2a				
EST12530	EST212	-166.1	C2a	50.5	29	25.0	1.5

Table 1. Depth, lithology, main mineralogy and strontium content of the samples selected for this study. The data are extracted from (GAUCHER et al., 2004b) and from the database of geochemical data of the Callovian-Oxfordian clays from Bure developed in the FUNMIG project (LEROUGE et al., 2006).

Sample	Extracted Sr (ppm)					Total Sr (ppm)
	CEC	Na-Acetate	EDTA	Tri-acid attack	HF + HCl + HNO <sub>3</sub>	
EST21400	10	130	20		190	350
EST05485	210	290	90		210	800
K108	30	170	20		150	370
EST05554	140	140	nd		nd	280*
EST05545	110	100	nd		nd	210*
EST21439	90	130	nd		nd	220*
EST05583	180	110	nd		nd	290*
EST12190	160	110	0		70	340
EST05632	150	160	nd		nd	310*
EST20714	170	150	70		50	440
EST25687	160	120	10		50	330
EST28099	100	100	20		60	280
EST05724	180	110	nd		nd	290*
EST25380	110	100	10		50	270
EST28210	100	130	10		80	320
EST12530	100	130	0		90	320

Table 2. Strontium concentrations in leachates extracted at each step of the sequential extraction procedure applied to the samples of the Callovian-Oxfordian clayey formation.

n.d. = not determined, \* indicates that the total Sr content is calculated by adding strontium extracted at the first two steps of the sequential extraction procedure.

Sample	Unit	$^{87}\text{Sr}/^{86}\text{Sr}$ celestite
EST05433	C3a	0.706945
EST05485	C2d	0.707373
EST20714	C2b1	0.707040
Bure1		0.706935
Bure2	gallery -490m	0.706932
Bure3		0.706872

Table 3. Strontium isotopic ratios of celestite separates.



Sample	$^{87}\text{Sr}/^{86}\text{Sr}$ Cobalt hexamine trichloride	$^{87}\text{Sr}/^{86}\text{Sr}$ Na- acetate	$^{87}\text{Sr}/^{86}\text{Sr}$ EDTA	$^{87}\text{Sr}/^{86}\text{Sr}$ tri-acid attack
EST21400	0.707494	0.706936		0.708290
EST05485	0.707272	0.707156	0.707150	0.708927
K108	0.707503	0.706988		0.712499
EST05554	0.707406	0.707050		
EST05545	0.707484	0.707029		
EST21439	0.707421	0.707004		
EST05583	0.707413	0.707096		
EST12190	0.707447	0.707087		0.731470
EST05632	0.707420	0.707077		
EST20714	0.707332	0.707043	0.707185	0.729947
EST25687	0.707472	0.707053	0.707200	0.734169
EST28099	0.707419	0.707113		0.735005
EST05724	0.707417	0.707155		
EST25380	0.707465	0.707163	0.707352	0.733841
EST28210	0.707493	0.707050		0.731915
EST12530	0.707526	0.707088		0.724621

Table 4 .  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios measured in the successive leachates of the sequential extraction procedure applied to the clayey samples.

Sample	Cobalt hexamine trichloride		Na-acetate		EDTA		Tri-acid attack	
	Rb content (µg/L)	$^{87}\text{Sr}/^{86}\text{Sr}$ (160 Ma)	Rb content (µg/L)	$^{87}\text{Sr}/^{86}\text{Sr}$ (160 Ma)	Rb content (µg/L)	$^{87}\text{Sr}/^{86}\text{Sr}$ (160 Ma)	Rb content (µg/L)	$^{87}\text{Sr}/^{86}\text{Sr}$ (160 Ma)
E 21400	16	0.707351	6	0.706930			22	0.707526
EST05485	20	0.707260	24	0.707148	10	0.707135	28	0.708034
K108	27	0.707396	11	0.706979			55	0.710120
EST12190	59	0.707397	21	0.707063			107	0.720694
EST20714	91	0.707277	60	0.707002	32	0.706891	72	0.720005
EST25687	81	0.707406	57	0.707009	42	0.706706	82	0.722563
EST28099	41	0.707366	15	0.707094			131	0.721550
EST25380	54	0.707400	46	0.707121	48	0.706833	74	0.724675
EST28210	39	0.707440	18	0.707032			145	0.720020
EST12530	44	0.707473	17	0.707072			105	0.716583

Table 5.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios calculated at 160 Ma, taking into account the extracted Rb measured in the leachate.

Sample	Dissolved fraction (%)	Rb (ppm)	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ (160 Ma)
EST05485	9.6	0.19	207.02	0.707276	0.707270
EST20714	22.5	1.04	345.56	0.707236	0.707216
EST25687	18.8	1.15	308.84	0.707297	0.707273
EST25380	13.7	0.49	186.94	0.707345	0.707328

Table 6. Results of the leaching with 0.2N HCl for 30 minutes applied to four samples that had undergone the entire sequential extraction procedure.

Sample	Reagent/ solid ratio	Time of reaction	Exchangeable cations / 100 g dry sample					CEC cation sum	CEC colorimetry
			Na <sup>+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>		
			meq/100 g dry sample						
1 - EST 05485	20	30 mn	0.9	1.6	0.4	5.8	0.5	9.3	4.0
2 - EST 05485	40	30 mn	1.0	1.6	0.5	7.2	0.5	10.9	4.9
1 - EST 25687	20	15 mn	3.5	5.1	1.4	9.9	0.4	20.3	17.6
2 - EST 25687	20	30 mn	3.5	5.1	1.5	9.8	0.3	20.3	19.3
3 - EST 25687	20	4 hours	3.5	5.2	1.6	9.6	0.4	20.2	20.2
4 - EST 25687	20	24 hours	3.5	5.1	1.6	8.9	0.4	19.5	22.6

Electronic annex 1. Concentrations of exchangeable cations, sum of cations and CEC measured by colorimetry in a clay-rich limestone (EST05485) and a calcite-poor claystone (EST25687).

Pure phases	Exchangeable cations					CEC <sub>Σ</sub>	CEC colorimetry
	Na <sup>+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>		
	meq/ 100 g dry sample						
Calcite	-	0.05	-	1.81	-	1.9	-
Dolomite	-	1.75	-	4.2	-	6	1.25
Celestite	-	-	0.21	1.34	9.58	11.1	0.4

Electronic annex 2. Measured cations in leachates from the cobalt hexamine trichloride extraction applied to calcite, dolomite and celestite. The “-” indicates a measured value below the detection limit.

	[Ca]		[Mg]	
	Step 1 - CEC	Step 2 - acetate	Step 1 - CEC	Step 2 - acetate
Leachate (mg/g of solid)	0.84	34.07	0.22	17.49
% of extracted dolomite	0.4	16	0.2	13

Electronic annex 3. Partial sequential extraction procedure applied to pure dolomite.

Concentrations of calcium and magnesium in the leachates 1 and 2 allowing the estimation of the percentage of dolomite dissolution at the first two steps of the sequential extraction applied to dolomite.

	Step 1 - CEC	Step 2 - acetate	Step 3 - EDTA
Leachate ([Sr] mg/g of solid)	4.20	5.48	14.49
% of extracted celestite	0.88	1.15	3.04

Electronic annex 4 . Partial sequential extraction procedure applied to pure celestite.

Concentration of strontium in the leachates 1, 2 and 3, allowing the estimation of the percentage of celestite dissolution at the first three steps of the sequential extraction.

Sample	[Ca] mg/g leachate 2	Corresponding extracted Cc %	Extraction yield
EST21400	177.9	44	81
EST05485	126.1	32	69
K108	151.6	38	nd

EST05554	75.0	19	94
EST05545	97.2	24	85
EST21439	117.3	29	73
EST05583	41.4	10	86
EST12190	53.0	13	nd
EST05632	59.2	15	85
EST20714	92.4	23	64
EST25687	81.3	20	90
EST28099	66.7	17	nd
EST05724	67.9	17	81
EST25380	71.1	18	88
EST28210	82.2	21	nd
EST12530	91.8	23	88

Electronic annex 5. Calcium concentration in leachate 2, corresponding percentage of extracted calcite and extraction yield of calcite taking into account the calcite content of the sample (given in table 1).

## References

- ANDRA, 2005. Evaluation de la faisabilité du stockage géologique en formation argileuse, Dossier 2005 *Collection Les Rapports*.
- Armstrong-Altrin, J. S., Lee, Y. I., Verma, S. P., and Worden, R. H., 2009. Carbon, oxygen, and strontium isotope geochemistry of carbonate rocks of the upper Miocene Kudankulam Formation, southern India: Implications for paleoenvironment and diagenesis. *Chemie der Erde - Geochemistry* **69**, 45-60.
- Baker, P. A., Gieskes, J. M., and Elderfield, H., 1981. Diagenesis of carbonates in deep sea sediments-evidence from ratios and interstitial dissolved Sr<sup>++</sup> data. *J. Sed. Petrol.* **52** 71-82.
- Banner, J. L., 2004. Radiogenic isotopes: systematics and applications to earth surface processes and chemical stratigraphy. *Earth-Science Reviews* **65**, 141-194.
- Bathurst, R. G. C., 1975. Carbonate sediments and their diagenesis. *Elsevier, New York*, 658 p.
- Blanc, P., Legendre, O., and Gaucher, E. C., 2007. Estimate of clay minerals amounts from XRD pattern modeling: The Arquant model. *Physics and Chemistry of the Earth, Parts A/B/C* **32**, 135-144.
- Brand, U., 1991. Strontium isotope diagenesis of biogenic aragonite and low-Mg calcite. *Geochimica et Cosmochimica Acta* **55**, 505-513.
- Brigaud, B., Durllet, C., Deconinck, J.-F., Vincent, B., Thierry, J., and Trouiller, A., The origin and timing of multiphase cementation in carbonates: Impact of regional scale geodynamic events on the Middle Jurassic Limestones diagenesis (Paris Basin, France). *Sedimentary Geology* **222**, 161-180..
- Buschaert, S., Giannesini, S., Lavastre, V., Benedetti, F., Gaucher, E. C., Lacroix, M., Lavielle, B., Michelot, J.-L., France-Lanord, C., Bourles, D., Lancelot, J., Benabderrahmane, H., Dewonck, S., and Vinsot, A., 2007a. The contribution of water geochemistry to the understanding of the regional hydrogeological system. *Mémoire de la Société Géologique de France* **178**, 91-114.
- Buschaert, S., Giannesini, S., Lavastre, V., Benedetti, L., Gaucher, E. C., Lacroix, M., Lavielle, B., Michelot, J. L., France-Lanord, C., Bourlès, D. L., Lancelot, J., Benabderrahmane, H., Dewonck, S., and Vinsot, A., 2007b. The Contribution of Water Geochemistry to the Understanding of the Regional Hydrogeological System. *Mémoire de la Société Géologique de France, nouvelle série*. **178**, 91-114.
- Casanova, J., Négrel, P., Aranyosy, J. F., and Bruhlet, J., 1999. Callovo–Oxfordian argillites (Meuse, France): Isotope Geochemistry (O, C, Sr) *3rd International Symposium on Applied Isotope Geochemistry. Orléans, France. September 21–25, Orléans, France*.
- Chaudhuri, S., Broedel, V., and Clauer, N., 1987. Strontium isotopic evolution of oil-field waters from carbonate reservoir rocks in Bindley field, central Kansas, U.S.A. *Geochimica et Cosmochimica Acta* **51**, 45-53.
- Ciesielski, H. and Sterckeman, T., 1997. Determination of cation exchange capacity and exchangeable cations in soils by means of cobalt hexamine trichloride. Effects of experimental conditions. *Agronomie* **17**, 1-7.

- Claret, F., Sakharov, B. A., Drits, V. A., Velde, B., Meunier, A., Griffault, L., and Lanson, B., 2004. Clay minerals in the Meuse-Haute marne underground laboratory (France): Possible influence of organic matter on clay mineral evolution. *Clays and Clay Minerals* **52**, 515-532.
- Clauer, N., Fourcade, S., Cathelineau, M., Girard, J. P., Vincent, B., Elie, M., Buschaert, S., and Rousset, D., 2007. A review of studies on the diagenetic evolution of the Dogger-to-Tithonian sedimentary sequence in the Eastern Paris Basin : Impact on physical-chemical rock properties. *Mémoire de la Société Géologique de France, nouvelle série* **178**, 59-71.
- Elderfield, H., Gieskes, J. M., Baker, P. A., Oldfield, R. K., Hawkesworth, C. J., and Miller, R., 1982. and ratios, interstitial water chemistry and diagenesis in deep-sea carbonate sediments of the Ontong Java Plateau. *Geochimica et Cosmochimica Acta* **46**, 2259-2268.
- Fontes, J. C. and Matray, J. M., 1993a. Geochemistry and origin of formation brines from the Paris Basin, France : 1. Brines associated with Triassic salts. *Chemical Geology* **109**, 149-175.
- Fontes, J. C. and Matray, J. M., 1993b. Geochemistry and origin of formation brines from the Paris Basin, France : 2. Saline solutions associated with oil fields. *Chemical Geology* **109**, 177-200.
- Gaucher, E., Blanc, P., Matray, J. M., and Michau, N., 2004a. Modelling diffusion of an alkaline plume in a clay barrier. *Applied Geochemistry* **19**, 1505-1515.
- Gaucher, E., Robelin, C., Matray, J. M., Negrel, G., Gros, Y., Heitz, J. F., Vinsot, A., Rebours, H., Cassabagnere, A., and Bouchet, A., 2004b. ANDRA underground research laboratory: Interpretation of the mineralogical and geochemical data acquired in the Callovian-Oxfordian Formation by investigative drilling. *Physics and chemistry of the earth* **29**, 55-77.
- Gaucher, E. C., Blanc, P., Bardot, F., Braibant, G., Buschaert, S., Crouzet, C., Gautier, A., Girard, J. P., Jacquot, E., Lassin, A., Negrel, G., Tournassat, C., Vinsot, A., and Altmann, S., 2006. Modelling the porewater chemistry of the Callovian-Oxfordian formation at a regional scale. *Comptes Rendus Geoscience* **338**, 917-930.
- Gaucher, E. C., Lerouge, C., Blanc, P., and Tournassat, C., 2007. Caractérisation géochimique des forages PAC et nouvelles modélisations THERMOAR. BRGM, RP-54416-FR.
- Gaucher, E. C., Tournassat, C., Pearson, F. J., Blanc, P., Crouzet, C., Lerouge, C., and Altmann, S., 2009. A robust model for pore-water chemistry of clayrock. *Geochimica et Cosmochimica Acta* **73**, 6470-6487.
- Giannesini, S., 2006. Géochimie isotopique couplée des eaux des formations argileuses et calcaires du site ANDRA de Meuse/Haute Marne. PhD Thesis. in French., Univ. Paul Cézanne Aix-Marseille III.
- Hodell, D. A., Mead, G. A., and Mueller, P. A., 1990. Variation in the strontium isotopic composition of seawater (8 Ma to present) : Implications for chemical weathering rates and dissolved fluxes to the oceans. *Chemical Geology: Isotope Geoscience section* **80**, 291-307.
- Jones, C. E. and Jenkyns, H. C., 2001. Seawater strontium isotopes, oceanic anoxic events, and seafloor hydrothermal activity in the Jurassic and Cretaceous. *American Journal of Science* **301**, 112-149.
- Jones, C. E., Jenkyns, H. C., and Hesselbo, S. P., 1994. Strontium Isotopes in Early Jurassic Seawater. *Geochimica Et Cosmochimica Acta* **58**, 1285-1301.
- Koepnick, R. B., Denison, R. E., Burke, W. H., Hetherington, E. A., and Dahl, D. A., 1990. Construction of the Triassic and Jurassic Portion of the Phanerozoic Curve of Seawater Sr-87/Sr-86. *Chemical Geology* **80**, 327-349.



- Lamiroux, C. and Mascle, A., 1998. Petroleum exploration and production in France. *Oil & Gas Science and Technology - Rev. IFP* **16**, 109-117.
- Lerouge, C., Michel, P., Gaucher, E. C., and Tournassat, C., 2006. A geological, mineralogical and geochemical GIS for the Andra URL: A tool for the water-rock interactions modelling at a regional scale. *FUNMIG - 2nd annual workshop - Stockholm - Sweden - 21-23/11/2006*.
- Mester, Z., Cremisini, C., Ghiara, E., and Morabito, R., 1998. Comparison of two sequential extraction procedures for metal fractionation in sediment samples. *Analytica Chimica Acta* **359**, 133-142.
- Morse, J. W. and Mackenzie, F. T., 1990. *Geochemistry of Sedimentary Carbonates*. Elsevier, Amsterdam.
- Négre, P., Casanova, J., and Brulhet, J., 2006. Re and Nd isotope stratigraphy of a Late Jurassic carbonate platform, eastern Paris Basin, France. *Journal of Sedimentary Research* **76**, 605-617.
- Négre, P., Casanova, J., and Njitchoua, R., 2001a. Tracage des apports terrigènes dans les mers épicontinentales par les systématiques isotopiques Sr et Nd : application au site de Bure (Meuse, France). 257-258. .
- Négre, P., Casanova, J., and Njitchoua, R., 2001b. Tracage des apports terrigènes dans les mers épicontinentales par les systématiques isotopiques Sr et Nd : application au site de Bure (Meuse, France). . , 257-258.
- Négre, P., Grosbois, C., and Kloppmann, W., 2000. The labile fraction of suspended matter in the Loire River (France): multi-element chemistry and isotopic (Rb-Sr and C-O) systematics. *Chemical Geology* **166**, 271-285.
- Neilson, J. E., Oxtoby, N. H., Simmons, M. D., Simpson, I. R., and Fortunatova, N. K., 1998. The relationship between petroleum emplacement and carbonate reservoir quality: examples from Abu Dhabi and the Amu Darya Basin. *Marine and Petroleum Geology* **15**, 57-72.
- Odin, G. S., 1994. Geological Time-Scale (1994). *Comptes Rendus De L Academie Des Sciences Serie Ii* **318**, 59-71.
- Pace, M. N., Mayes, M. A., Jardine, P. M., McKay, L. D., Yin, X. L., Mehlhorn, T. L., Liu, Q., and Gurleyuk, H., 2007. Transport of Sr<sup>2+</sup> and SrEDTA(2-) in partially-saturated and heterogeneous sediments. *Journal of Contaminant Hydrology* **91**, 267-287.
- Pellenard, P. and Deconinck, J. F., 2006. Mineralogical variability of Callovo-Oxfordian clays from the Paris Basin and the Subalpine Basin. *Comptes Rendus Geoscience* **338**, 854-866.
- Pin, C. and Bassin, C., 1992. Evaluation of a strontium specific extraction chromatographic method for isotopic analysis in geological materials. *Analytica Chimica Acta* **269**, 249-255.
- Rao, C. R. M., Sahuquillo, A., and Sanchez, J. F. L., 2008. A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. *Water Air and Soil Pollution* **189**, 291-333.
- Rémy, J. C. and Orsini, L., 1976. Utilisation du chlorure de cobaltihexamine pour la détermination simultanée de la capacité d'échange et des bases échangeables dans les sols. *Sciences du Sol* **4**, 269-275..
- Rigol, A., Roig, M., Vidal, M., and Rauret, G., 1999. Sequential Extractions for the Study of Radiocesium and Radiostrontium Dynamics in Mineral and Organic Soils from Western Europe and Chernobyl Areas. *Environmental Science & Technology* **33**, 887-895.

- Rousset, D. and Clauer, N., 2003. Discrete clay diagenesis in a very low-permeable sequence constrained by an isotopic (K-Ar and Rb-Sr) study. *Contributions to Mineralogy and Petrology* **145**, 182-198.
- Rushdi, A. I., McManus, J., and Collier, R. W., 2000. Marine barite and celestite saturation in seawater. *Marine Chemistry* **69**, 19-31.
- Tessier, A., Campbell, P. G. C., and Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* **51**, 844-851.
- Tournassat, C., Gailhanou, H., Crouzet, C., Braibant, G., Gautier, A., and Gaucher, E. C., 2009. Cation Exchange Selectivity Coefficient Values on Smectite and Mixed-Layer Illite/Smectite Minerals. *Soil Science Society of America Journal* **73**, 928-942.
- Tournassat, C., Lerouge, C., Blanc, P., Brendle, J., Greneche, J.-M., Touzelet, S., and Gaucher, E. C., 2008. Cation exchanged Fe(II) and Sr compared to other divalent cations (Ca, Mg) in the bure Callovian-Oxfordian formation: Implications for porewater composition modelling. *Applied Geochemistry* **23**, 641-654.
- Van Loon, L. R., Baeyens, B., and Bradbury, M. H., 2005. Diffusion and retention of sodium and strontium in Opalinus clay: Comparison of sorption data from diffusion and batch sorption measurements, and geochemical calculations. *Applied Geochemistry* **20**, 2351-2363.
- Veizer, J., Hoefs, J., Lowe, D. R., and Thurston, P. C., 1989. Geochemistry of Precambrian carbonates: II. Archean greenstone belts and Archean sea water. *Geochimica et Cosmochimica Acta* **53**, 859-871.
- Vidal, M. and Rauret, G., 1995. Use of sequential extractions to study radionuclide behavior in mineral and organic soils. *Quimica Analitica* **14**, 102-107.
- Vinsot, A., Mettler, S., and Wechner, S., 2008. In situ characterization of the Callovo-Oxfordian pore water composition. *Physics and Chemistry of the Earth, Parts A/B/C* **33**, S75-S86.
- Wersin, P., Soler, J. M., Van Loon, L., Eikenberg, J., Baeyens, B., Grolimund, D., Gimmi, T., and Dewonck, S., 2008. Diffusion of HTO, Br<sup>-</sup>, I<sup>-</sup>, Cs<sup>+</sup>, 85Sr<sup>2+</sup> and 60Co<sup>2+</sup> in a clay formation: Results and modelling from an in situ experiment in Opalinus Clay. *Applied Geochemistry* **23**, 678-691.

## Figure captions

- Fig. 1. Geological setting of the ANDRA Underground research Laboratory (URL). a. Geological map of the Paris Basin, location of the Bure URL, b. Geological and structural map of the eastern part of the Paris Basin, c. Lithostratigraphic column with the mineralogical detail of the Callovian-Oxfordian clayey formation and its strontium content. .... 21
- Fig. 2. Previous strontium isotopic data on the Callovian-Oxfordian clayey formation and surrounding limestones (overlying Oxfordian carbonate platform and overlaid Dogger carbonate platform). The line indicates the strontium isotope profile of the labile carbonate fraction obtained on bulk rock by weak HCl leaching. The points are strontium isotopic ratios obtained on separates of late diagenetic carbonates in vugs (Casanova et al. 2001). The shaded area shows the range of strontium isotope values of the Callovian-Oxfordian seawater, according to Jones et al. (1994).22
- Fig. 3. Sequential extraction protocol. Main phases or fractions extracted at each step and main corresponding strontium carriers. .... 23
- Fig. 4. Diagram showing the relationship between the strontium isotope ratio of cobalt hexamine trichloride leachate and the clay content of the samples..... 24
- Fig. 5. Diagram showing the relationship between the Sr content of the Na-acetate leachate and the calcite content of the samples. .... 24
- Fig. 6. Distribution of strontium among the main fractions in all the samples (x-axis). .... 25
- Fig. 7. Strontium isotope ratio and content of the cobalt hexamine trichloride leachate reported in a diagram of  $^{87}\text{Sr}/^{86}\text{Sr}$  as a function of  $1/\text{Sr}$ , providing evidence of mixing between exchangeable strontium and strontium due to celestite dissolution..... 26
- Fig. 8. Strontium isotopic signatures of the different fractions in claystones, compared with the local reservoirs: Callovian-Oxfordian seawater (JONES et al., 1994), natural and forced percolating COx waters (VINSOT et al., 2008), Oxfordian formation waters (BUSCHAERT et al., 2007a), the Dogger, Rhaetian and Keuper aquifers (FONTES and MATRAY, 1993a; FONTES and MATRAY, 1993b);(BUSCHAERT et al., 2007b) and the Varangeville brines (FONTES and MATRAY, 1993b). The shaded region represents the range of strontium isotope values of the exchangeable strontium.27
- Fig. 9. Strontium isotopic ratios of exchangeable strontium (cobalt hexamine trichloride) at equilibrium with present day porewaters, strontium in carbonates (Na-acetate) and separated celestite in the Callovian-Oxfordian clayey formation, reported as a function of the depth of the sample. Strontium isotopic ratios of the labile fraction after weak HCl leaching are reported for comparison. The black lines in the surrounding limestones (Dogger and Oxfordian aquifers) indicate the average strontium isotope ratio of the present-day groundwaters. The depth is relative to the surface and is given relative to the EST205 borehole. The equivalent  $Z_{\text{NGF}}$  (depth relative to the present-day sea level) can be calculated by 368 minus the depth for the EST205 borehole. .... 28



## Table captions

Table 1: Depth, lithology, main mineralogy and strontium content of the samples selected for this study. The data are extracted from (GAUCHER et al., 2004b) and from the database of geochemical data of the Callovian-Oxfordian clays from Bure developed in the FUNMIG project (LEROUGE et al., 2006).....	29
Table 2: Strontium concentrations in leachates extracted at each step of the sequential extraction procedure applied to the samples of the Callovian-Oxfordian clayey formation. ....	30
Table 3: Strontium isotopic ratios of celestite separates.....	31
Table 4 : $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured in the successive leachates of the sequential extraction procedure applied to the clayey samples. ....	32
Table 5: $^{87}\text{Sr}/^{86}\text{Sr}$ ratios calculated at 160 My, taking into account the extracted Rb measured in the leachate. ....	33
Table 6: Results of the leaching with 0.2N HCl for 30 minutes applied to four samples that had undergone the entire sequential extraction procedure. ....	34

## Annex cations

Annex 1 : Concentrations of exchangeable cations, sum of cations and CEC measured by colorimetry in a clay-rich limestone (EST05485) and a calcite-poor claystone (EST25687). ....	35
Annex 2 : Measured cations in leachates from the cobalt hexamine trichloride extraction applied to calcite, dolomite and celestite. The “-” indicates a measured value below the detection limit. ...	35
Annex 3 : Partial sequential extraction procedure applied to pure dolomite. ....	36
Annex 4 : Partial sequential extraction procedure applied to pure celestite.....	36
Annex 5 : Calcium concentration in leachate 2, corresponding percentage of extracted calcite and extraction yield of calcite taking into account the calcite content of the sample (given in table 1).37	