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Interaction of europium and nickel with calcite studied by Rutherford Backscattering Spectrometry and Time-Resolved Laser Fluorescence Spectroscopy

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ABSTRACT

This study aims at elucidating the mechanisms regulating the interaction of Eu and Ni with calcite (CaCO₃). Calcite powders or single crystals (some mm sized) were put into contact with Eu or Ni solutions at concentrations ranging from 10⁻³ to 10⁻⁵ mol L⁻¹ for Eu and 10⁻³ mol L⁻¹ for Ni. The sorption durations ranged from 1 week to 1 month. Rutherford Backscattering Spectrometry (RBS) well adapted to discriminate incorporation processes such as: (i) adsorption or co precipitation at the mineral surfaces or, (ii) incorporation into the mineral structure (through diffusion for instance), has been carried out. Moreover, using the fluorescence properties of europium, the results have been compared to those obtained by Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) on calcite powders. For the single crystals, complementary SEM observations of the mineral surfaces at low voltage were also performed. Results showed that Ni accumulates at the calcite surface whereas Eu is also incorporated at a greater depth. Eu seems therefore to be incorporated into two different states in calcite: (i) heterogeneous surface accumulation and (ii) incorporation at depth greater than 160 nm after 1 month of sorption. Ni was found to accumulate at the surface of calcite without incorporation.

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1. Introduction

Calcium carbonate minerals are present in the French Callovo Oxfordian shales where the radioactive waste should be disposed of. An important number of waste repository concepts enclose cement base components and calcite is the main secondary alteration product formed during the degradation of cement over geological time scales [1]. Europium is a fission product (¹⁵⁴Eu and ¹⁵⁵Eu, with $t_{1/2} = 8.6$ and 4.7 years, respectively) also used as analogue of trivalent actinides. Nickel is an activation product (⁶³Ni and ⁵⁹Ni, with $t_{1/2} = 100.1$ years and 7.6×10^4 years, respectively). Therefore, for safety reasons, the evaluation of the retention capabilities of calcite

with respect to these radionuclides has to be fully understood. Interactions between cations and natural or synthetic calcite may include incorporation processes, resulting in the irreversibility of some sorption reactions. Understanding and quantification of poorly to non-reversible trapping mechanisms can be considered as a significant improvement in the description of a geological barrier or a backfill material performance in the safety assessment. Little is known about the mechanism of the transfer process from the surface to the bulk. Trapping of ions can proceed either via progressive incorporation into the lattice of the solid, including continuous dissolution/precipitation processes and diffusion or via irreversible surface precipitation.

Rutherford Backscattering Spectroscopy (RBS) is an analysis technique that is widely used to follow the incorporation or migration of different elements in minerals. For example, the incorporation of rare earth elements (REE) and Pb and Sr into

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calcite and into apatite has been studied by Cherniak [2–5]. The comparison of the results of these studies proves that these elements diffuse rather rapidly into calcite in comparison to other minerals. Alonso et al. [6] investigated the diffusion of Eu, U, Sr and Re into clay by means of RBS, and clearly showed different behaviors for Eu and U (strong adsorbing elements) compared with Sr and Re. Carroll [7] combined a RBS study to SEM and EDS measurements and observed the incorporation of U(VI), Nd and Th(IV) in calcite as solid solutions.

Europium's luminescent properties enable the use of TRLFS to elucidate interaction mechanisms with calcite. Fernandes et al. [8] successfully demonstrated the formation of solid solution between Eu^{3+} with calcite, by substitution of Ca^{2+} on the lattice site [9]. Calcite presented both surface sorption and incorporation capacities for Eu(III) [9]. The incorporation had already been evidenced by Piriou et al. [10]. Schmidt et al. [11] studied Eu sorption onto aragonite (metastable CaCO_3) and found only structural incorporation of Eu^{3+} , without any surface sorption. The reactivity of CaCO_3 was thus shown to be dependent on its polymorphism. Substitution of divalent Ca^{2+} by trivalent Eu^{3+} was found to be accompanied by a charge compensation which proceeds via a coupled substitution mechanism, originating from the simultaneous substitution of two Ca^{2+} by one Eu(III) and one Na^+ ion [8,9].

Our work aims at studying the different mechanisms leading to a potential incorporation of europium and nickel in calcite. We have decided to work on the $\text{Eu-CO}_2\text{-NaCl-CaCO}_3$ and $\text{Ni-CO}_2\text{-NaCl-CaCO}_3$ system at $\text{pH} \sim 8.3$, buffered by calcite under air and corresponding to the typical pH range of natural interstitial groundwaters. Our study relies on the RBS technique to comprehensively characterize the $\text{Eu-CO}_2\text{-NaCl-CaCO}_3$ and the $\text{Ni-CO}_2\text{-NaCl-CaCO}_3$, and associates TRLFS analyses for Eu. The investigated samples were prepared under atmospheric conditions, on different calcite samples (powders and millimetric crystals), for different initial concentrations of europium and nickel, these parameters being assumed to be amongst the most important controlling the sorption mechanisms.

2. Materials and methods

2.1. Materials

At first, an appropriate material for sorption experiments was selected based on characterization studies. From a variety of sources, the attention was focused on two calcite powders from SOLVAY (SOCAL U1-R) and from OMYA (Hydrocarb 90). The particle size was estimated by Scanning Electron Microscopy (SEM) to be, respectively, ~ 0.2 and ~ 50 μm . The specific surface areas were determined to be, respectively, 18.4 and 0.66 $\text{m}^2 \text{g}^{-1}$ by applying the Brunauer–Emmet–Teller (BET) equation with nitrogen adsorption isotherms at 77 K (Multi-point Beckman Coulter Surface Analyzer SA 3100). Purity of the calcite samples and absence of polymorphic CaCO_3 compounds (i.e. vaterite and aragonite) were confirmed by XRD (X-ray Diffraction), DRIFT (Diffuse Reflectance Infra-Red Fourier Transform Spectroscopy) and TEM (Transmission Electron Microscopy). Elemental analysis performed by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry, ELAN 9000 Perkin Elmer) after digestion showed the absence of Ni in the SOLVAY sample ($< 0.01 \mu\text{g g}^{-1}$) and the presence of a very low concentration of Eu ($5.83 \times 10^{-2} \mu\text{g g}^{-1}$), whereas in the OMYA sample a small amount of Ni was detected ($13.11 \mu\text{g g}^{-1}$), whereas Eu was not detected ($< 0.01 \mu\text{g g}^{-1}$). Single crystals provided by Alfa Aesar were also investigated, with a surface size around $1 \times 1 \text{mm}^2$ and a thickness of 2–3 mm. Small amounts of Eu ($< 0.07 \mu\text{g g}^{-1}$) and for Ni ($0.41 \mu\text{g g}^{-1}$) were determined by ICP-MS after digestion of 50 mg of single crystals.

2.2. Sample preparation

The europium ($5 \times 10^{-3} \text{M}$) and nickel ($2 \times 10^{-3} \text{M}$) stock solutions were prepared by dissolving $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (Sigma–Aldrich, trace elements basis, 99.99%) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma–Aldrich, 99%) in UHQ water. All experiments were carried out using diluted fractions of these solutions. All sorption experiments were done under atmospheric conditions ($\text{pCO}_2 = 10^{-3.5} \text{atm}$) and carried out in duplicate.

For powder samples, 500 mg of calcite was suspended in 100 mL of 0.1 mol L^{-1} NaCl solution in Teflon vials, to get a mass–volume ratio of 5 g L^{-1} . A first step resulting in the pre-equilibration of calcite was performed, i.e. the calcite suspension was stirred until an equilibrium pH of ~ 8.3 was reached. Required amounts of europium were then added to reach a europium concentration of 10^{-3} and $10^{-4} \text{mol L}^{-1}$ and a nickel concentration of $10^{-3} \text{mol L}^{-1}$ at ambient pressure and temperature and the samples were subsequently stirred during 1 month. After sorption, the suspension was directly measured by TRLFS and for RBS experiments, samples were centrifuged at 5000 rpm for 30 min, the solid was dried in air for 4 days and then compacted to pellets about 1 cm in diameter.

For millimetric single crystals, 10–12 crystals (resulting in a solid/liquid ratio of 0.3 g L^{-1}) were directly immersed in 100 mL of a Eu or Ni-enriched solution (10^{-5} and $10^{-4} \text{mol L}^{-1}$ for Eu, 10^{-4} and $10^{-3} \text{mol L}^{-1}$ for Ni), since the pre-equilibration could not be reached easily; the pH was adjusted using a dilute NaOH solution to reach a value of ~ 8.3 . Two contact times (1 week and 1 month) were selected, during which the solution was periodically stirred by hand. For the RBS measurements, powders were pressed to pellets and were, as well as the single crystals, coated with a layer of carbon (about 10 nm) prior to the measurement in order to prevent charging of the surface.

2.3. TRLFS

The TRLFS measurements were carried out with a pulsed flash lamp pumped Nd:YAG-OPO laser system (Powerlite Precision II 9020 laser equipped with a Green PANTHER EX OPO from Continuum, Santa Clara, CA, USA) at an excitation wavelength of 394 nm and a constant time gate width of 1 ms (10^{-5} and $10^{-4} \text{mol L}^{-1} \text{Eu}^{3+}$) or 0.1 ms ($10^{-3} \text{mol L}^{-1} \text{Eu}^{3+}$). Details on the laser system are given elsewhere [12]. Static and time-resolved luminescence spectra of Eu^{3+} were recorded in the range of 570–650 nm (1200 lines mm^{-1} grating, 0.2 nm resolution) and 550–740 nm (300 lines mm^{-1} grating, 0.7 nm resolution), respectively. For time-resolved measurements, 61 spectra with delay steps of 20, 50, 250 or 500 μs , depending on the luminescence lifetime, were recorded per sample. The luminescence spectra were analyzed using OriginPro 7.5G (OriginLab, Northampton, MA, USA) to obtain peak positions and lifetimes. The lifetimes were calculated by fitting the integrated luminescence signal to a sum of exponential decay functions:

$$E(t) = \sum_i E_i \cdot \exp(-t/\tau_i) \quad (1)$$

where E is the total luminescence intensity at the time t , E_i the initial luminescence intensity of the species i at $t = 0$, and τ_i the corresponding lifetime.

The number of water molecules in the first coordination shell of Eu^{3+} was determined from the luminescence lifetimes τ (in ms) using the linear relationship developed by Horrocks and Sudnick [13] and the resultant empirical formula from Kimura and Choppin [14]. This equation is only valid for lifetimes higher than 110 μs .

$$n(\text{H}_2\text{O}) \pm 0.5 = 1.07 \cdot \tau^{-1} - 0.62 \quad (2)$$

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