Available online at www.sciencedirect.com

ScienceDirect

Journal of Colloid and Interface Science 321 (2008) 323–331

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

# Site-selective time-resolved laser fluorescence spectroscopy of $Eu^{3+}$ in calcite

M. Marques Fernandes [a,*], M. Schmidt [a], T. Stumpf [a,b], C. Walther [a], D. Bosbach [a], R. Klenze [a], Th. Fanghänel [b,c]

[a] *Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe, P.O. Box 3640, Karlsruhe 76021, Germany*
[b] *Ruprecht-Karls-Universität Heidelberg, Physikalisch-Chemisches Institut, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany*
[c] *European Commission, Joint Research Center, Institute for Transuranium Elements, P.O. Box 2340, Karlsruhe 76125, Germany*

Received 24 September 2007; accepted 13 January 2008

## Abstract

Three samples of calcite homogeneously doped with $Eu^{3+}$ were synthesized in a mixed-flow reactor. By means of selective excitation of the $^5D_0 \rightarrow {}^7F_0$ transition at low temperatures ($T < 20$ K), three different $Eu^{3+}$ species (species A, B, and C, respectively) could be discriminated. For each one, the emission spectrum and lifetime were obtained after selective excitation of the single species. On the basis of these data, species C could be identified as $Eu^{3+}$ incorporated into the calcite lattice on the (nearly) octahedral $Ca^{2+}$ site. Species B was also identified as $Eu^{3+}$ incorporated into the calcite lattice, but the ligand field shows a much weaker symmetry. Species A, however, is not incorporated into the crystal's bulk, having 1–2 $H_2O$ ligands left in its first coordination sphere and showing very little symmetry, and is considered as $Eu^{3+}$ adsorbed onto the calcite surface. The emission spectra of species C for Eu:calcite grown in the presence of $Na^+$ were found to differ from those of Eu:calcite synthesized in the presence of $K^+$. The latter revealed a strong distortion in site symmetry, which was not observed in the samples grown in $Na^+$ solutions. This finding provides spectroscopic evidence in favor of an incorporation mechanism based on the charge–balanced coupled substitution of $Na^+ + Eu^{3+} \leftrightarrow 2Ca^{2+}$.

*Keywords:* Lanthanides/actinides; TRLFS; Incorporation; Calcite; Charge compensation

## 1. Introduction

Assessing the geochemical long-term safety of a nuclear waste repository requires a molecular level understanding of the behavior of radionuclides in the geosphere. This is needed in order to establish reliable thermodynamic data, which are then used in safety assessment models to predict radionuclide retention and transport in the near and far field of radioactive waste repositories. In particular, the interaction of radionuclides with mineral phases (adsorption, structural incorporation) strongly affects their mobility and sequestration. In the environment of deep geological nuclear waste repositories, reducing conditions prevail and the radionuclides are present in their low oxidation states. In particular trivalent actinides like Am(III), Cm(III), and Pu(III) contribute highly to the radiotoxicity of a high level radioactive waste (HLW) disposal. This work focuses on the interaction of trivalent radionuclides with the mineral calcite $CaCO_3$.

Calcite is an omnipresent crystalline mineral phase in many soil and sedimentary formations. It plays an important role in the retention of toxic and radiotoxic elements [1–11].

Geological clay formations (Bure, Boom clay, Opalinus) containing a high percentage of calcite (up to 40%) are intensively discussed as a host rock formation for a nuclear waste repository. Moreover, many waste repository designs include cement-based components of which calcite is a major secondary alteration product formed over geological time scales [12,13]. Besides its importance as a potential host phase for radionuclides, calcite also serves, due its relatively simple crystal structure with a single cation site, as a model phase for investi-

---

[*] Corresponding author. Present address: Laboratory for Waste Management, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.
*E-mail address:* maria.marques@psi.ch (M. Marques Fernandes).

0021-9797/$ – see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2008.01.017

gating heterovalent solid solutions (e.g., substitution of $Ca^{2+}$ by a higher charged cation). In calcite, $Ca^{2+}$ occupies regular centrosymmetric octahedra with monodentate sixfold coordination to oxygen belonging to adjacent $CO_3^{2-}$ groups.

Because of their electronic 4f configuration, the trivalent lanthanides are frequently used in laboratory studies as nonradioactive chemical analogues of 5f trivalent actinides (Am(III), Cm(III), and Pu(III)).

Several studies have dealt with the interaction of trivalent lanthanides resp. actinides with calcite. Empirical partition coefficients for rare earth elements (REE) have been determined from sorption and coprecipitation experiments [3,4,14,15]. Spectroscopic studies (EXAFS, TRLFS) on synthetic calcite crystals containing lanthanides [9,16,17] or actinides (Cm(III), Am(III)) provided structural information (coordination number, bond distances, hydration state) [18,19]. Curti et al. [20] used a thermodynamic "inverse" modeling approach to model the Eu/calcite solid solution–aqueous solution (SSAS) system based on different experimental data. Based on the studies noted above various substitution mechanisms have been discussed but so far no unambiguous evidence could be provided for any of the proposed mechanisms. Zhong and Mucci [4] observed a positive correlation between REE content and Na partition coefficients in REE-doped calcites, which suggests that $Na^+$ might serve to balance the excess charge generated by the incorporation of trivalent REE. A substitution scheme with the end-members $CaCO_3$–$Eu_{2x}(CO_3)_3$, where $x$ represents a $Ca^{2+}$ vacancy in the calcite lattice has been proposed by Lakshtanov and Stipp [15]. To explain the data obtained by EXAFS, Withers et al. [17] suggested mechanisms like bidentate linkage of one carbonate group, or retention of an $OH^-/H_2O$ from the hydration shell of REE. Curti et al. [20] proposed the formation of a ternary solid solution. At low pH, $Ca^{2+}$ is substituted by $H^+$ and $Eu^{3+}$. At higher pH, EuO(OH) is incorporated into the calcite lattice.

The optical properties of 4f elements, in particular of $Eu^{3+}$, have been widely used as luminescent probes to gain structural information, thus allowing identification of the number of the main crystallographic sites, their hydration state, and their point symmetry, to determine the energy of the electronic sublevels/transitions induced by different crystal fields for crystal field calculations, to investigate the correlation between the crystal field and the resulting optical features [9,21–26]. The $Eu^{3+}$ ion is particularly well suited for luminescence studies because of the simplicity of its energy levels and their sensitivity to its crystal field environment [21,27].

In the present work, the fluorescence properties of the trivalent lanthanide $Eu^{3+}$ are used to investigate its coordination environment after the interaction with calcite, with special focus on the structural incorporation and charge compensation mechanisms. Because the ionic radii of sixfold coordinated trivalent actinides ($Cm^{3+}$, 97 pm; $Am^{3+}$, 98 pm) and lanthanides ($Eu^{3+}$, 95 pm; $Nd^{3+}$, 98 pm) is close to that of $Ca^{2+}$ (100 pm) [28] it is assumed that cations are incorporated into the Ca sites in the calcite structure. However, an important question for any heterovalent substitution is the charge compensation mechanism in the vicinity of the substituting cation ($Ca^{2+} \rightarrow Eu^{3+}$). In this paper, site-selective time-resolved laser fluorescence investigations are presented, which were carried out on Eu(III)-doped calcite samples synthesized in the presence of either $Na^+$ or $K^+$ electrolytes to investigate the nature of the different sites induced by the substitution of $Ca^{2+}$ by $Eu^{3+}$ and to verify in particular the charge compensation mechanism proposed by Zhong and Mucci [4]: $2Ca^{2+} \leftrightarrow Na^+ + Eu^{3+}$. Since $K^+$ has a much larger ionic radius (138 pm in sixfold coordination) than $Na^+$ (102 pm) and $Ca^{2+}$ (100 pm) [28], it is assumed that the incorporation of $K^+$ or the vacancy site that must form to provide charge balance if $K^+$ is not incorporated will locally distort the calcite structure and thus modify the crystal field around $Eu^{3+}$ ion. To our knowledge site-selective time-resolved laser fluorescence has been applied only once to investigate the interaction of $Eu^{3+}$ with calcite [9]; however, no particular attention has been given to potential charge compensation mechanisms.

## 2. Eu(III) optical properties [21,27,29,30]

Most luminescence spectra recorded for Eu(III) complexes are emission spectra of the $^5D_0 \rightarrow {}^7F_J$ (J = 0–6) transitions obtained after exciting the $^7F_0 \rightarrow {}^5L_6$ transition. The f–f transitions of $Eu^{3+}$ consist mainly of magnetic dipole (MD) and induced electric dipole (ED) transitions. The most intensive transitions are $^5D_0 \rightarrow {}^7F_{1,2,4}$. The intensity of the MD transition $^5D_0 \rightarrow {}^7F_1$ is independent of the chemical environment of Eu(III), whereas the intensity of the ED transition $^5D_0 \rightarrow {}^7F_2$, referred to as hypersensitive, strongly depends on the local crystal field and local symmetry of the ion. Thus, for europium-containing systems, the time-resolved laser fluorescence analysis of the $^5D_0 \rightarrow {}^7F_J$ fluorescence transitions yields both structural and chemical information (number of sites, local site symmetry, and hydration state).

The ground state $^7F_0$ is not degenerated; the same applies to the $^5D_0$ state. The number of components observed in the $^5D_0 \rightarrow {}^7F_0$ region is necessarily related (as far as they can be observed, weak or no $F_0$ transition indicates high site symmetry) to the number of chemically different (nonequivalent) sites occupied by $Eu^{3+}$.

By making use of the selection rules for induced electric dipole (ED) and magnetic dipole (MD) transitions, that is, from the comparison between the derived number of possible and experimentally observed sublevels of the $^5D_0 \rightarrow {}^7F_J$ transitions (obtained after selectively exciting the $^5D_0 \rightarrow {}^7F_0$ transitions), it is in principle likely to discriminate between different symmetry point groups for $Eu^{3+}$ optical centers in the investigated system [21]. The maximum splitting of the $F_J$ levels for a given site is 2J + 1. The higher the splitting magnitude of the $^5D_0 \rightarrow {}^7F_{1,2,3,4}$ transitions of one Eu(III) site, the lower the symmetry of the site. In highly symmetric sites or when an inversion center is present, the ED transitions $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ are forbidden or weak (symmetry selection rules).

Furthermore the analysis of the Eu(III) fluorescence decay rate allows determination of the hydration state of Eu(III) in a given site. If no other quench processes (e.g., metal to ligand transfer) are present in the vicinity of Eu(III), the rate of radiationless deexcitation is directly proportional to the number