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## Role of carbonate minerals in the distribution of trace elements in marine clay formations

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### Abstract

Anthropogenic radionuclides (RN) are generated by a wide range of industrial and medical activities. In the contexts of waste storage, the quantification of RN migration is of paramount importance. RN migration is partly ruled by the interaction of RN with the solid surfaces. Usually experiments are conducted at various scales from laboratory to the field in order to measure retention and retardation parameters of radiotracers. Whereas this experimental approach is mandatory to tackle the issue of RN migration, the understanding of the natural speciation of stable isotopes that are analog to RN brings additional useful information. In particular, the RN natural speciation sheds light on RN isotopic exchange and “irreversible” trapping mechanisms. This study aims at overviewing the association of natural trace elements (U, Th, Ni, I, Sr and Zn) with carbonate minerals in the Callovian-Oxfordian sedimentary formation that is under consideration for deep nuclear waste disposal in France. The combined use of sequential extraction techniques, microscopic and spectrometric techniques, as well as laser-ablation coupled to chemical analysis techniques made it possible to establish the distribution of I, Sr, U, Th and Ni in the various mineral and organic phases present in the clay rock. I and Sr and in a less extent U and Th are mainly carried by carbonates while Ni is distributed in a variety of phases including pyrite, sphalerite, chlorite, organic matter and muscovite.

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### 1. Introduction

Carbonate minerals are among the most studied minerals for decade because they are fast-reacting minerals present

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in many rocks (sedimentary, hydrothermal, metamorphic, magmatic), soils and in anthropic systems (clay barriers, reservoirs, polluted sediments and soils, mining environment, cement materials). The investigations span several aspects: mineral structure and chemistry, large stability conditions, reactivity and thermodynamic constants of interest for fields such as nuclear waste management, carbon capture and storage. The carbonate system in marine clay formations is especially of great interest for deep waste storage at least for three aspects. First of all, carbonate formation in a sediment is informative on the pH, alkalinity, partial pressure of CO<sub>2</sub> and on major cations and carbonate species present in fluids from which they precipitated. For this reason, they are used to control pH, alkalinity and major cations of pore water chemistry in pore water models [1]. Secondly for their chemical buffering capabilities in various natural and anthropic contexts of perturbation as for instance oxidizing disturbance, acidification, alkaline perturbation at clayrock/cementitious material interfaces. A third aspect which is sometime evoked is its capacity to retain trace elements by sorption or incorporation. Batch experiments have strongly suggested that sorption is dominantly controlled by fast and reversible sorption onto clay minerals but slow incorporation/sorption/complexation of trace elements with other phases, such as calcite cannot be neglected [2, 3]. Although carbonates cannot incorporate high amounts of trace elements, their important content in marine clay formations such as Callovian-Oxfordian (COx) makes them a fraction which carried trace elements, as demonstrated for I [4, 5], Ni [2], Sr [6, 7]. This work aims at 1) summarizing the results of the different sequential extractions performed to better constrain the trace element distribution in the Callovian-Oxfordian claystone, and hereafter the data concerning more specifically the calcite fraction, and 2) presenting new *in situ* analyses performed on calcite grains using techniques adapted to the measurements of traces elements, such as EPMA and high resolution ICP-MS coupled to a laser.

## 2. Materials and methods

Two technics were used to measure trace element contents in the different clayrock fractions: sequential extraction procedures and *in situ* analyses on minerals. The first ones are also currently applied to polluted sediments and soils. The second ones are electron microprobe, ICP-MS coupled with laser,  $\mu$ XRF, depending of the mineral size and content. Different extracting sequences were applied to COx clayrocks to determine the distribution of trace elements (Sr, Ni, Zn, U, I, Th) among the minerals present in the rock [2, 4, 6]. All the chemical extractions were performed in a glove box under nitrogen to avoid any mineral change (i.e. oxidation) as pristine clayrock is in reduced form. A first extraction is dedicated to exchangeable cations sorbed on the clay fraction. The reactants commonly used are ammonium acetate [2, 4] or cobalt hexamine [1, 6]. The second step using sodium acetate buffered with acetic acid at pH 5 allows extracting calcite and thus the elements it contains. *in situ* analyses of major and trace elements (EPMA) were performed on polished thin sections using a Cameca SX Five electron microprobe equipped with a 20 kV acceleration voltage, a current beam of 300 nA and a 1–2  $\mu$ m beam width, for trace element contents down to 40 ppm. Counting times were 10 s for major elements and between 60 and 240 s for trace elements. Microanalyses of trace elements (U, Th, Ni, Zn) in calcite from two COx samples (EST5738 and EST26536) were performed using an Element XR high resolution ICP-MS (Thermo Scientific) coupled to a UP213 Nd-YAG laser ablation system (New Wave Research). Soft laser ablation conditions were chosen to limit the reactivity of the calcite under the beam. Systematic analyses of the NIST612 standard were performed during the course of the analysis session to validate the stability of the analytical conditions and to calculate trace element contents using <sup>42</sup>Ca for internal standardisation.

## 3. Sequential extractions and the calcite fraction

Sr is a major trace element in marine clay formations. The Sr content in COx clayrocks ranges between 210-370 ppm, whose 100 to 180 ppm are attributed to the calcite content (i.e. 33-41 % of the bulk Sr), indicating a Sr content of calcite ranging between 323 to 917 ppm [6].

Iodine content in COx clayrocks is about 1-5 ppm. 1.7 to 2.5 ppm corresponds to the carbonate fraction, indicating that calcite is one of the major carrier mineral of iodine [4].

Uranium content is  $\sim 2 \pm 0.5$  ppm in COx clayrocks. The content of uranium extracted during the acetic acid /acetate step was around 333-392 ppb in clay richest samples, corresponding to about 11-13 wt % of bulk U and to a U content in calcite of about 1.5-3.8 ppm.

In carbonate rich samples the content of extracted U was around 701 ppb U, corresponding to about 35 wt % of bulk U and to a U content in calcite of about 1.7 ppm.

Ni content in COx clayrock is  $\sim 33 \pm 11$  ppm. The Ni content extracted during acetic acid /acetate step was around 2 ppm Ni, corresponding to about 5 % of the bulk Ni and to a Ni content in calcite of about 10 ppm [2].

Sequential extraction procedures applied on marine COx clayrocks provided evidence that the carbonate fraction is an important reservoir of trace elements such as strontium, iodine, uranium, nickel, although the trace element contents recalculated in calcite taking account the percent of calcite in the clayrock are low.

#### 4. *In-situ* analyses of diagenetic calcite

While sequential extractions allow obtaining data easily but without information on the element speciation within the solid, spot analyses of phases remain a challenge in clayrocks due to the small size of particles, and because of the very low content of trace elements. However *in situ* analyses are required to cross-check data obtained by sequential extraction procedures, and allow considering the type of calcite: detrital calcite forming bioclasts and diagenetic calcite (micrite, microsparite) [7].

**Strontium:** About 500 Sr analyses measurements were performed in diagenetic calcite and bioclasts (shell of bivalves and brachiopods) using electron microprobe, the content of Sr in calcite being significantly higher than the detection limit of the technique (dl  $\sim 130$  ppm) [7]. Calcite bioclasts contain 500-1700 ppm. Diagenetic calcite has systematic lower Sr contents ( $<130 - 800$  ppm). The lowest values measured in bioclasts correspond to bioclasts which are partially recrystallized into diagenetic calcite.

**Iodine:** The measurement was uneasy due to the very low content of iodine in both rock and calcite. However electron microprobe analyses provided evidence of high contents of iodine up to 2000 ppm in calcite bioclasts. Iodine contents in recrystallized bioclast and in diagenetic calcite are lower and more heterogeneous [5]. A major difficulty of iodine analyse with electron microprobe was also the interference between the I La line and the Ca K $\beta$ ; the resolution of this problem was to measure iodine on the I L $\beta$  [4].

**Uranium:** U and Th contents were measured in calcite with the high resolution ICP-MS coupled with a laser. Laser ablation line mode analyses on calcite bioclast and microsparite filling a bioclast in two claystone samples (EST5738 and EST26536) were acquired with the following laser parameters (Frequency= 5 Hz, Output Energy=35-40% ,pulse energy= 0.03mJ, spot diameter= 40  $\mu$ m). The measured  $^{238}\text{U}$  and Th signals were significant but lower than those of the NIST612 standard. U contents of calcite clast and of diagenetic calcite calculated using  $^{42}\text{Ca}$  as internal standard were almost similar and were  $\sim 0.4 - 0.7$  ppm; however some spots with higher contents up to 15 ppm were found in bioclast. Th contents of calcite ranged between 0.1 and 0.6 ppm (cf. Figure 1).

**Nickel and zinc:** Ni and Zn contents were measured in calcite with the ICP-MS-HR coupled with a laser. Several line mode analyses on the same microsparite from the sample EST26536 were acquired with laser operating conditions: Frequency=5 Hz, output energy=70%, pulse energy=0.6mJ and spot diameter= 55  $\mu$ m. The measured  $^{62}\text{Ni}$  and  $^{64}\text{Zn}$  signals are significant but lower than those of the NIST612 standard. Ni contents of diagenetic calcite calculated with  $^{42}\text{Ca}$  as standard are almost similar and generally lower than 1 ppm (0.4-0.7). Zn contents ranged between 2.3 and 4.9 ppm.

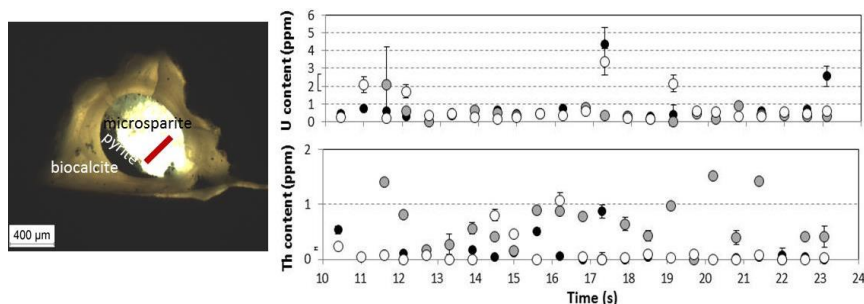


Figure 1: Micrograph of a calcite bioclast filled with limpid diagenetic microsparite and pyrite in transmitted light and analytical profiles through the microsparite (uncertainties 4 %).

## 5. Discussion

Sequential extractions help to discriminate the carrier (clay, carbonates, pyrite, etc) in clayrocks. The results report that calcite fraction can scavenge a large part of the natural Sr (33-41 %) and I contents of the COx clayrock, and in a less extent U (11-13 %), Th, Ni (5 %) and Zn. Sr contents estimated from sequential extractions and spot analyses are almost similar; moreover Sr content is fairly homogeneous. On the opposite, the other elements display an important discrepancy between extraction and spot analyses. In this way, spot analyses of iodine demonstrate heterogeneous amounts in calcite with locally high content (up to 2000 ppm). *In situ* analyses with ICP-MS HR evidenced low amount of U and Ni carried by microsparite (< 1 ppm) and lower than those estimated by sequential extraction. As U and Ni mean contents in calcite estimated by sequential extraction procedure are significantly higher than U and Ni measured by ICP-MS-HR, it is assumed that acid attack performed with acetate buffer (pH 5) allows extracting U from another phase than calcite such as surface complexation sites on clay minerals. It is also noteworthy that bioclasts are systematically richer in trace elements than diagenetic calcite. Finally, Th content in calcite is only measurable by ICP-MS-HR proving the high relevance to use this analytical technique to determine reservoir of trace elements in clayrocks.

Spot analyses using EPMA and high resolution ICP-MS laser are a good complement to the sequential extractions and are of major interest for interpretation of sorption data. As an example, sorption capacity of COx clay with regards to radioactive  $^{63}\text{Ni}$  was tested using batch experiments. Indirect evidences point out the possible sorption/incorporation of Ni in calcite although pyrite and organic matter may also be involved [2, 3]. Investigations of Ni in microsparite by spot analyses with ICP-MS HR coupled with a laser show that Ni carried by this type of calcite is very low (< 1 ppm) and lower than those estimated by sequential extraction (10 ppm). These new data suggest that calcite may possibly be a minor mineral in the control of the Ni sorption. However, the influence of the external surface of calcite, which might have a chemical composition different from the bulk, remains to be investigated.

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