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**Investigation of Europium Retention on Callovo-Oxfordian Clay Rock (France) by
Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and
percolation experiments in microcells.**

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Abstract

Clay-rock formations are under investigation in several countries as a potential host of radioactive waste repositories. In order to assess the long-term safety of these concepts, retention distribution data (Rd) are needed to describe the interaction between radionuclides and natural rock. While Rd values obtained from batch-type experiments with dispersed material are essential for the development of retention models, it is also important to generate retention data under more realistic conditions, in particular with compact samples. Specifically, the literature data on strongly retained radionuclides proves to be very scarce. The present study

focuses on the retention of europium at trace concentrations on clay samples extracted from the Callovo-Oxfordian (COx) formation in France. R_d values obtained with compact COx samples are assessed by a methodology coupling percolation experiments (in pressurized microcells), performed using submillimeter-sized samples in thickness, and Laser Ablation Inductively Coupled Plasma Mass Spectrometry measurements. The R_d found at trace concentrations under non-transient conditions are high ($R_d > 10^4 \text{ mL g}^{-1}$) and in agreement with those recorded under classical batch-type conditions or those deduced from the distribution of naturally-occurring Eu between the pore water and the clay rock. They can be described by modeling with existing sorption databases, considering an adsorption process only on the clay fraction. This was validated by solid state LA-ICP-MS analyses of one of the Eu-spiked COx samples; the added europium was found exclusively in the COx clay fraction.

Keywords: Retention, Clay rock, Europium, (LA)-ICP-MS, Percolation.

I. Introduction

The development of nuclear energy requires safe solutions for managing radioactive waste. The worldwide consensus on the best way to protect human life and the environment is to dispose of this radioactive waste in deep geological repositories. In France, the Callovo-Oxfordian claystone formation (COx) is under investigation as a geological barrier to lower the fluxes from the waste towards the geosphere, the hydrosphere and biosphere (ANDRA, 2005a; Sellin and Leupin, 2013). This clay-rich formation, located in the Meuse/Haute-Marne site (Eastern France), is characterized by low permeability, mineralogical homogeneity, high retention capacities for radionuclides and little variation in other physicochemical properties (ANDRA, 2005b; Grambow, 2016).

To assess the long-term safety of this repository site, it is important to understand, characterize and quantify the retention and transport properties of radionuclides in the host clay rock. Retention processes, such as adsorption on mineral surfaces, precipitation as poorly soluble pure solid phases, co-precipitation in the formation of minerals (neo-formation of a solid solution) or incorporation into solid phases, can delay the radionuclides migration (Maes et al., 2008) for a sufficient time to allow for radioactive decay.

"Safety analyses" generally consider adsorption processes (typically described by a list of retention distribution data, or R_d values) leading to retardation of mass transfer. Scientifically, for clayey rocks, these R_d values can be understood by cation exchange and surface complexation reaction describing the concentration of labile species in rapid equilibrium with a surface and a solution as a function of a number of environmental variables such as pH, pCO_2 , ionic strength, etc. The formation of these labile species can be described by thermodynamic approaches. The modeling of radionuclide adsorption processes in the clay formation requires numerous input parameters, many of which have been determined under laboratory conditions with pure clay minerals. Experiments are carried out in batch-type mode in a state where the solid is dispersed in large quantities of synthetic pore water for reasons of either duration or ease of experimental implementation. The experiments are quite simple, relatively fast (a few days) and able to be performed under a variety of well-controlled conditions; also, the data can be used for assessing the dependency of retention parameters on the local mineralogy of the host rock and its variation, on temperature, or on parameters describing the pore water chemistry such as pH, pCO_2 , redox, other chemical species as aqueous silica or salinity variations. However, it is essential to ensure that the adsorption parameters obtained on dispersed materials are capable of describing adsorption processes on the actual compact rock/pore water systems.

A relatively recent review (Miller and Wang, 2012) on the subject highlights various aspects that can lead to differences depending on the state of compactness of the sample (surface-water reactivity, accessibility of sorption sites, electrostatic considerations, double-layer overlapping, etc.). For the case of Cs, Van Loon and Glaus (2008) critically examined the application of thermodynamic models on highly compacted states whose ion hydration energies may differ from those in the dispersed state. This important subject must therefore be treated for each class of key radionuclides, which entails developing methods capable of determining retention parameters for compact states.

In the ideal case, it would be possible to carry out batch-type retention experiments in a compact system, i.e. waiting until a non-transient state is reached when the radionuclide concentration in aqueous solution (in contact with the water-saturated porous system) and the radionuclide concentration in pore water are equal. Under these conditions, the concentrations of radionuclides both in pore water and retained on the solid surface can be measured, which serves to calculate the distribution coefficient describing the retention (R_d) value. However, achieving a non-transient state can take a long time due to the low permeability of the studied compact clay materials. This approach appears to be feasible for highly compact states with poorly or moderately retained radionuclides. A few number of studies can be found in the literature for: I^- (Montavon et al., 2014), Cs^+ (André et al., 2009; Chen et al., 2014b; Oscarson, 1994; Van Loon et al., 2009), Ni^{2+} (Montavon et al., 2020), and Sr^{2+} (Van Loon et al., 2005). Overall, no clear evidence suggests that increasing clay compaction will lead to a fundamentally different uptake of radionuclides.

For strongly sorbed ions/radionuclides, like trivalent metal ions, retention data are often deduced from in-diffusion experiments, where information is derived from a transient state (Descostes et al., 2017; Glaus et al., 2020; Kasar et al., 2016; Wang et al., 2004). The information on metal retention is reliable provided species mobility has been adequately

described since compaction potentially affects both diffusive mass transfer and retention. Therefore, it is fundamental to develop for strongly sorbed elements, in parallel with transport/diffusion experiments, a set of methodologies yielding retention data in a non-transient state (i.e. concentrations of radionuclides both in pore water and retained on the solid surface can be measured), in order to assess the compaction effect on retention processes.

The objective of this work is to propose a non-transient method adapted to the retention study of strongly sorbed elements on compact clay rock samples. It combines the use of pressurized PEEK (Polyetheretherketone) micro cells, thereby limiting adsorption phenomena (Aertsens et al., 2003) and accommodating submillimeter-thick samples, with a percolation mode to accelerate transport so as to overcome the disadvantages of a long experimental duration by using diffusion cells (Montavon et al., 2020 ; Chen et al., 2014b). After the experiment, the strongly sorbed element is analyzed quantitatively on the (inlet) surface and in depth of the compact sample by means of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). This technique turns out to be essential in the present context (due to its high sensitivity and spatial resolution) to determining metal ion concentration in metal-spiked compact samples as well as to assessing its distribution among the various mineral phases present in the clay rock.

The methodology adopted in this study is applied to the Eu/COx system. Indeed, Eu is considered to be a chemical homologue of certain trivalent actinides, such as Am or Cm, present in radioactive waste (Kautenburger and Beck, 2010). Europium retention values published in the literature are high and range from 5×10^4 to 10^5 L kg⁻¹ for trace concentrations, thus reflecting a strong interaction with COx clay rock (ANDRA, 2005a; Descostes et al., 2017; Schott et al., 2012). Retention data obtained in the compact state are compared herein with data measured in the dispersed state and then discussed in light of both modeling results and a study of naturally-occurring Eu in COx clay rock.

II. Materials and methods

A summary of the experiments carried out in the present study is given in Table 1.

Two types of experiments were performed as part of this study, namely: batch-type sorption experiments on crushed COx samples in a dispersed state, and percolation experiments with compact clay rock. All experiments were conducted at $T = 22 \pm 2^\circ\text{C}$ in the presence of a synthetic pore water (SPW) whose simplified composition was based on geochemical modeling exercises on *in situ* samples (Vinsot et al., 2008; Gaucher et al., 2009): $[\text{Na}^+] = 4.6 \times 10^{-2} \text{ M}$, $[\text{K}^+] = 10^{-3} \text{ M}$, $[\text{Ca}^{2+}] = 7.4 \times 10^{-3} \text{ M}$, $[\text{Mg}^{2+}] = 6.7 \times 10^{-3} \text{ M}$, $[\text{Sr}^{2+}] = 2 \times 10^{-4} \text{ M}$, $[\text{Cl}^-] = 4.1 \times 10^{-2} \text{ M}$, $[\text{SO}_4^{2-}] = 1.6 \times 10^{-2} \text{ M}$, inorganic carbon = $4.5 \times 10^{-3} \text{ M}$ (in equilibrium with calcite), and $\text{pH} = 7.3$. Inorganic carbon was controlled by use a N_2/CO_2 (1%) gas mixture ($P_{\text{CO}_2} = 10^{-2} \text{ atm}$) either in a glove box (batch-type experiments) or by bubbling inlet solution (percolation experiments).

All solutions were prepared with ultra-pure deionized water ($18.2 \text{ M}\Omega\cdot\text{cm}$) and with commercially available chemical products of analytical grade or superior. For the SPW preparation, analytical grade $\geq 99\%$ ACS reagents (NaCl , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaHCO_3 , KCl) and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ product from Sigma Aldrich (99.995% trace metals basis) were used.

A stock solution of EuCl_3 (99.99% trace metals basis, Sigma Aldrich) was used to obtain initial concentrations of Eu between 1.9×10^{-9} and $1 \times 10^{-7} \text{ mol L}^{-1}$. Sources of ^{152}Eu (Eckert & Ziegler) in 0.5M HCl (with $10 \mu\text{g/g}$ of carrier) and HTO (Eckert & Ziegler) served as radioactive tracers.

II.1 COx samples

The COx samples used were obtained from the Meuse/Haute-Marne Underground Laboratory (depth: ≈ 500 m) located in the eastern part of the Paris basin. They originated from boreholes drilled by Andra (French Radioactive Waste Management Agency). The mineralogical composition and proportions of the major phases have been extensively described in Gaucher et al. (2004), ANDRA (2005b) and Lerouge et al. (2011). This composition mainly consists of phyllosilicates (40-60 wt%, mainly illite and mixed layer illite/smectite, kaolinite and chlorite), carbonates (15-45 wt%, mainly calcite and dolomite), tectosilicates (10-40 wt%, mainly quartz and feldspars) and minority phases such as sulfides (0-3 wt%, mainly pyrite) and natural organic matter (0.5-1 wt%).

After drilling, the samples were conditioned in airtight aluminum foil filled with nitrogen, transported to the laboratory and then stored until their opening in a N₂/CO₂ (1%) glove box.

For the measurement of natural Eu concentrations in the pore water of COx, seepage water from the Callovo-Oxfordian clay-rich rock was collected from borehole GIS1002 in Andra's Meuse/Haute-Marne underground research laboratory. This 16-m long horizontal borehole was drilled at a depth of 490 m in the clay-rich layer. The water sample analyzed was collected 10 years after the borehole began to produce water (Grangeon et al., 2015).

II.2 Batch-type experiments

Europium retention on COx was investigated by means of batch-type experiments as a function of Eu concentration at a fixed solid/liquid (S/L) ratio (0.5 g L⁻¹). An appropriate amount of COx powder (grain size < 200 μ m) was dispersed in SPW in 35-mL Nalgene® Polypropylene Copolymer (PPCO) centrifugation tubes. After one day of mechanical agitation to equilibrate the "SPW/COx/atmosphere" system, Eu was added to the suspension. The Eu concentration domain was chosen (by modeling) so as to avoid any precipitation of Eu hydroxide or carbonate solid phases (see Table 1). Preliminary experiments showed that a contact time of at least 4

days was necessary to reach sorption equilibrium, as indicated by constant Eu concentrations in the aqueous phase, within the uncertainties, as a function of the time (data not shown). The supernatant was recovered using 0.22- μm surfactant-free cellulose acetate filters for Eu analysis.

The solid/liquid distribution coefficient, R_d (in L kg^{-1}), and associated error (Err_{R_d}) were determined according to the following equations:

$$R_d = \frac{C_s}{C_{eq}} = \frac{C_0 - C_{eq}}{C_{eq}} \times \frac{V}{m} \quad (1)$$

where C_s (mol g^{-1}), C_0 (mol L^{-1}), C_{eq} (mol L^{-1}), V (L) and m (kg) are respectively: the amount of Eu adsorbed onto the solid, the initial and equilibrium aqueous concentrations of Eu, the volume of the aqueous solution, and the mass of the COx powder.

the associated error is calculated according to the equation:

$$Err_{R_d} = \sqrt{\left(\frac{V}{m} \frac{C_0}{C_{eq}}\right)^2 \times \left(\left(\frac{Err_{C_0}}{C_0}\right)^2 + \left(\frac{Err_{C_{eq}}}{C_{eq}}\right)^2\right) + R_d^2 \times \left(\frac{Err_{V/m}}{V/m}\right)^2} \quad (2)$$

with Err_{C_0} , $Err_{C_{eq}}$ and $Err_{V/m}$ being the uncertainties linked to C_0 , C_{eq} and V/m , respectively.

In parallel to the sorption experiments, "blanks" were systematically performed with SPW in the presence of Eu without COx to quantify the total Eu content (C_0); no significant adsorption of Eu on either the tube surfaces or the filters under the experimental conditions of this study was observed (<5%).

Each point on the isotherm corresponds to the result of a single test.

II.3 Percolation experiments

II.3.1 Experimental strategy

The methodology applied for percolation experiments involves injecting the element of interest (at a given concentration) under pressure through the compact clay medium saturated with synthetic pore water (in equilibrium with the phases present) (see Table 1 for more details). We recall that the objective is to obtain a non- transient state, i.e. that element concentration at the output of the assembly is equal to the injected concentration. Since the solution concentration is known, a value for R_d can be calculated by determining the concentration of the element in the adsorbent phase, here COx. It is also worth mentioning here that the transient /non- transient state is not related to the notion of the establishment of an equilibrium state between the soluble and adsorbed fractions of the element. This equilibrium state, which allows the application of thermodynamic models, is dependent on the rate of adsorption of the element onto the material. Such a state of equilibrium for the adsorption process is assumed with clays, whether we are working under transient or non-transient conditions.

If we come back to our percolation experiences, a non-transient state can be obtained for Cs/COx (Chen et al., 2014b) or Ni/COx (Montavon et al., 2020) systems. For the case of Eu, which is a strongly retained element, this condition is more complicated to achieve. By way of illustration, Fig. 1 shows initial simulations that were carried out with literature data, i.e. a value of R_d around 10^5 L kg^{-1} (ANDRA, 2005a; Descostes et al., 2017; Schott et al., 2012). It can be seen that the non-transient state is reached after about 6 years of experiments, even though the work is being carried out in advective mode with submillimeter-sized samples in thickness (Fig. 1).

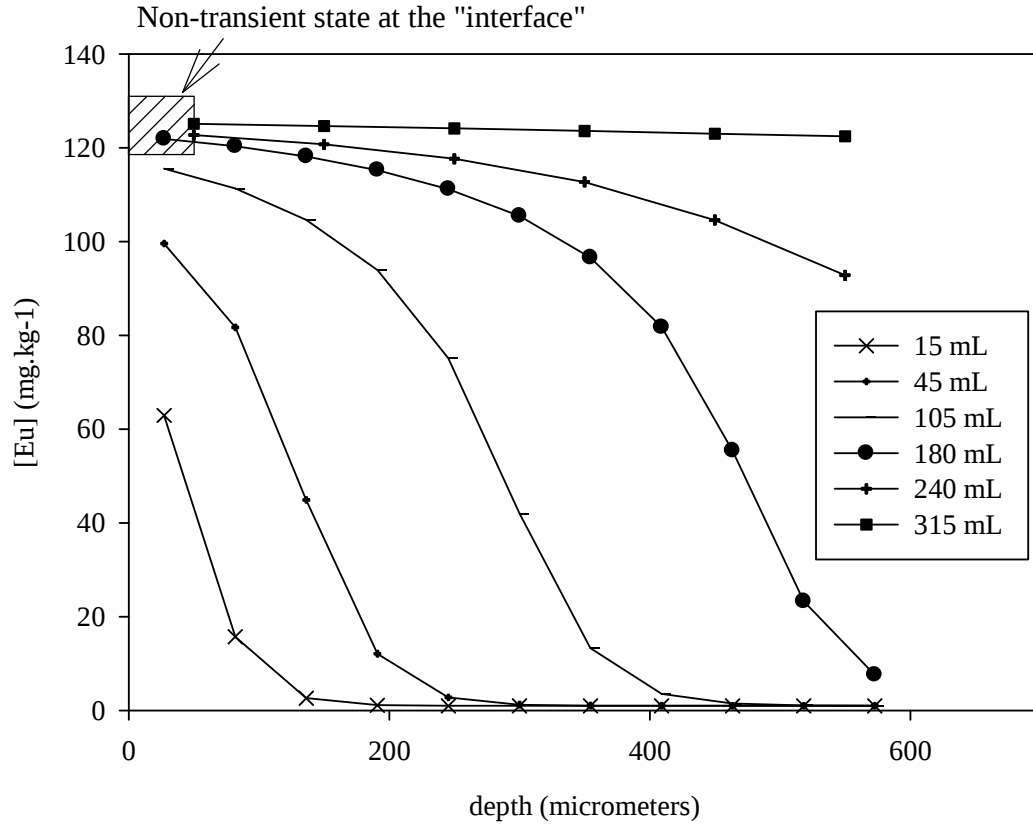


Fig.1: Simulations of Eu profile evolution in a compact COx sample vs. depth for different percolation volumes (for roughly 6 years of experiment). Flow rate: 0.15 mL day^{-1} ; sample thickness: 0.6 mm ; $[\text{Eu}]_{\text{injected}} = 8.2 \times 10^{-8} \text{ M}$; $\text{Rd} = 7.8 \times 10^4 \text{ L kg}^{-1}$. Information for the simulation is available in Table A1.

In order to limit the experimental time (i.e. a few months), the strategy adopted in our study sought a non-transient state at the inlet surface, or at least within the first few micrometers. By measuring Eu concentration at the surface by LA-ICP-MS ($[\text{Eu}]_{\text{clay,COx}}$, in mol per mass of COx) with a known Eu concentration in the injection loop ($[\text{Eu}]_{\text{injected}}$, in mol per volume of SPW) it is then be possible to calculate a Rd value:

$$\text{Rd} = \frac{[\text{Eu}]_{\text{clay,COx}}}{[\text{Eu}]_{\text{injected}}} \quad (3)$$

The amount of spiked Eu in the COx was systematically corrected from the amount of Eu naturally present.

The retention parameter obtained can subsequently be used as a fixed value in an attempt to reproduce the Eu “percolation depth profiles” using a reactive transport model (see part II.5).

II.3.2 CO_x clay rock samples

Naturally highly compact samples were used (bulk density of $\sim 2.3 \text{ g cm}^{-3}$). The sample preparation methodology was adapted from Montavon et al. (2020, 2014). First, a 1-cm diameter piece (several centimeters long) was manufactured through core drilling; next, a lathe (Caseneuve HB55) was used to obtain a diameter of $4.99 \pm 0.02 \text{ mm}$. Lastly, the piece was fastened onto a support and cut into slices (thickness: $0.5 - 0.8 \pm 0.05 \text{ mm}$) by means of a precision diamond wire saw (Escil® W3032; wire diameter = 0.3 mm). These steps were performed under air, but the potential superficial oxidation of the minerals was minimized by using a nitrogen flow around the rock samples. Note that a possible partial oxidation of the sample will not have a direct effect on the retention of Eu: Eu is not a redox sensitive element and neither is the clay fraction of CO_x.

The dry bulk densities of the pellets output ranged from 2.18 to 2.28 g cm^{-3} .

The samples were initially qualitatively characterized by Optical Microscopy (Olympus BH2) and Scanning Electron Microscopy (Tescan Mira 3 XMU) (SEM) in order to select the "right candidates" (Fig. A1). The aim of this initial characterization was to discard CO_x pellets with cracks or those with crumbled edges and then select only those pellets characterized by a homogeneous distribution of CO_x mineral phases (compared to average compositions).

II.3.3 Percolation experiment set-up

The percolation experiment set-up is presented in Figure 2. The reactors have been designed to ensure total system tightness and allow for total sample recovery once the experiment has been completed. The material used to make the reactors and the capillary tubes are made of PEEK

in order to avoid or limit Eu adsorption phenomena (Molera and Eriksen, 2002). An assembly of three reactors R1, R2 and R3 connected in parallel was installed for the purpose of performing several experiments with just a single pump. Each part of the percolation cell was cleaned successively with HNO₃ 5% (v/v), Milli-Q water and Normapur 96% ethanol before drying (in the glove box) and use.

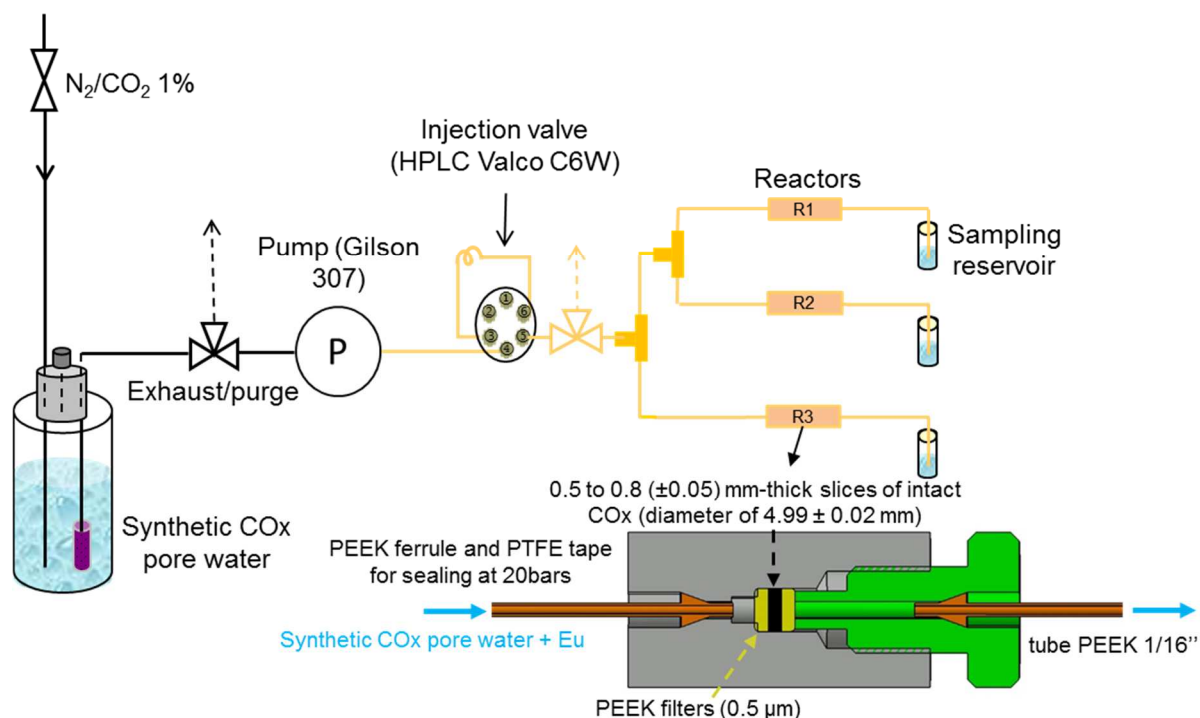


Fig. 2: The percolation experiment set-up

Once the samples had been inserted into the cells (between two PEEK filters), they were first hydrated and equilibrated with SPW. Sample hydration proceeded in stages, initially at low pressure (1 bar) for 3 days before pressure was gradually increased to 20 bar so as to determine the permeability and verify the applicability of Darcy's Law (Fig. A2). Average flows were 158 ± 10 , 132 ± 7 and 101 ± 9 mg d⁻¹ for R1, R2 and R3, respectively. In order to maintain the pH and carbonate concentration of the SPW constant throughout the duration of the experiment, a bubbling with a N₂/CO₂ (1%) gas mixture was carried out for at least 15 min twice a week. In the meantime, pH was measured from time to time in the sampling reservoir to ensure that the

system remained in equilibrium. SPW with Eu at $(8.8 \pm 0.9) \times 10^{-8} \text{ mol L}^{-1}$ was injected into the percolation cell at a constant pressure of 20 bar. In order to avoid Eu adsorption on the pump head, the solution was injected via a 7.85 mL injection loop (made of PEEK) (Fig. 2). In other words, the Eu-free SPW solution in the vessel in Fig. 2 “pushes” the Eu-doped SPW solution (present in the loop) into the compacted COx pellet. Note that the loops were changed in time to ensure a constant supply in Eu concentration in the COx. The outlet solution was analyzed regularly to both control the possible presence of Eu and measure pH values and alkalinity.

Europium solution percolation through samples R1, R2 and R3 was stopped after 174, 365 and 694 days, respectively. The collected solution volumes were of 25, 49 and 58 mL for R1, R2 and R3, respectively. Compact COx samples extracted from R1 and R2 reactors were recovered and cut in half using a sterilized scalpel (washed in AnalaR Normapur® 96% vol. ethanol (VWR BDH Prolabo) and 5% (v/v) Teflon distilled nitric acid and then rinsed with Milli-Q water).

The Eu “percolation depth profiles” were obtained by analyzing the side of the pellet in depth (from the surface in contact with the input solution to the end of the pellet from which the solution was recovered).

Each half-sample piece was fastened onto a thin petrographic plate with a double-sided adhesive disc for the Eu microanalysis of sample surface and depth profile by means of Laser Ablation Inductively Coupled Plasma Mass Spectrometry. For R1 and R2 samples, Eu concentrations were measured in relation to the mass of COx ablated. For R3, the analysis was concentrated on the clay fraction of the COx.

Results were compared with the distribution of Eu naturally present.

Table 1: Summary of the experimental conditions in effect during this study

Sample	Type of sample	Type of experiment	Focus	Contact time (days)	Figure(s)
EST45989 (R1)	Compact	Spiked by percolation	Eu concentration at the surface and as a function of depth. $[\text{Eu}]_{\text{injected}} = (2.4 - 2.7) \times 10^{-8} \text{ mol L}^{-1*}$	174	5, 6, A1-2, 5
EST45989 (R2)				365	5, 6, A1-2, 5
EST45989 (R3)			Eu in clay fraction at the surface. $[\text{Eu}]_{\text{injected}} = 9.1 \times 10^{-8} \text{ mol L}^{-1*}$	694	5, A1-2, A6
EST51779	Crushed	Spiked in the dispersed state	Rd measurement: $[\text{Eu}]_0 = 1.9 \times 10^{-9} - 10^{-6} \text{ mol L}^{-1}$ (experiments with the radioactive tracer)	4	3
EST51779	Compact	Naturally-occurring Eu	Eu distribution in COx mineral phases	-	3, 4, A1, A3

* concentrations measured at the end of the experiment; the initial concentration injected was $(8.8 \pm 0.9) \times 10^{-8} \text{ mol L}^{-1}$

II.4 Analytical techniques

The SPW composition was measured by ionic chromatography (Dionex ICS1000). A pH electrode (Inlab), freshly calibrated with standard pH buffers (pH 4, 7 and 10, Fisher), was used to measure pH values. The alkalinity was determined by colorimetric analysis using Bromocresol Green-Methyl Red Indicator Powder Pillow as color indicator and a Digital Titrator (Hach method 8203) with a digital titrator cartridges containing 0.16 N of H_2SO_4 . Analyses of radioactive Eu (^{152}Eu) in solution (8 mL) were performed by liquid scintillation counting with a Packard TriCarb 3170 TR in adding an Ultima Gold LLT[®] (Perkin Elmer) scintillation cocktail (12 mL).

Direct analyses of Eu concentration in COx samples were conducted by LA-ICP-MS on thin samples polished under dry conditions in order to avoid any contamination or loss of trace element with reagents. Analyses of both natural (surface Eu concentration) and compact spiked COx R1 and R2 (depth profile and surface Eu concentration) samples were measured by LA-HR-ICP-MS at the SUBATECH Laboratory. Analyses of Eu concentration in the clay fraction of the compact Eu-spiked COx sample from the R3 reactor were performed by LA-Q (quadrupole)-ICP-MS at the BRGM (French Geological Survey) facility.

In order to identify the phases at the origin of Eu retention (Eu-COx sample from R3, natural COx sample), mineral phases (pyrite, calcite and clay fractions) were first characterized using an Olympus BH2 optical microscope (Fig. A3) and then localized by diamond strapping to assist with the analyses.

Note that the ability of the LA-ICP-MS technique to accurately quantify the amount of Eu was assessed with the natural sample by comparison with the amount measured in solution after sample acid digestion (Fig. A6).

II.4.1 LA-HR-ICP-MS

Micro-analyses of Eu in the natural COx or Eu-spiked COx (R1 and R2) samples were undertaken using a Nd-YAG UP213 laser system (NewWave Research) coupled with the Element XR single collector high resolution ICP-MS (Thermo Scientific). The HR-ICP-MS was synchronized to the laser ablation device in external trigger mode. The laser system was equipped with a standard ablation cell ($V=30$ ml) mounted on a motorized xyz stage with sub-micron resolution for sample movement. The ablated material was removed from the sample chamber by helium carrier gas, then mixed with argon gas and directly introduced into the hot plasma of the HR-ICP-MS instrument. Operating conditions have been detailed elsewhere (Hassan Loni et al., 2019). The Eu concentration was determined by external calibration using two standard reference materials, i.e. the NIST 610 synthetic glass with $[Eu] \text{ (mg kg}^{-1}\text{)} = 447 \pm 10$ ($k=2$) and the matrix-matched NIST 679 brick clay with $[Eu] \text{ (mg kg}^{-1}\text{)} = 1.9 \pm 0.2$ ($k=2$) prepared in a compacted disc-shaped pellet. The quantification procedure was carried out according to two distinct approaches, namely: internal standardization with a major element of known concentration used as internal standard, and the 100% oxide normalization in applying the total matrix (58 elements) as an internal standard (Lin et al., 2016; Liu et al., 2008; Šelih and Van Elteren, 2011; Van Elteren et al., 2009).

The Eu depth profiles of R1 and R2 COx samples were analyzed in either line scan or single-spot ablation modes according to the 100% oxide (w/w) normalization strategy. The laser was operated at a pulse repetition rate of 10 Hz, with an output energy of 50% (≈ 0.5 mJ) and beam diameter of 65 μm (line scan) or 50 μm (single spot). A total analysis time of 3 min was defined for the line ablation mode (2 min for the single-spot mode), including 2.25 min (or 1 min) and 1.7 min (or 1 min) for laser ablation sample and gas blank measurements, respectively.

Micro-analyses of Eu in polished thin sections of natural COx mineral phases were performed by both external calibration and internal standardization (^{29}Si or ^{27}Al for clay fraction, ^{42}Ca for calcite and ^{57}Fe for pyrite). The laser settings were as follows: output energy = 50% (≈ 0.5 mJ), frequency = 10 Hz, and beam diameter = 55 μm . Each optimal laser analysis lasted 2 min, encompassing 30 s to 60 s of laser sample ablation (depending on the beam length, with beam diameter = 55 μm) and 60 s of background measurement. The laser beam length was adapted to the size of the mineral phase being analyzed.

All time-resolved raw data were exported in ASCII or FIN2 format and processed offline by in-house subroutines written in VBA language for Microsoft Excel 2010TM. The average gas blank signal intensities for all elements were calculated and then subtracted from the signal intensities measured during the standard and sample ablation step. A signal drift correction was applied with a linear interpolation over time by using normalized ^{151}Eu signal intensities from the bracketing standard reference materials. A two-sigma rejection test of outliers was applied to all normalized sample Eu signal intensities. The Eu concentration of each analysis were calculated from the following equations:

$$C_{\text{SMP}}^i(\text{norm}) = 100 \times \frac{\hat{I}_{N_X}^{i,\text{SMP}}}{\frac{[\hat{I}_{N_2}^{i,\text{STD}} \times (N_X - N_1) + \hat{I}_{N_1}^{i,\text{STD}} \times (N_2 - N_X)]}{(N_2 - N_1)}} \times \frac{C_{\text{STD}}^i}{\sum_{i=1}^n C_{\text{SMP}}^i(\text{unnorm})} \quad (4)$$

$$\text{with: } C_{\text{SMP}}^i(\text{unnorm}) = \frac{\hat{I}_{\text{SMP}}^i}{\hat{I}_{\text{STD}}^i / C_{\text{STD}}^i}$$

where $\hat{I}_{\text{SMP}}^i$, $\hat{I}_{\text{STD}}^i$ and C_{STD}^i are the signal intensity (in cps) for each of the sample-containing elemental oxides i (1 to n), the signal intensity and the elemental oxide concentration i (in % (w/w)) of elemental oxide i in NIST 610, respectively. N_1 , N_2 and N_x denote the analysis numbers in the sequence.

II.4.2 LA-ICP-Q-MS

The microanalysis of Eu in the clay fraction of the spiked COx sample (R3) was performed by a UV Laser-Ablation micro sampler CETAC[®] Excite (193 nm) coupled with a ThermoScientific[®] X series II quadrupole plasma mass spectrometer, according to the laser configuration set forth by (Monnier et al., 2018). The analytical protocol involved combinations of ^{27}Al , ^{29}Si , ^{44}Ca and ^{151}Eu analyses. Ablation spots 35 μm in diameter were introduced at an 8-Hz frequency with an energy of $\approx 2 \text{ J cm}^{-2}$. The analysis time for each spot was 60 s, including 20 s of background measurement with the laser off and 40 s of analysis time with the laser on. The Eu concentration was calibrated against the external standard NIST 612, the internal standard of the Si value for clay minerals and the Ca value for carbonates.

II.5 Reactive transport and sorption models

All calculations were carried out using the PhreeqC code (Version 3.3) (Parkhurst and Appelo, 2013) using the Davies Equation (Davies, 1964) to account for the ionic strength correction of solutes.

Reactions occurring in the aqueous phase as well as saturation states with respect to solid phases were calculated using the thermodynamic database ThermoChimie v9b (Giffaut et al., 2014) (Grivé et al., 2015; <https://www.thermochimie-tdb.com/>) (Table A2).

To model Eu adsorption, two assumptions were introduced: 1) the clay fraction governs Eu retention in assuming that illite and interstratified IS were the reactive phases with IS-combined illite (50% in weight) and smectite (50% in weight) properties (Chen et al., 2014a; Grangeon et al., 2015; Tournassat et al., 2008); and 2) the additivity (Davis et al., 1998) approach is valid, whereby the models developed for the clay model phases illite and montmorillonite (smectite) can be directly applied to the COx material without considering additional reactive phases or modifying interaction parameters in the complex multi-mineral assemblage including mixed layer illite-smectite (IS). The 2-site protolysis, non-electrostatic surface complexation and cation exchange model (2 SPNE SC/CE) (Bradbury and Baeyens, 2011) was implemented for the COx clay rock. According to the 2 SPNE SC/CE model, the surface complexation phenomenon is controlled by both weak (i.e. high quantity, limited affinity) and strong (low quantity, high affinity) sites. No competitive effect was considered between Eu and other trace metals at the adsorption sites (Bradbury and Baeyens, 2011; Marques Fernandes et al., 2015). Unless otherwise indicated, calculations were performed for COx with the lower and upper clay content limits. This approach introduces the greatest error sources, while other uncertainties associated with model parameters were not considered (Table A3). Considering in the clay-rich zone the variation in clay (40-60 wt%), the variation in illite and I/S, and a percentage of 55% of smectite in I/S (Chen et al., 2014a; Gaucher et al., 2004), range of 20–44% and 9–18% for illite and montmorillonite respectively were used in the calculations.

For the percolation experiments, the 1D coupled chemical/transport model (reactive code) implemented in phreeqC was used. For the modeling step, the two filters in PEEK, with a porosity of 9.4 vol%, were taken into account, along with the length of capillary tubes at both the cell inlet and outlet. Dead volumes were estimated by simulating HTO injection through the samples (Fig. A5). Note that results indicate the absence of dilution in the HTO solution injected through the capillary loop.

The relative magnitudes of advection and dispersion are characterized by the Peclet number, as defined by:

$$Pe = vL / (D_p + \lambda v) \quad (5)$$

where L is the sample length (m), v the pore water velocity (m s^{-1}), D_p the pore diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), and λ the dispersivity (m). $D_p + \lambda v$ represents the dispersion coefficient.

The D_p value was set at $1.5 \cdot 10^{-11} \text{ m}^2 \text{s}^{-1}$ (Altmann et al., 2014). Peclet numbers were estimated in the range of 2 - 4 for compact COx samples, thus indicating the predominance of the advection mode over the diffusion mode.

The column hydrodynamic characteristics required for modeling (porosity, samples dimension,...), as well as the data used for describing Eu adsorption, can be found in Tables A1-A3.

III. Results

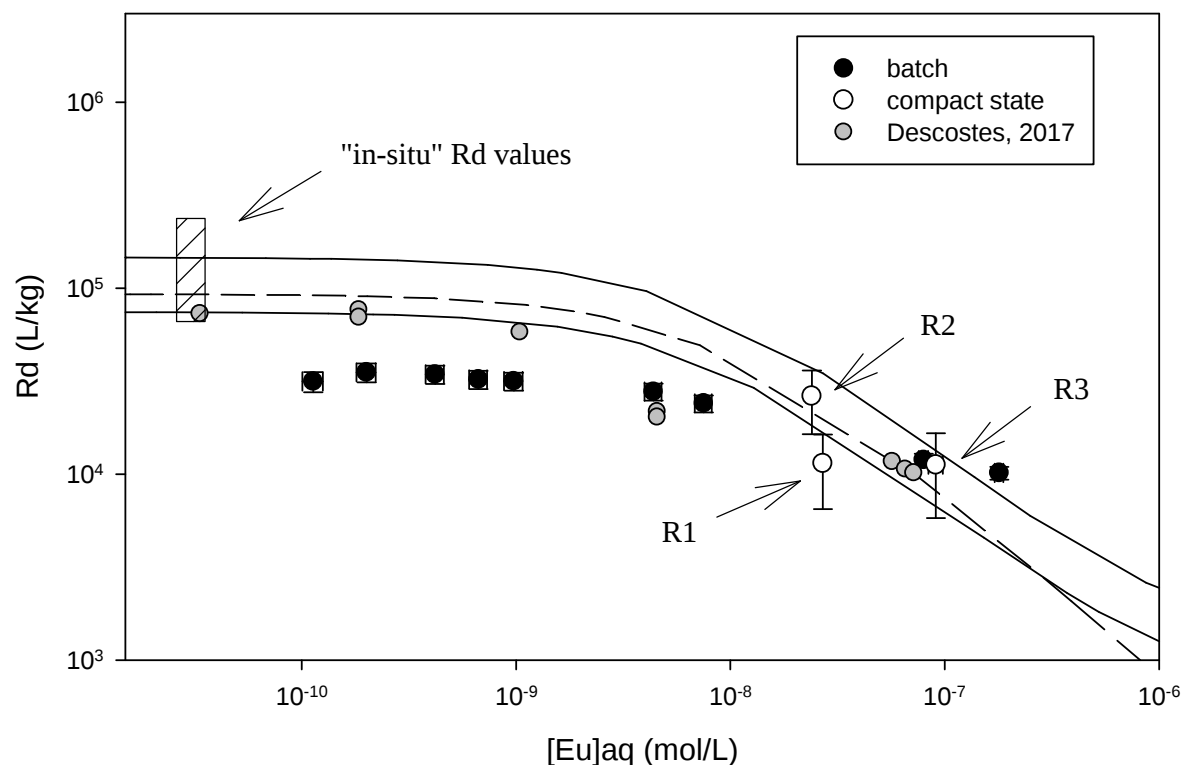
III.1 Batch-type experiments in the COx dispersed state

Figure 3 presents the sorption isotherm of Eu on COx as well as those published for the Eu/COx system by Descostes et al. (2017) under similar conditions. The pH and alkalinity values of the supernatant were: 7.3 ± 0.1 and $2.64 \pm 0.14 \text{ meq L}^{-1}$, respectively. Europium sorption is constant at the lowest concentration, with R_d values around $(3.5 \pm 0.5) \times 10^4 \text{ L kg}^{-1}$. These values are of the same order of magnitude as those given for similar experimental conditions by both García-Gutiérrez et al. (2009) ($> 3.8 \times 10^4 \text{ L kg}^{-1}$) and ANDRA (2005b) ($\approx 5 \times 10^4 \text{ L kg}^{-1}$) yet lower than that obtained by Descostes et al. (2017) ($\approx 1 \times 10^5 \text{ L kg}^{-1}$).

423 Rd values then decrease to approx. 10^4 L kg^{-1} at the highest concentration studied ($\approx 2 \times 10^{-7} \text{ mol}$
424 L^{-1} for aqueous Eu concentration). Under these conditions, our data are consistent with those of
425 Descostes et al. (2017).

426 The simulation results are represented by the solid lines for the lower and upper clay fraction
427 limits. Under the experimental conditions of this study, Eu speciation in solution is dominated
428 by carbonate complexes. Carbonate ions also appear to be important in describing the
429 adsorption of Eu; at the lowest Eu concentrations, adsorption is controlled by the formation of
430 two carbonate surface complexes with strong sites ($\text{sOEu}(\text{CO}_3)$ and sOEuOHCO_3^- , Table A2).
431 In this range, the model overestimates our retention data by about one order of magnitude. For
432 the highest concentrations studied, i.e. the zone where the percolation experiments were carried
433 out, the simulation and experimental results are consistent. Under these conditions, the
434 contribution of weak sites to retention becomes significant ($\approx 15\%$).

435 Given this study's objective, no further work has been carried out in search of an explanation
436 for this discrepancies observed at the lowest Eu concentrations.



438

439 *Fig. 3: Eu adsorption onto a COx sample in the presence of SPW and modeling results. (●) Batch-type*
 440 *experiments; (O) Percolation experiments in the compact state (R1, R2 and R3). (▲) Data from*
 441 *Descostes et al. (2017). Solid lines depict simulations performed for the lower and upper clay fraction*
 442 *limits. The dashed line represents the contribution of the two carbonate surface complexes ($s\text{OEu}(\text{CO}_3)$*
 443 *and $s\text{OEuOHCO}_3^-$) to the overall retention for the mean COx clay fraction. Simulation details are given*
 444 *in Tables A2 and A3.*

445

446 III.2 Naturally-occurring Eu

447 The two analytical approaches (the direct analysis on the solid vs. the analysis of the solution,
 448 after digestion) yield similar values, i.e. an Eu concentration of $0.9 \pm 0.2 \mu\text{g g}^{-1}$. As expected,
 449 Eu is present at trace levels in the clay formation; to the best of our knowledge, this is the first
 450 reported value for Eu.

451 The various constituent mineral phases (i.e. clay, calcite, pyrite) were analyzed by means of
 452 LA-HR-ICP-MS in order to assess the distribution of naturally-occurring Eu in the COx. These
 453 mineral phases were chosen for their recognized ability to trap metals through various retention

processes (Descostes et al., 2017); results are provided in Figure 4. The mass balance calculations performed from the direct analyses carried out on individual phases did appear to be consistent, given the uncertainties present, with the total quantity of Eu in the sample. The main mineral phases with more affinity to Eu have therefore been identified.

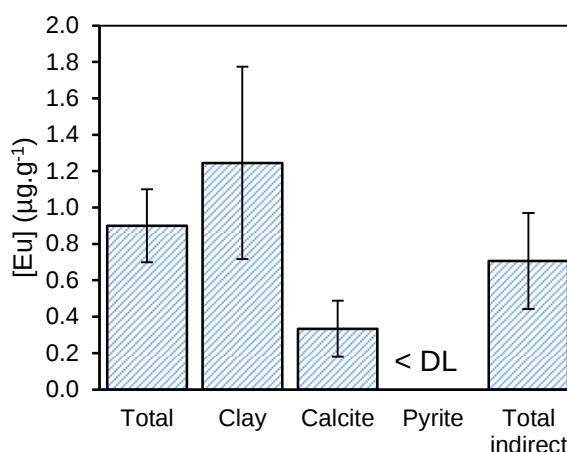


Fig. 4: Distribution of naturally-occurring Europium studied by LA-HR-ICP-MS (the number of analyses are 10, 5 and 3 for clay, calcite and pyrite, respectively). "Total indirect" corresponds to the Eu content in the COx determined by summing the Eu concentrations measured in the individual phases (normalized to their % in COx). (DL = Detection Limit)

Europium is mainly present in the clay fraction (1.2 ± 0.5 µg per g of clay fraction) and contributes to about 70% of the inventory (0.9 µg per g of COx) if the average clay content found in the COx (≈ 50 wt%) is taken into account. For calcite (≈ 25 wt%), the average Eu concentration obtained (0.33 ± 0.15 µg per g of calcite) is less than that determined in the clay phase. The contribution of calcite to average Eu concentration in the COx has been estimated at roughly 10%. No Eu was detected in the pyrite phase (i.e. $< DL = 0.001$ µg g⁻¹). These results indicate that the clay fraction is the main "reservoir" for Eu in the COx.

In assuming that the clay fraction controls adsorption (i.e. the starting hypothesis of the adsorption model), it is then possible to revert to Rd values as long as the concentration of Eu in the pore water remains known. A value of $(3.0 \pm 0.4) \times 10^{-11}$ mol L⁻¹ was experimentally measured by means of HR-ICP-MS for the GIS1002 borehole. With these concentrations in

water and clay fraction, a range of R_d values can be estimated from around $6 \cdot 10^4$ to $2 \cdot 10^5 \text{ L kg}^{-1}$ (hatched area in Figure 3).

III.3 Percolation experiments

For all samples, the linearity obtained between flow rate and pressure gradient serves to validate the applicability of Darcy's Law under our experimental conditions. The measured permeability values varied between $3.3 \cdot 10^{-13}$ and $4.2 \cdot 10^{-13} \text{ m s}^{-1}$ (Fig. A2); these values are in good agreement with data for compact rock found in the literature (ANDRA, 2005b; Vinsot et al., 2008). The CO_x/SPW equilibrium was checked throughout the experiment; more specifically, the alkalinity and pH measured on aliquots at the reactor outlet showed values equivalent to those obtained for SPW, i.e. between 2.1 and 2.4 meq L^{-1} and 7.2-7.4, respectively. The Eu concentration at the outlet of all reactors remained very low and stable over time, with average values below $7 \cdot 10^{-11} \text{ mol L}^{-1}$.

III.3.1 Europium quantification at the surface of spiked samples (R1 and R2)

The analyses of Eu concentrations carried out on the surface at the inlet side of samples are given in Figure 5. The ablation depth by the laser beam was estimated at about 10 μm . The average Eu concentration at the surface of spiked samples equals 47 ± 19 and $95 \pm 32 \mu\text{g g}^{-1}$ for R1 and R2, respectively ($n = 9$). Europium appears to be homogeneously distributed on the inlet faces even though the uncertainties associated with the derived concentrations are quite high.

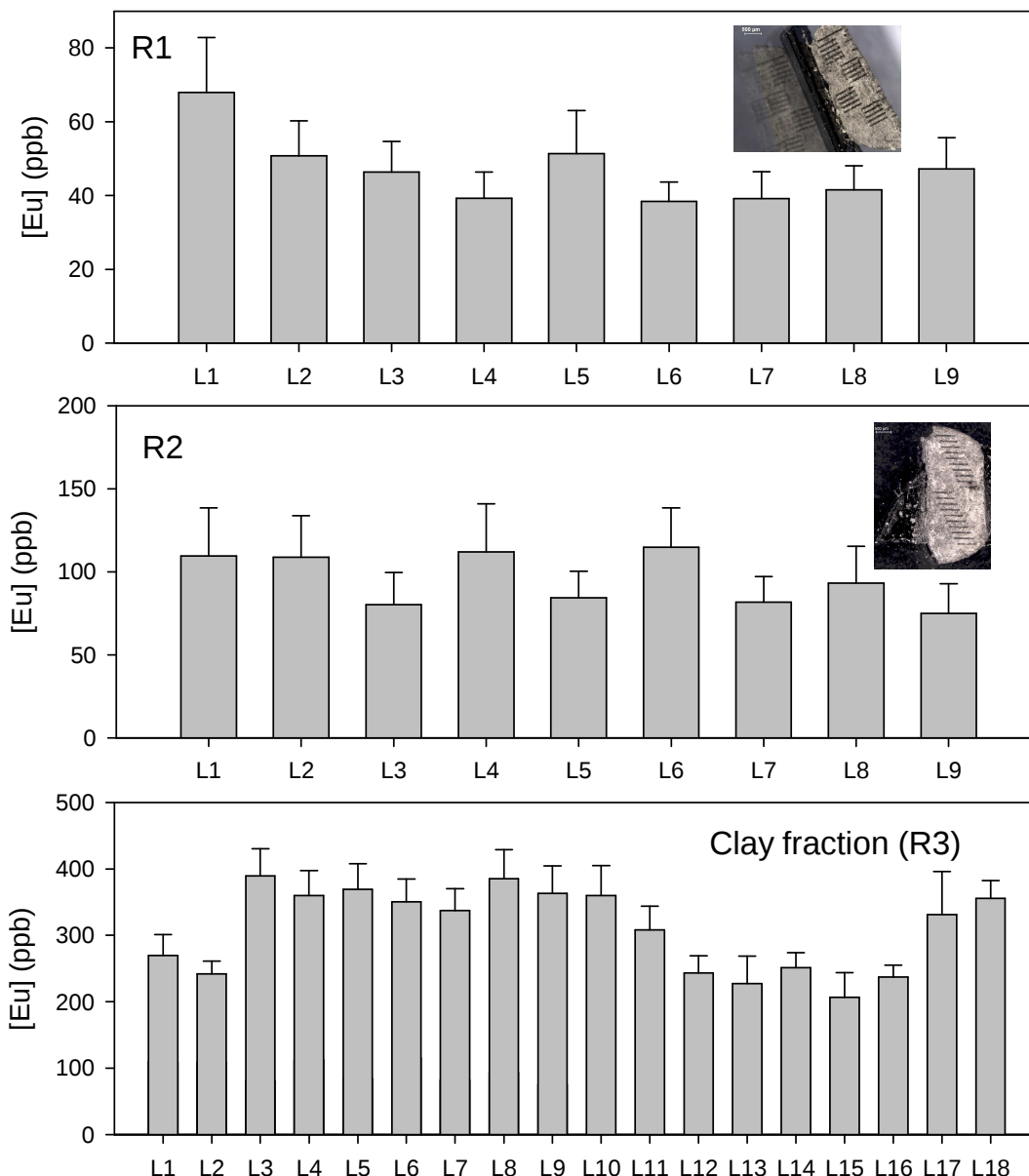


Fig. 5: Europium concentration at the surface of Eu-spiked COx samples for bulk material (R1 and R2) and clay fraction (R3). L stands for the ablation line number (average concentration over around 0.65 mm length).

During dismantling, a few drops of the aqueous solution in the immediate vicinity of the inlet surface were collected, under pressure, in order to measure the Eu concentration as close as possible to the sample surface. This analysis showed a decrease by a factor of about 3 with respect to the concentration of injected solution ($8.8 \times 10^{-8} \text{ mol L}^{-1}$ initially), i.e. between 2.4×10^{-8} and $2.7 \times 10^{-8} \text{ mol L}^{-1}$. This decrease in concentration is not easily explained. Experiments

conducted with HTO do not indicate any significant dilution resulting from the solution injection protocol (Fig. A5); moreover, the experimental set-up was designed to limit Eu adsorption on the surface of the materials used.

Regardless of the reason (e.g. possible slight adsorption of Eu on the PEEK material of the capillary loop), the measured concentrations injected into the COx sample constitute the data required to revert to the Rd values. Considering that a non-transient state was reached at the surface where pore water concentration corresponds to injected concentration, Rd values of $11,500 \pm 5,000 \text{ L kg}^{-1}$ and $26,300 \pm 9,500 \text{ L kg}^{-1}$ were obtained for R1 and R2, respectively. Although a factor of close to two lies between the values, they do agree, within the limits of uncertainty, with the predicted range of Rd values, within which the adsorption data recorded in the dispersed state all lie (open symbols in Fig. 3).

III.3.2 Eu localization at the surface of the spiked sample R3

Since no significant compaction effect was observed and given that the sorption model satisfactorily predicts the experimental retention data, Eu was expected to be adsorbed by the clay fraction. This outcome was assessed directly on the R3 sample. Note that for this reactor, unlike reactors 1 and 2, the Eu concentration measured at the reactor inlet ($9.1 \pm 0.7 \cdot 10^{-8} \text{ mol L}^{-1}$) corresponded to the Eu concentration injected into the loop.

The areas rich in clay were previously identified by optical microscopy. Several laser ablation lines were carried out (see Fig. 5 for results). Note that the analysis of the major elements indeed confirms that the clay fraction has been appropriately targeted (Fig. A6). As expected, the Eu concentration measured in the clay matrix of the Eu-spiked COx sample ($[\text{Eu}]_{\text{clay,R3}}$) is clearly higher than that for the natural COx ($[\text{Eu}]_{\text{clay,COx}}$), i.e. $311 \pm 62 \mu\text{g g}^{-1}$ vs. $1.2 \pm 0.5 \mu\text{g g}^{-1}$. In taking into account the percentage of clay in the COx ($P_{\text{clay,COx}}$), as well as the concentration of Eu injected into the compact system ($[\text{Eu}]_{\text{injected}}$), the molecular weight of Eu (MM_{Eu}) and the

fact that a non-transient state has been reached at the "interface", an Rd value can be calculated according to the following:

$$Rd = 10^{-3} \frac{([Eu]_{clay,R3} - [Eu]_{clay,COx})P_{clay,COx}}{MM_{Eu}[Eu]_{injected}} \quad (6)$$

The Rd value obtained ($11,200 \pm 5,700 \text{ L kg}^{-1}$) also appears to be consistent with the retention data previously determined for reactors R1 and R2 and with the values measured in the dispersed state. These results are entirely consistent with the hypothesis that clay fraction governs Eu adsorption.

III.3.3 Europium concentration along the spiked COx samples

In a final step, the Eu concentration was assessed along the samples as a function of depth for both the R1 and R2 reactors. The "percolation depth profiles" obtained are shown in Figure 6; let's note that although the profiles resemble one another, the data are rather scattered. As expected, Eu reaches its highest concentrations within the first few micrometers ($< 50 \mu\text{m}$) of the sample, even though migration was detected up to a depth of approx. $200 \mu\text{m}$. From a depth of $200 \mu\text{m}$ and beyond, the geochemical background of Eu in COx is in fact being analyzed, i.e. approx. $0.9 \mu\text{g g}^{-1}$.

The percolation profiles were then simulated by coupling the chemistry model applicable for the Eu concentrations investigated (solid lines in Fig. 3, see Tables A2 and A3 for the parameters) with an advective transport model (see Table A1 for detailed information). No adjustment was attempted, as this multi-parametric model lacking constraints does not output precise parameters. The simulation results (solid lines in the figure) are in good agreement with experience, provided the trends are well reproduced.

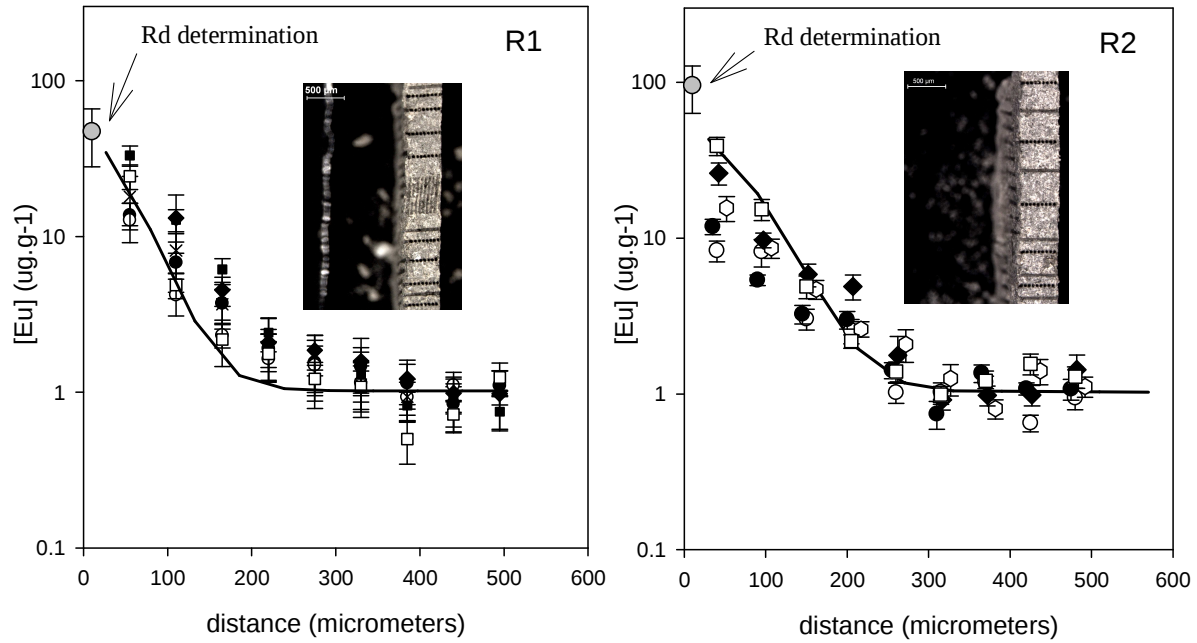


Fig. 6: Europium concentration along the COx sample for R1 (25 mL of percolated Eu-spiked SPW) and R2 (49 mL of percolated Eu-spiked SPW). The various series represent different laser ablation spot lines. The lines reflect simulations made with reactive transport model. The gray symbols correspond to the surface analysis ($\approx 10 \mu\text{m}$).

IV. Discussion

With regard to the key question raised in this work, thanks to the proposed methodology, Rd values could be proposed to describe Eu adsorption on compact COx samples. The objective of this work has been to determine these values in a non-transient state, where the thermodynamic model can be directly applied without considering the transport part. This condition is anticipated at the sample surface after a certain contact time, when the pore water concentration corresponds to that of the injected solution (dashed zone in Fig. 1).

The contact time required to reach this non-transient state at the COx pellet entry surface has not been evaluated experimentally, as this step would have required excessive experimental work given the difficulty of setting up these experiments. In this context, the simulation results prove to be quite important. As revealed by the depth profile simulation results (Fig. 6), the level of agreement between experiment and calculation is satisfactory, especially when

considering that no parameters have been adjusted. A more detailed examination indicates that the extrapolation of simulation curves out to the surface explored by laser ablation coincides with the measured Eu concentration values. Recall that these measured values are the origin of the experimental R_d values, which themselves are accurately reproduced by the chemical model (Fig. 3). It can thus be concluded that simulations confirm that the experimental time was sufficient to achieve the desired non-transient state at the interface for R1 and R2, as proposed in our strategy. Since the percolated volume is even greater for R3, the conditions are therefore logically applicable to this reactor as well.

Europium adsorption onto COx was shown to be strong ($R_d > 10^4 \text{ L kg}^{-1}$) at trace concentrations. Similar behavior would be expected for the trivalent actinides Am and Cm, as well for Pu under highly reducing conditions. Furthermore, the three R_d values obtained for the compact spiked COx samples are consistent, within the experimental uncertainties, with those deduced from conventional batch experiments carried out in dispersed state (black symbols in Fig. 3). Similar results had already been obtained for compact COx with iodine (I) (Montavon et al., 2014), cesium (Cs) (Chen et al., 2014b) and nickel (Ni) (Montavon et al., 2020), thus suggesting that this trend seems *a priori* applicable to the retention of metal ions by COx clay rock. The result also appears to be consistent with the recent results of Glaus et al. (2020), derived from diffusion experiments vs. pH for an Eu/compacted illite system. They demonstrated that adsorption models are valid for describing the equilibrium distribution of Eu between aqueous solution and clay phase in the compacted state, provided an electrical double layer is considered to describe the behavior of mobile species in the diffuse layer.

A combination of the various methods also leads to conclude that the clay fraction effectively governs Eu adsorption. This finding has been indirectly confirmed by modeling the data; in using a bottom-up approach along with the assumption that the clay fraction is responsible for element adsorption on COx (Table A2), it was possible to explain experimental adsorption data

in the conditions chosen for the percolation experiments, during which both strong and weak sites contribute to Eu adsorption. This finding was also validated by direct analysis on the compact Eu-spiked sample (R3); the additional Eu is derived quantitatively, within uncertainties, in the clay fraction. This result is in agreement with qualitative data already published by Menut et al. (2006) on Eu-spiked COx samples obtained from a diffusion experiment and Laser-Induced Breakdown Spectroscopy (LIBS) measurements.

The importance of the clay fraction in Eu retention also corroborates the results of the study conducted with naturally-occurring Eu. The clay fraction represents the main reservoir, with some 70% of the inventory of naturally-occurring Eu found at trace concentrations in the COx ($\approx 0.9 \text{ mg kg}^{-1}$). Using this value and the natural pore water concentration of Eu, Rd values ranging from 6.10^4 to 2.10^5 L kg^{-1} are determined. The domain in Rd values is consistent with predictive simulations yet lies beyond the values potentially extrapolated from adsorption data recorded at the trace scale (in dispersed state); the Rd values over such a range are assumed to be constant ($\approx 3.5 \times 10^4 \text{ L kg}^{-1}$). However, adsorption is not the only process leading to metal retention and one shall recall that the total content of Eu in the clay rock is larger than the fraction bound to the clay phases. On the other hand, only a fraction of the retained Eu is labile and has to be taken into account for the evaluation of the Rd to be compared with the laboratory retention experiments. Other processes leading to non-labile species, such as incorporation of metals into matrices, are likely to occur, in particular for the long times characteristic of sedimentary rocks (e.g. COx) (McKinley and Alexander, 1993). This outcome was recently shown for the Ni/COx system (Montavon et al., 2020), whereby only $\approx 13\%$ of the Ni found in the rock appeared to be labile/adsorbed (and only 24% of Ni found in the clay fraction). The proposed *in situ* range of Rd values ($\approx 6.10^4$ to 2.10^5 L kg^{-1}) therefore represents an upper limit, which cannot be simply compared to Rd values measured in the laboratory over short time

periods. On the other hand, the deviation between prediction and experiment for equilibrium Eu concentrations below $\approx 10^{-8}$ mol L⁻¹ still needs to be elucidated.

V. Conclusion

Thanks to our methodology, and the use of LA-ICP-MS, it was possible to derive R_d values for Eu on compact COx samples under non-transient conditions, i.e. without considering the transport process. Within the uncertainties present, these values are of the same order of magnitude as those derived in the dispersed state for the aqueous concentration range explored for both states ($\sim 3 \cdot 10^{-8}$ - 10^{-7} mol/L). From a mechanistic point of view, retention can be described by the reversible adsorption of Eu on the surface of clays (illite and illite/smectite) based on existing adsorption models (for equilibrium Eu concentrations above $\approx 10^{-8}$ mol L⁻¹) through carbonate surface complexes with strong sites. This finding was also shown directly by mapping on the compact spiked sample (R3); the additional Eu is found quantitatively, again within uncertainties, in the clay fraction. The magnitude of the clay fraction in Eu retention is also observed for naturally-occurring Eu, with about 70% of the inventory found in the latter. However, only a portion of this natural Eu in the clay fraction seems to be present in labile (reversible) form, thus suggesting the existence of other retention mechanisms capable of leading to metal entrapment. Further studies would be needed to assess the impact of this irreversible entrapment of Eu and of other trivalent elements in minerals for the long-term safety of radioactive waste disposal sites. Yet even when ignoring this additional margin of safety, our data clearly demonstrate the strong retention of trivalent elements on clay rock, which makes them very little mobile in the COx formation.

Acknowledgments

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