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# Formation of mixed Eu(III)-CO<sub>3</sub>-fulvic acid complex: spectroscopic evidence and NICA-Donnan modeling.

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## Abstract

Humic substances impact the fate of radionuclides in the environment. The formation of mixed complexes between lanthanides(III), carbonates, and humic substances is still a matter of debate and further studies are needed. Time-resolved luminescence spectroscopy (TRLS) is used to evidence the presence of Eu(III)-CO<sub>3</sub>-SRFA ternary complexes in media representative of environmental conditions. The evolutions of the Eu(III) luminescence spectra from the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub> to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transitions are showing

modifications of the asymmetry ratio — area ratio of the  ${}^5D_0 \rightarrow {}^7F_2$  over the  ${}^5D_0 \rightarrow {}^7F_1$  transition — that indicates the presence of several species in addition to the  $\text{EuCO}_3^+$  and Eu-SRFA complexes. The occurrence of bi-exponential decay times, with one decay time faster than the one from  $\text{Eu}^{3+}$ , is typical of the occurrence of fulvic complex, even in the presence of carbonate. The analyses of the indirect excitation of the Eu- $\text{CO}_3$ -SRFA system are used to build complexation isotherms varying either SRFA or total carbonate concentrations in the framework of the NICA-Donnan modeling of the Eu(III)-SRFA system. In view of the restricted pH range, no strict attribution to the different possible types of sites can be done. Different complex(es) formations are considered and discussed.

## **1. Introduction**

Natural organic matter (NOM) plays an important role on geochemical cycle of trace metal elements. In natural waters and soils, NOM is mainly composed of humic substances (HS) that consists of humic (HA), fulvic (FA) acids, and humin (Thurman, 1985). Among other elements, radionuclides involved in the nuclear cycle — e.g. lanthanides (Ln) and actinides (An) at their +III redox state — are known since long to be impacted by HS (Bertha and Choppin, 1978; Brevet et al., 2009; Buckau et al., 1992; Czerwinski et al., 1996; Dierckx et al., 1994; Glaus et al., 1995; Janot et al., 2011; Janot et al., 2013; Johannesson et al., 2004; Kim et al., 1989; Kim et al., 1991; Kim et al., 1993; Kouhail et al., 2016; Lead et al., 1998; Marang et al., 2008; Marang et al., 2009; Morgenstern et al., 2000; Moulin et al., 1987; Panak et al., 1996; Pourret et al., 2007a; Pourret et al., 2007b; Rabung and Geckeis, 2009; Reiller and Brevet, 2010; Tang and Johannesson, 2003; Torres and Choppin, 1984). Lanthanides(III), part of the rare earth family and widely used in the industry (Binnemans et al., 2013), are good chemical

analogues of actinides(III) for complexation with oxygen containing functions (Pearson, 1963), due to their similar ionic radii over charge ratios. Some lanthanides(III) isotopes are also fission products from nuclear fuels. Therefore, the knowledge of their speciation in presence of HS is a key point for the global understanding of their aqueous geochemistry. In near neutral and mildly alkaline solutions, hydroxides and carbonates are the main inorganic ligands of lanthanides, and carbonate complexes are known to be predominant (Goldstein and Jacobsen, 1988; Smedley, 1991; Tang and Johannesson, 2010). Competition reactions between these inorganic ligands and organic matter for lanthanides complexation are not always well known. Simulation and modeling calculation done previously (Tang and Johannesson, 2003) report that organic complexes are predominant over a wide range of pH.

HS interactions with metals as a function of pH and anionic ligands concentration could lead to the formation of ternary complexes (Dierckx et al., 1994; Glaus et al., 1995; Morgenstern et al., 2000; Panak et al., 1996; Tipping et al., 2002; Weber et al., 2006b). Panak et al. (1996) and Morgenstern et al. (2000) highlighted the formation of ternary complexes of Am(III) and Cm(III) from spectroscopic data and proposed interaction constants for  $An(III)(OH)_nHA$  (Morgenstern et al., 2000; Panak et al., 1996), and  $Cm(CO_3)HA$  (Panak et al., 1996) in the framework of the charge neutralization model (Kim and Czerwinski, 1996). The carbonate mixed complex has been applied to Eu(III) by direct analogy (Tan et al., 2008) with no account of the slight difference between  $(Ln, An)(CO_3)_n^{(3-2n)+}$  complexes (Fanghänel et al., 1999; Hummel et al., 2002; Thoenen et al., 2014). Because of this strong analogy between Am/Cm(III) and Eu(III), same types of complexes are expected for Eu(III). Pourret *et al.* (2007a; 2007b) showed that rare earth elements are predominantly complexed with HS up to pH approx. 7.5, and stated that

there were no  $\text{Ln}(\text{CO}_3)_n\text{HA}$  mixed complexes — contradicting other propositions (Dierckx et al., 1994; Glaus et al., 1995) — starting from  $\text{Ln}(\text{CO}_3)_2^-$  species under their experimental conditions. It is worthy to notice that the authors did not compare their results with the ones from Panak et al. (1996). However, analysis of the raw data from Pourret et al. (2007a) moderates the conclusions on the non-existence of these mixed complexes (Reiller, 2015).

One of the most effective model that describes metal complexation by NOM is the Non-Ideal Competitive Adsorption model coupled to a Donnan approach of electrostatic behavior (NICA-Donnan) (Benedetti et al., 1995; Benedetti et al., 1996a; Benedetti et al., 1996b; Kinniburgh et al., 1999). Generic and origin specific parameters have been estimated for HA and FA in Milne et al. (2001) for  $\text{H}^+$  interaction, and in Milne et al. (2003) for metal cations interactions. The formation of mixed complexes between metals, and particularly Ln/An(III), inorganic anions, and humic substances is thus still not completely settled. If the formation of Eu(III)-OH-FA complexes is not needed in the framework of NICA-Donnan modeling (Janot et al., 2013; Kouhail et al., 2016), the competition, or mixed complex formation, with  $\text{CO}_3^{2-}$  still remains under controversy.

In order to provide further information, the system Eu(III)- $\text{CO}_3$ -FA at pH ca. 7 is studied using time-resolved luminescence spectroscopy (TRLS), with Suwannee River fulvic acid (SRFA) as a proxy for NOM reactivity, and Eu(III) as a representative of Ln(III) and An(III). Starting from our former characterization of the Eu-SRFA system (Kouhail et al., 2016), the evolution of both the Eu(III) fluorescence spectra and decay times at varying  $\text{CO}_3^{2-}$  and SRFA concentrations are obtained and analyzed. From these experiments, calculations are done using the NICA-Donnan model to discuss on complexation

constants that should be incorporated in speciation models to account for the formation of these complexes in natural environment.

## **2. Materials and methods**

### ***2.1. Reagents and chemicals***

Stock solutions and reagents are the same as those used in Kouhail et al. (2016). Europium(III) stock solution ( $10^{-4}$  mol L<sup>-1</sup> or M) is obtained from the dissolution of Eu<sub>2</sub>O<sub>3</sub> (Johnson Matthey, 99.99%) in HClO<sub>4</sub>. All solutions are prepared using milli-Q water from a Direct Q3 Millipore. Suwannee River fulvic acid (2S101F) is purchased from the International Humic Substances Society and used as received. Carbonate solutions are prepared using Na<sub>2</sub>CO<sub>3</sub> (Fluka, 99.5%). The ionic strength is fixed with NaClO<sub>4</sub> (Sigma Aldrich, >98%) at 0.1 M. The pH values are fixed at values ca. 7 by the addition of small amounts of freshly prepared 0.1 M NaOH and/or HClO<sub>4</sub>. Measurements are done using a pH meter Seven Easy (Mettler Toledo) with a combined glass electrode Inlab micro, filled with NaClO<sub>4</sub> 3 M to avoid KClO<sub>4</sub> precipitation in the frit of the electrode with the original KCl filling and outer calibration — plotting E vs. pH at  $(22 \pm 1)$  °C — is done using commercial buffer solutions (pH 4.01, 7.01, and 10.00). The uncertainties are better than 0.08 pH-units — the grand average of all the experiments gives pH  $6.99 \pm 0.03$ .

### ***2.2. Time-resolved luminescence spectroscopy***

The experimental set-up and luminescence decay times fitting have already been described elsewhere (Brevet et al., 2009; Janot et al., 2011; Janot et al., 2013; Kouhail et al., 2016; Reiller and Brevet, 2010). Spectra were obtained in a thermostated room ( $22 \pm 1$  °C) in quartz fluorescence cuvettes (Hellma QS-111-10-40) with a minimum free space

to consider the system as closed to the atmospheric CO<sub>2</sub>. The 600 lines/mm grating of the Acton spectrometer (slit 1 mm) is used. The luminescence signal is collected during a gate width ( $W$ ) of 300  $\mu$ s, at a gate delay ( $D$ ) of 10  $\mu$ s after the excitation by the laser flash. To increase the signal to noise ratio 2 000 to 5 000 accumulations are performed for each spectrum, the background noise is subtracted, and the luminescence is divided by the average of 100 laser-shots energy, and by the number of acquisitions (accumulations).

Because of the weak energy received by the system during the experiments, photochemical reactions of humic substances (Monsallier et al., 2001) can be excluded. The excitation wavelength is set using an optical parametric oscillator. Several excitation wavelengths ( $\lambda_{exc}$ ) were used either to excite selectively Eu(III) through the  $^5L_6 \leftarrow ^7F_0$  transition ( $\lambda_{exc} = 393.7$  nm), to take advantage of the antenna effect from the ligand (Alpha et al., 1990) — here the fulvic acid chromophores ( $\lambda_{exc} = 390$  nm) —, or to minimize the excitation of the fulvic complex ( $\lambda_{exc} = 532$  nm). The energy is typically < 1 mJ for all excitation wavelengths. We typically focused our attention on three transitions: the  $^5D_0 \rightarrow ^7F_0$  transition ( $\lambda_{max} \approx 578.8$  nm), forbidden by the selection rules but apparent when Eu(III) chemical environment loses its centro-symmetry; the  $^5D_0 \rightarrow ^7F_1$  transition ( $\lambda_{max} \approx 591.1$  nm), a magnetic dipole transition; and the  $^5D_0 \rightarrow ^7F_2$  electric dipole transition ( $\lambda_{max} \approx 615.1$  nm), which is very sensitive to europium speciation (Jørgensen and Judd, 1964), and known as a hypersensitive transition. The luminescence decay parameters are obtained from the peak area of either the  $^5D_0 \rightarrow ^7F_1$  or the  $^5D_0 \rightarrow ^7F_2$  transition at varying  $D$  values with the same  $W$ . The obtained decay is described by a first order kinetics, and for a purely integrative system like a CCD camera, the luminescence signal of a species  $i$  is given by equation (1):

$$F_i = \sum_{i=1}^n \int_D^{D+W} F_i^0 \exp\left(-\frac{t}{\tau_i}\right) dt = \sum_{i=1}^n F_i^0 \tau_i \exp\left(-\frac{D}{\tau_i}\right) \left[1 - \exp\left(-\frac{W}{\tau_i}\right)\right] \quad (1)$$

where  $F_i^0$  and  $\tau_i$  are the initial luminescence intensity and decay time of the species  $i$ , respectively. They were obtained by a non-linear fitting of the experimental results ( $F_i$ ), at varying  $D$  values — typically 15  $\mu$ s steps — to equation (1).

The area of the transitions, and according uncertainties, are calculated using the trapezoid method. The uncertainty of the  ${}^5D_0 \rightarrow {}^7F_2 / {}^5D_0 \rightarrow {}^7F_1$  area ratio — the asymmetry ratio denoted  ${}^7F_2 / {}^7F_1$  —, is calculated from the propagation of errors.

### ***2.3. Thermodynamic constants***

The inorganic side reactions and solubility of Eu(III) with  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  selected in Hummel et al. (2002), and kept in Thoenen et al. (2014), given in Table 1 were used — these data were used in coherence with our other studies (Fromentin and Reiller, 2018; Janot et al., 2013; Kouhail et al., 2016). No enthalpy of reaction for the formation of  $\text{EuCO}_3^+$  or  $\text{Eu}(\text{CO}_3)_2^-$  were selected in Hummel et al. (2002).

**Table 1. Thermodynamic constants used in this work.**

Equilibrium	$\log_{10}\beta^\circ$	References
$\text{Eu}^{3+} + \text{OH}^- \rightleftharpoons \text{EuOH}^{2+}$	$6.36 \pm 0.04^a$	Hummel et al. (2002)
$\text{Eu}^{3+} + 2\text{OH}^- \rightleftharpoons \text{Eu}(\text{OH})_2^+$	$12.9 \pm 0.2^a$	Hummel et al. (2002)
$\text{Eu}^{3+} + 3\text{OH}^- \rightleftharpoons \text{Eu}(\text{OH})_3(\text{aq})$	$18.3 \pm 0.1^a$	Hummel et al. (2002)
$\text{Eu}^{3+} + \text{CO}_3^{2-} \rightleftharpoons \text{EuCO}_3^+$	$8.1 \pm 0.2$	Hummel et al. (2002)
$\text{Eu}^{3+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Eu}(\text{CO}_3)_2^-$	$12.1 \pm 0.3$	Hummel et al. (2002)
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	$-6.35 + 0.02$	Guillaumont et al. (2003)
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + 2\text{H}^+$	$-16.68 \pm 0.02$	Guillaumont et al. (2003)
Solubility	$\log_{10}K_s^\circ$	
$\text{Eu}(\text{OH})_3(\text{am}) \rightleftharpoons \text{Eu}^{3+} + 3\text{OH}^-$	$-24.4 \pm 0.8$	Hummel et al. (2002)
$\text{EuOHCO}_3(\text{cr}) \rightleftharpoons \text{Eu}^{3+} + \text{OH}^- + \text{CO}_3^{2-}$	$-21.7 \pm 0.1$	Hummel et al. (2002)

<sup>a</sup> Original constants in Hummel et al. (2002) are given relative to H<sub>2</sub>O; as constants used in ECOSAT (Keizer and van Riemsdijk, 1994) are better given relative to OH<sup>-</sup>, thermodynamic constants are calculated using  $K_w$ , and the number of significant digits from the original constants relative to H<sub>2</sub>O.

## 2.4. NICA-Donnan modeling

The NICA-Donnan model merges the Non-Ideal Competitive Adsorption (NICA) model with a continuous distribution of sites — see Benedetti et al. (1995), and references therein —, and a Donnan potential description to account for electrostatic interactions within the structure of HS (Benedetti et al., 1996a). The model extensively described and discussed elsewhere (Benedetti et al., 1996a; Benedetti et al., 1996b; Kinniburgh et al., 1999; Koopal et al., 2005), accounts for sites heterogeneity, non-ideality of the metal-HS complexation, and competition between metals. It will be briefly recalled here.

In the Donnan approach, humic substances are considered as an electrostatically neutral gel phase with a constant electrostatic Donnan potential,  $\Psi_D$ . The “structural charges” of humic substances are compensated by the counter-ions. Outside the Donnan gel structure,  $\Psi_D = 0$ . The activities in the gel phase in the gel  $a_{i,D}$  and in the bulk solution  $a_i$  are linked by a Boltzmann factor.

$$C_{i,D} = C_i \exp\left(-\frac{z_i F \Psi_D}{RT}\right) \quad (2)$$

As the phase is electrically neutral:

$$\frac{q}{V_D} + \sum_i z_i (a_{i,D} - a_i) = 0 \quad (3)$$

where  $V_D$  is the volume of the Donnan phase,  $q$  is the charge of the humic substance extract and  $z_i$  the charge on the considered cation. For  $q$  values vs. pH for a known concentration of electrolyte,  $\Psi_D$  can be determined if  $V_D = f(\text{pH}, C_s)$  is known — where  $C_s$  is the concentration of the background electrolyte. Practically, this value can only be estimated by the Einstein law, with the approximation of a “simple” form. Benedetti et al. (1996a) showed a logarithmic dependence between  $V_D$  and ionic strength.

$$\log_{10} V_D = b (1 - \log_{10} V_D) - 1 \quad (4)$$

Within the Donnan phase, the cations complexation occurs with a distribution of sites.

The quantity of fixed cations on the total number of sites  $\theta_{i,T}$  is described by

$$\theta_{i,T} = \int_{\Delta \log_{10} K_i} \theta_{i,L} f(\log_{10} K_i) d(\log_{10} K_i) \quad (5)$$

where  $\theta_{i,L}$  is the fixed quantity on a site  $i$ ,  $f(\log_{10} K_i)$  is the continuous distribution function of sites.

From the Sips' equation (Sips, 1948; Sips, 1950), Koopal et al. (1994) have applied a Henderson-Hasselbach treatment and proposed a general equation in the case of a cation  $i$  in competition with other species on a distribution of sites. As the model requires the electroneutrality of the phase, the complexation of an ion must be followed by the release

of another cation. Kinniburgh et al. (1999) have proposed the normalization to the following expression for two distributions,

$$Q_{i,T} = \sum_j \left( \frac{n_{i,j}}{n_{H,j}} Q_{\max i,j} \right) \frac{(\tilde{K}_{i,j} C_{D,i})^{n_{i,j}}}{\sum_i (\tilde{K}_{i,j} C_{D,i})^{n_{i,j}}} \frac{(\sum_i (\tilde{K}_{i,j} C_{D,i})^{n_{i,j}})^{p_j}}{1 + (\sum_i (\tilde{K}_{i,j} C_{D,i})^{n_{i,j}})^{p_j}} \quad (6)$$

with  $Q_{i,T}$  the total quantity of a compound  $i$  fixed to humic substances ( $\text{mol kg}_{\text{HS}}^{-1}$ ),  $Q_{\max}$  the maximum number of available sites ( $\text{mol kg}_{\text{HS}}^{-1}$ ),  $C_{D,i}$  the concentration of  $i$  in the Donnan phase,  $\tilde{K}_i$  the median affinity value of species  $i$  in the distribution,  $p_j$  the width of the  $j$ th distribution or its intrinsic heterogeneity (the same for all the cations) ( $0 \leq p_j \leq 1$ ), and  $n_{i,j}$  the heterogeneity or non-ideality of the ion  $i$  within the  $j$ th distribution ( $0 \leq n_{i,j} \leq 1$ ). The parameter  $n_{i,j}$  can be viewed as an inverse of stoichiometry (Koopal et al., 2005). This expression is actually rather equivalent to a Langmuir-Freundlich isotherm. In the case of  $\text{H}^+$ , only the product  $m_{\text{H}^+,j} = n_{\text{H}^+,j} \cdot p_j$  can be experimentally obtained. Parameters  $n_{\text{H}^+,j}$ ,  $p_j$ , and  $n_{i,j}$  for other cations are determined from titration of the humic substance and from complexometric experiments.

Calculations — simulation and modeling — of Eu-SRFA interactions were performed using ECOSAT software (Keizer and van Riemsdijk, 1994), which includes speciation of inorganic ligands — activity coefficients calculated through the Davies (1962) equation, and humic substances through the NICA-Donnan model; generic data for HA and FA interaction with protons (Milne et al., 2001), and several metal cations of interest, including Ln(III) (Milne et al., 2003) were proposed. Thermodynamic constants from Table 1 were implemented in the ECOSAT database. Site densities of the two distributions of sites of SRFA, parameters representing the intrinsic heterogeneity ( $p_j$ ), generic proton median affinity constants ( $\log_{10} \tilde{K}_i$ ), non-ideality parameter ( $n_{i,j}$ ) and Donnan volume

parameter (b) for low-affinity type of sites,  $S_1$ , and high-affinity type of sites ( $S_2$ ) (Milne et al., 2001) and the same parameters for europium(III) (Kouhail et al., 2016) are recalled in Table 2.

**Table 2. NICA-Donnan parameters for proton binding to a fulvic acid from Milne et al. (2001), and Eu(III) given in Kouhail et al. (2016).**

	$Q_{\max,1}$ (mol.kg <sub>FA</sub> <sup>-1</sup> )	$n_{M,1}$	$\log_{10}\tilde{K}_{M,1}$	$p_1$	$Q_{\max,2}$ (mol.kg <sub>FA</sub> <sup>-1</sup> )	$n_{M,2}$	$\log_{10}\tilde{K}_{M,2}$	$p_2$	b	References
H <sup>+</sup>	5.88	0.66	2.34	0.59	1.86	0.76	8.60	0.70	0.57	Milne et al. (2001)
Eu <sup>3+</sup>		0.53	-1.11			0.40	6.92			Kouhail et al. (2016)

### 3. Results

Varying total carbonate,  $[\text{CO}_3]_{\text{total}} - [\text{CO}_2(\text{aq})] = 15.07\%$ ,  $[\text{HCO}_3^-] = 84.85\%$  and  $[\text{CO}_3^{2-}] = 0.08\%$  at pH ca. 7,  $I = 0.1 \text{ M}$ , and  $22^\circ\text{C}$  from thermodynamic data in Guillaumont et al. (2003) —, and SRFA concentrations,  $C_{\text{SRFA}}$ , it is possible to favor some europium complexes from others. Results for Eu(III)-SRFA from Kouhail et al. (2016) are recalled, then Eu(III)-CO<sub>3</sub> binary systems are presented. Afterwards, comparisons are done with Eu-CO<sub>3</sub>-SRFA ternary systems, for various  $C_{\text{SRFA}}$  and  $[\text{CO}_3]_{\text{total}}$ . Spectra, decay times, variations of the relative intensity of the area  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  to the area  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition — referred thereafter as the asymmetry ratio  $^7\text{F}_2/^7\text{F}_1$  — and NICA-Donnan calculations of the different europium complexes are presented below, where spectral and temporal interpretations will be attempted. For the sake of comparison, the luminescence spectra are normalized to the peak area of the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition. Eu(III) luminescence decay times are measured with  $D = 10 \mu\text{s}$ , a gate step of  $15 \mu\text{s}$ , and  $W = 300 \mu\text{s}$  for  $C_{\text{Eu(III)}} = 10 \mu\text{M}$ , pH ca. 7,  $I = 0.1 \text{ M NaClO}_4$ .

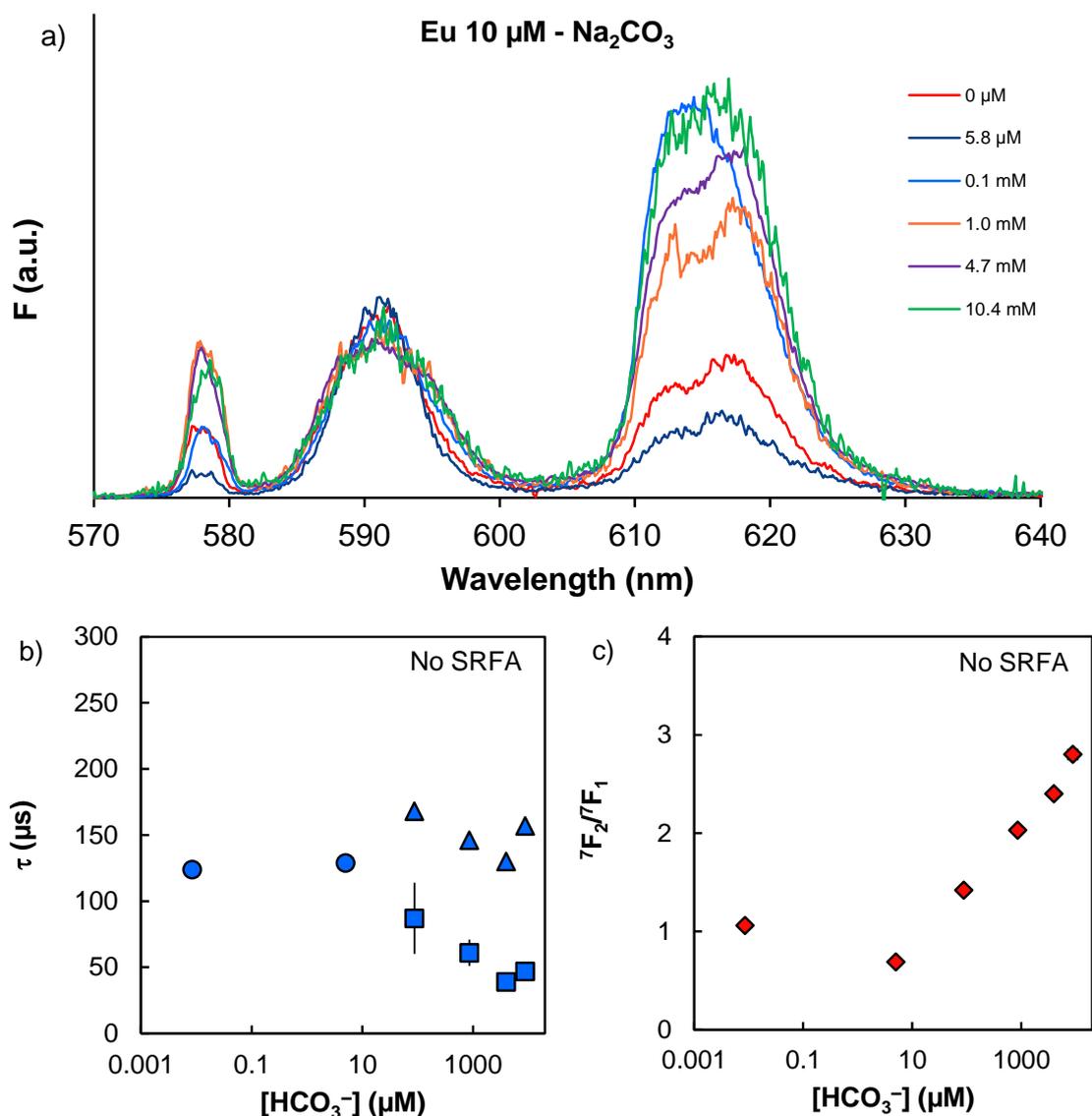
### **3.1. Binary systems**

#### **3.1.1. Eu-SRFA binary system**

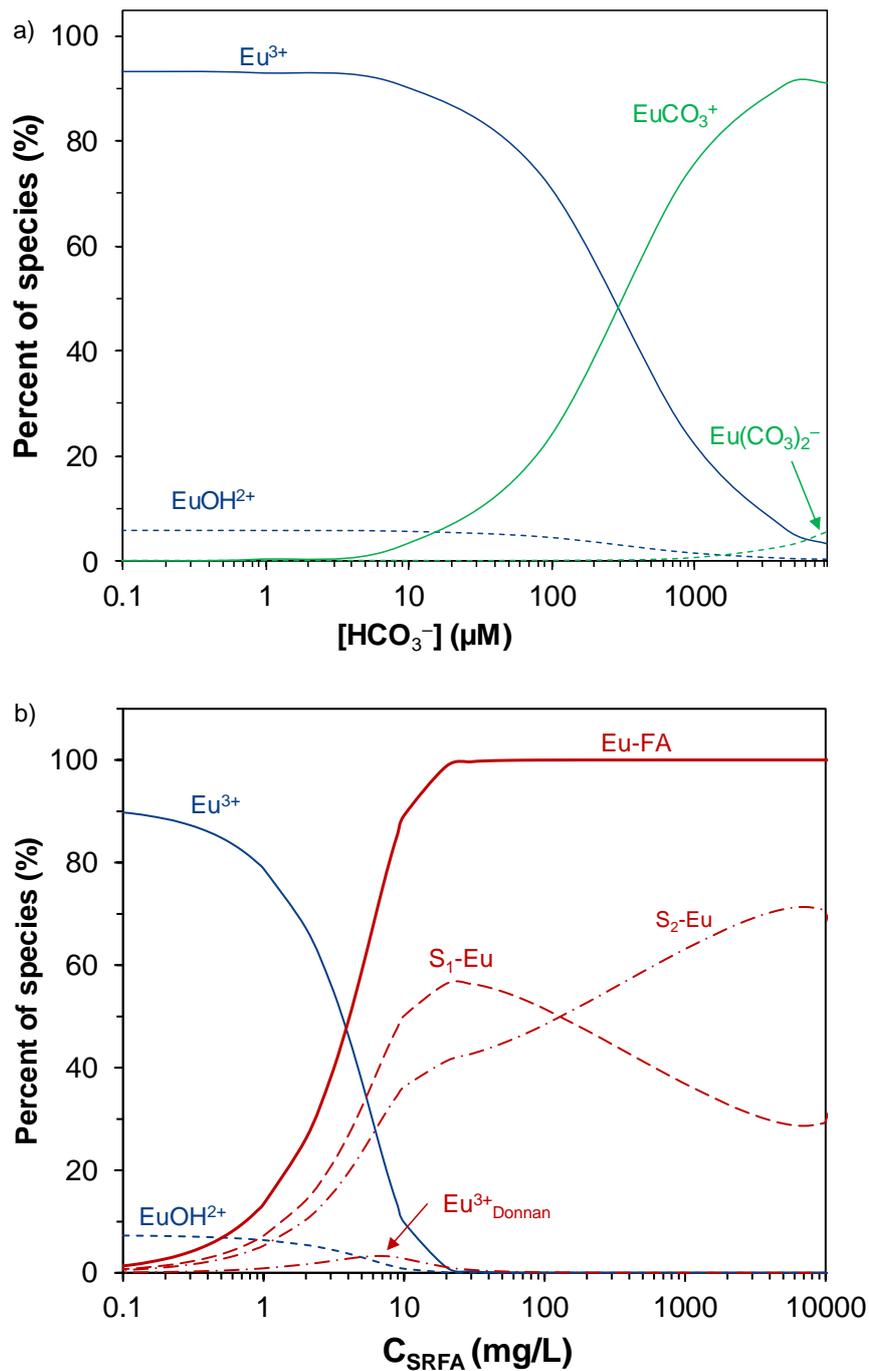
Eu(III)–SRFA complexation has been investigated in Kouhail et al. (2016) at different  $C_{\text{Eu(III)}}$ , pH and ionic strength values. Complexation of Eu(III) in this system was evidenced by the typical increase of both the forbidden  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  and the hypersensitive  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transitions (cf. Figure S1 from Kouhail et al., 2016). More details about spectra, decays and modeling of the Eu-SRFA complexation were given in Kouhail et al. (2016).

#### **3.1.2. Eu-CO<sub>3</sub> binary system**

The Eu-CO<sub>3</sub> binary system is first studied before further characterization of Eu-CO<sub>3</sub>-SRFA ternary systems. From spectra with various total carbonate concentrations (Figure 1a) and from theoretical speciation calculations (Figure 2a), it is possible to identify the influence of the different inorganic complexes. Within the  $\text{HCO}_3^-$  concentration range in Figure 2a, the proportion of  $\text{Eu}(\text{CO}_3)_n^{(3-2n)+}$  is always minor compared to total inorganic carbon. When adding  $[\text{CO}_3]_{\text{total}} = 5.8 \mu\text{M}$  — i.e.  $[\text{HCO}_3^-] = 4.9 \mu\text{M}$  —, both  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition intensities are decreasing due to the presence of carbonates — although  $< 1\%$  of  $\text{EuCO}_3^+$  is predicted. For a  $[\text{CO}_3]_{\text{total}}$  of  $0.1 \text{ mM}$  — i.e.  $[\text{HCO}_3^-] = 85 \mu\text{M}$  —, the intensity of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  is similar to the one of Eu(III) without carbonate, whereas the relative intensity of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  hypersensitive transition strongly increases.



**Figure 1.** Spectroscopic data of Eu(III)-CO<sub>3</sub> binary system vs. carbonate concentrations: (a) luminescence spectra normalized to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> transition area for total carbonate concentrations; (b) luminescence decay times for mono exponential decay (circles), and for bi-exponential decay times (squares and diamonds) vs. HCO<sub>3</sub><sup>-</sup> concentration; (c) Evolution of <sup>7</sup>F<sub>2</sub>/<sup>7</sup>F<sub>1</sub> area ratio vs. HCO<sub>3</sub><sup>-</sup> concentration; C<sub>Eu(III)</sub> = 10 μM, I = 0.1 M NaClO<sub>4</sub>, pH ca. 7, λ<sub>exc</sub> = 393.7 nm, D = 10 μs, W = 300 μs, 600 lines/mm grating.



**Figure 2. Speciation of Eu(III) in solution in Eu- $\text{CO}_3$  binary system depending on  $[\text{HCO}_3^-]$  (a), and speciation of Eu(III) in Eu-SRFA binary system depending on  $C_{\text{SRFA}}$  (b):  $C_{\text{Eu(III)}} = 10 \mu\text{M}$ , pH ca. 7, and  $I = 0.1 \text{ M NaClO}_4$ ; species  $< 2\%$  are not plotted; thermodynamic constants from Table 1, and NICA-Donnan parameters from Table 2.**

For higher  $[\text{CO}_3]_{\text{total}}$ ,  $\text{EuOHCO}_3(\text{s})$  becomes oversaturated and may precipitate. All our experiments were done under oversaturated conditions, i.e. up to two days after sample preparation. After that timeframe, TRLS signals were varying and solutions were changed if necessary. For a  $[\text{CO}_3]_{\text{total}}$  of 1 mM, the relative intensity of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  increases compared to the one of  $\text{Eu(III)-CO}_3$  at 0.1 mM of  $\text{CO}_3 - [\text{HCO}_3^-] = 85 \mu\text{M}$  —, and the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition intensity decreases. For higher  $[\text{CO}_3]_{\text{total}}$ , the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  remains constant while the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  increases. For  $[\text{CO}_3]_{\text{total}} = 4.7$  and 10.4 mM —  $[\text{HCO}_3^-] = 4.0$  and 8.8 mM, respectively —, 90% of Eu is calculated to be under the form of  $\text{EuCO}_3^+$  complexes (Figure 2a). The differences observed on the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  are likely due to the increase of  $\text{Eu}(\text{CO}_3)_2^-$  complex in solution —  $\text{Eu}(\text{CO}_3)_2^-$  complexes should represent around 3% of Eu(III) at  $[\text{CO}_3]_{\text{total}} = 4.7$  mM, and 6% at  $[\text{CO}_3]_{\text{total}} = 10.4$  mM — see above for corresponding  $[\text{HCO}_3^-]$ . The occurrence of sub-structures in the spectra is revealing changes in the symmetry around Eu(III). The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition is showing a broadening with  $[\text{CO}_3]_{\text{total}}$ . We estimated the wavelength evolution of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition maxima from a fit of the luminescence emission spectra  $F(\lambda)$  for the different experiments, as previously done in the literature for Eu-HS systems (Brevet et al., 2009; Janot et al., 2013). The spectra were considered as a sum of Lorentz-Gaussian function (Davis et al., 1972; McNemar and Horrocks, 1989) where the luminescence emission spectra  $F(\lambda)$  are given by equation (7),

$$F(\lambda) = \sum_i F_{\text{max},i} \frac{\exp \left[ -0.5 \left( \frac{\lambda - \lambda_{0,i}}{\sigma_i} \right)^2 \right]}{\left( \frac{\lambda - \lambda_{0,i}}{\sigma_i} \right)^2 + 1} \quad (7)$$

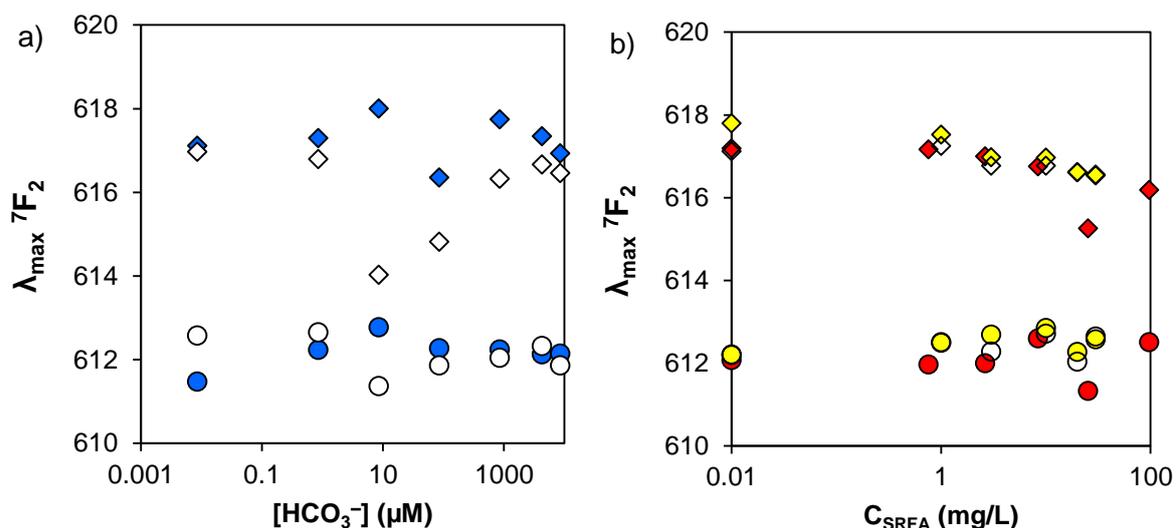
where  $F_{\text{max},i}$  is the maximum intensity,  $\lambda_{0,i}$  is the center wavelength and  $\sigma_i$  is the standard deviation, linked to the full-width at mid-height  $w_i = 1.46 \sigma_i$ , of the  $i^{\text{th}}$  component's

luminescence. Two to four components were needed to fit the  ${}^5D_0 \rightarrow {}^7F_2$  transition, as shown in Figure S1 to Figure S5 of the SI — no attribution to Stark levels were made —, and the fitting parameters and correlation matrices are given in Table S1 to Table S10 the SI. The  ${}^5D_0 \rightarrow {}^7F_2$  hypersensitive transition splits into two main contributions centered approximately around 612 and 618 nm (Figure 3), the latter being slightly more intense as observed previously (Vercouter, 2005). These observations on spectra are typical to the presence of  $\text{EuCO}_3^+$  complexes in solution (Moulin et al., 1999; Vercouter, 2005).

Decay times of Eu-CO<sub>3</sub> binary system (Figure 1b) are showing two different features. Eu(III) is showing a mono-exponential decay up to  $[\text{CO}_3]_{\text{total}} = 10 \mu\text{M}$  —  $[\text{HCO}_3^-] = 8.5 \mu\text{M}$ . The  $\tau$  approx. 130  $\mu\text{s}$  values are slightly higher than the free  $\text{Eu}^{3+}$  one. For higher  $[\text{CO}_3]_{\text{total}}$ , bi-exponential decays are obtained. The first decay  $\tau_1$  is faster than free  $\text{Eu}^{3+}$ , the second decay,  $\tau_2$ , is slower than free  $\text{Eu}^{3+}$ , and is ranging from 130 to 168  $\mu\text{s}$  — from 7.6 to  $5.7 \pm 0.5$  remaining H<sub>2</sub>O molecules using equation from Kimura and Choppin (1994). Bi-exponential decay time evolutions were not reported in previous spectroscopic studies of Eu(III)-CO<sub>3</sub> systems (Moulin et al., 1999; Vercouter, 2005). A non-exponential behavior of the decay time suggests the existence of two different excited states. The faster than  $\text{Eu}^{3+}$  decay time was up to now only observed in the case of organic complexes that contained phenolic moieties (Brevet et al., 2009; Burek et al., 2017; Kuke et al., 2010; Moreau et al., 2015; Plancque et al., 2005; Primus and Kumke, 2012; Reiller and Brevet, 2010). This should require further works.

The asymmetry ratio  ${}^7F_2/{}^7F_1$  of Eu-CO<sub>3</sub> binary system (Figure 1c) is increasing with  $[\text{CO}_3]_{\text{total}}$ . Since no plateau is reached, the asymmetry ratio cannot be used as a spectral titration curve (Dobbs et al., 1989). The asymmetry ratio keeps on increasing with  $[\text{CO}_3]_{\text{total}}$  as observed by Vercouter (2005). One can notice that the asymmetry ratio

values for Eu-SRFA and Eu-CO<sub>3</sub> binary systems, when Eu(III) is fully bound to SRFA (Figure 2b) or fully bound to CO<sub>3</sub><sup>2-</sup> (Figure 2a), are very close — <sup>7</sup>F<sub>2</sub>/<sup>7</sup>F<sub>1</sub> approx. 3 for C<sub>SRFA</sub> ca. 20 mg<sub>SRFA</sub>/L (cf. Figure 1c from Kouhail et al., 2016) and for a total carbonate concentration of 10 mM ([HCO<sub>3</sub><sup>-</sup>] = 8.5 mM, Figure 1c).



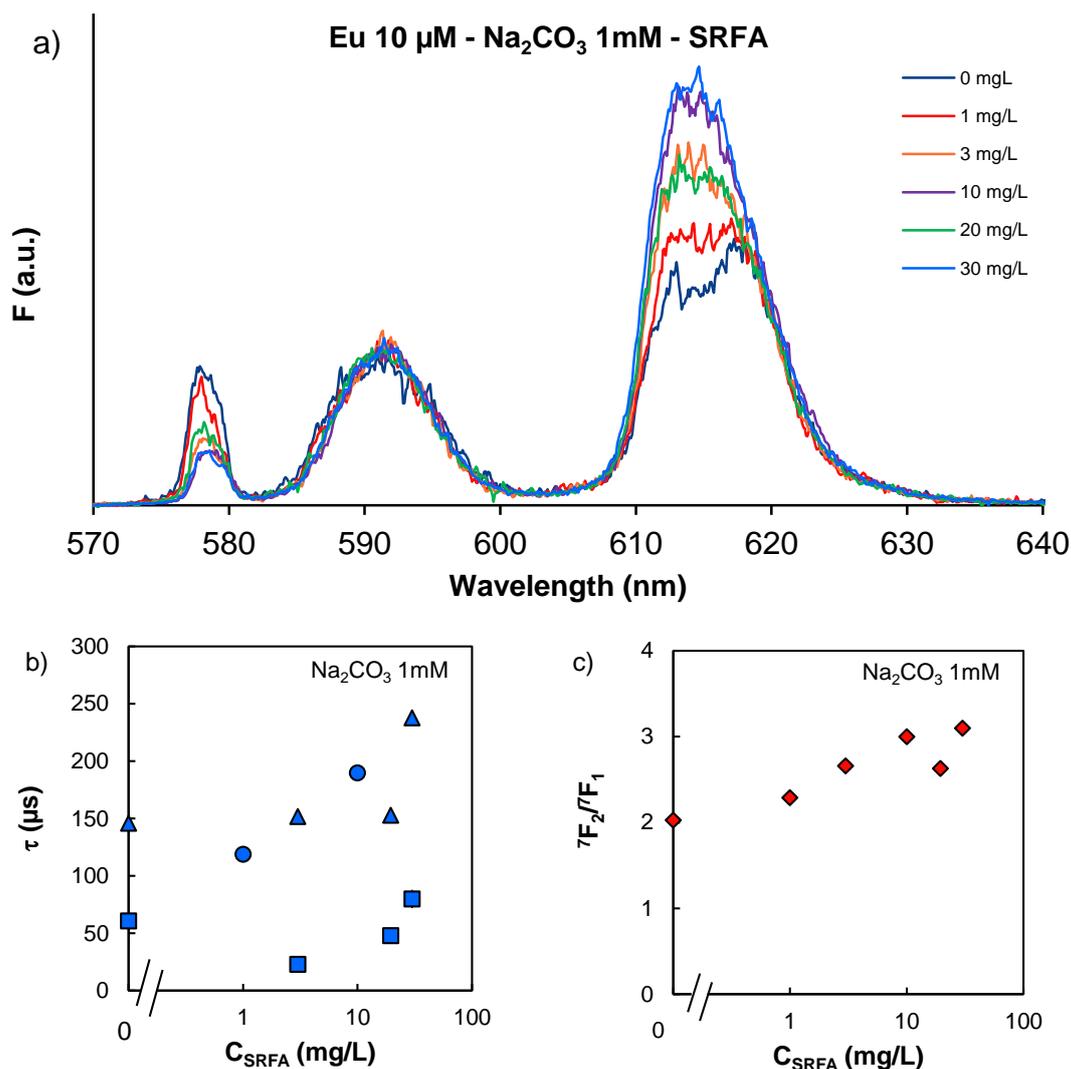
**Figure 3. Wavelength evolution of the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition maxima estimated from a fit to a sum of Lorentz-Gaussian function vs. pH in the different systems studied: C<sub>Eu(III)</sub> = 10 μM, I = 0.1 M NaClO<sub>4</sub>, pH ca. 7, λ<sub>exc</sub> = 393.7 nm, D = 10 μs, W = 300 μs, 600 lines/mm grating: a) the wavelengths maxima of the Eu-CO<sub>3</sub> binary system and the Eu-CO<sub>3</sub>-SRFA ternary system with a fixed C<sub>SRFA</sub> of 20 mg/L are represented respectively in blue and in white symbols; b) the wavelengths maxima of the Eu-SRFA binary system and the Eu-CO<sub>3</sub>-SRFA ternary system with a fixed carbonate concentration of 1 and 10 mM — i.e. [HCO<sub>3</sub><sup>-</sup>] = 0.85 and 8.5 mM, respectively — are represented respectively in red, yellow, and empty symbols. The fits to Lorentzian-Gaussian peaks, the parameters of the fits and the correlation matrices for each system are given in Figure S1 to S5 and Table S1 to Table S10 of the SI, respectively.**

### **3.2. *Eu-CO<sub>3</sub>-SRFA ternary systems: influence of total CO<sub>3</sub> concentration***

As noted earlier, the possible precipitation of  $\text{EuOHCO}_3(\text{cr})$  is monitored through the loss of the TRLS signal. For lower  $[\text{CO}_3]_{\text{total}}$ , the experiment were done in less than two days, but for higher  $[\text{CO}_3]_{\text{total}}$ , no change in the TRLS signal was noted. Nevertheless, no solutions older than two days are reported in the following.

#### **3.2.1. Eu-CO<sub>3</sub>-SRFA ternary system with fixed $[\text{CO}_3]_{\text{total}} = 1 \text{ mM}$**

The aim of this experiment is to evaluate the influence of increasing  $C_{\text{SRFA}}$  on Eu-CO<sub>3</sub> complexes. A total carbonate concentration of 1 mM —  $[\text{HCO}_3^-] = 0.85 \text{ mM}$  — was chosen because in the binary system,  $\text{EuCO}_3^+$  is the major complex in solution at pH ca. 7 (Figure 5a). Several evolutions can be seen in Figure 4a, which represents the Eu-CO<sub>3</sub>-FA spectra normalized to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition when varying  $C_{\text{SRFA}}$ . The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ , and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transitions show a progressive narrowing with  $C_{\text{SRFA}}$ . The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  transition relative intensity shows a decrease with  $C_{\text{SRFA}}$  until 10  $\text{mg}_{\text{SRFA}}/\text{L}$ , then an increase at 20  $\text{mg}_{\text{SRFA}}/\text{L}$ , and a decrease again at higher  $C_{\text{SRFA}}$ . The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition relative intensity is showing the exact opposite feature, i.e. an increase with  $C_{\text{SRFA}}$  until 10  $\text{mg}_{\text{SRFA}}/\text{L}$ , then a decrease at 20  $\text{mg}_{\text{SRFA}}/\text{L}$ , and an increase again at higher  $C_{\text{SRFA}}$ . From these observations, one can suppose that Eu(III) is successively under 4 different states: (i)  $\text{EuCO}_3^+$  complex; an intermediate states where Eu(III) is either involved in (ii)  $\text{CO}_3^{2-}$  complexation and in SRFA complexes, or (iii) in a ternary complex with  $\text{CO}_3^{2-}$  and SRFA; and (iv) a final state where  $C_{\text{SRFA}}$  is so important that only Eu-SRFA complexes could exist in solutions. These observations on spectra strongly suggest the presence of Eu-CO<sub>3</sub>-SRFA ternary complexes.

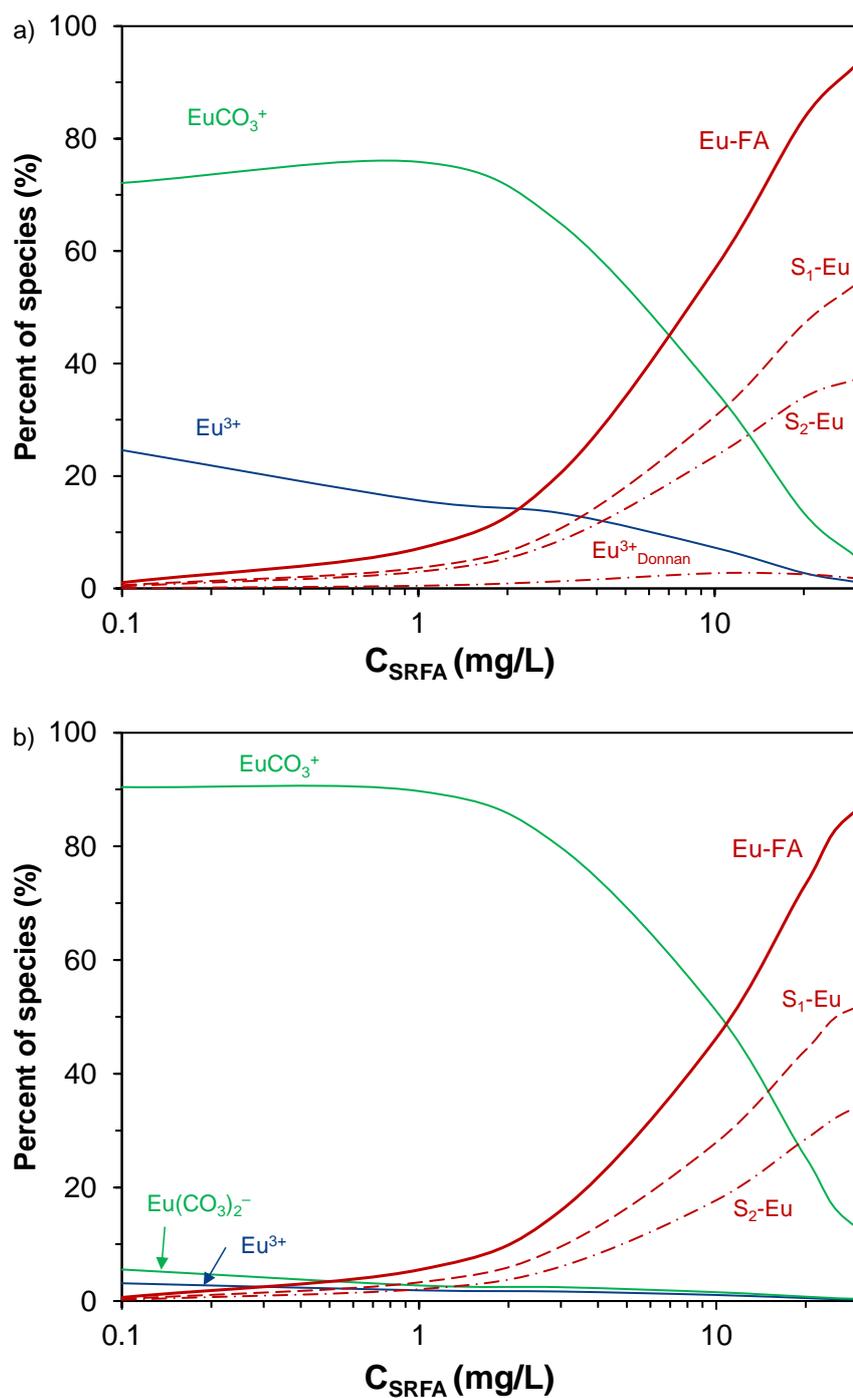


**Figure 4. Spectroscopic data of Eu(III)-CO<sub>3</sub>-SRFA ternary system with fixed [CO<sub>3</sub>]<sub>total</sub> at 1 mM — i.e. [HCO<sub>3</sub><sup>-</sup>] = 0.85 mM —: (a) luminescence spectra normalized to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition; (b) luminescence decay times, with circles symbols for mono exponential decay times, diamonds and squares for bi-exponential decay times; (c) evolution of <sup>7</sup>F<sub>2</sub>/<sup>7</sup>F<sub>1</sub> area ratio; C<sub>Eu(III)</sub> = 10 μM, I = 0.1 M NaClO<sub>4</sub>, pH ca. 7, λ<sub>exc</sub> = 393.7 nm, D = 10 μs, W = 300 μs, 600 lines/mm grating.**

Eu(III) is showing bi-exponential decays for most cases but it is not possible to fit bi-exponential decays for C<sub>SRFA</sub> = 1 and 10 mg<sub>SRFA</sub>/L, conceivably the proportion of one of the decays is not sufficiently prominent (Figure 4b). We can notice that τ<sub>2</sub> seems to

increase up to 238  $\mu\text{s}$  with  $C_{\text{SRFA}}$  — i.e.  $3.9 \pm 0.5$  remaining  $\text{H}_2\text{O}$  molecules according to Kimura and Choppin (1994) — except for  $C_{\text{SRFA}} = 20 \text{ mg}_{\text{SRFA}}/\text{L}$ .

The asymmetry ratios presented in Figure 4c are show an increase with  $C_{\text{SRFA}}$  except for  $C_{\text{SRFA}} = 20 \text{ mg}_{\text{SRFA}}/\text{L}$ . From NICA-Donnan calculations (Figure 5a), one can see that between 10 and 30  $\text{mg}_{\text{SRFA}}/\text{L}$ , only the decrease of inorganic complexes and the increase of SRFA complexes is predicted. This prediction cannot explain the evolutions on Eu- $\text{CO}_3$ -FA spectra when varying  $C_{\text{SRFA}}$ . It seems clear that a ternary Eu- $\text{CO}_3$ -FA complex is needed to explain these evolutions of spectra and decay times.



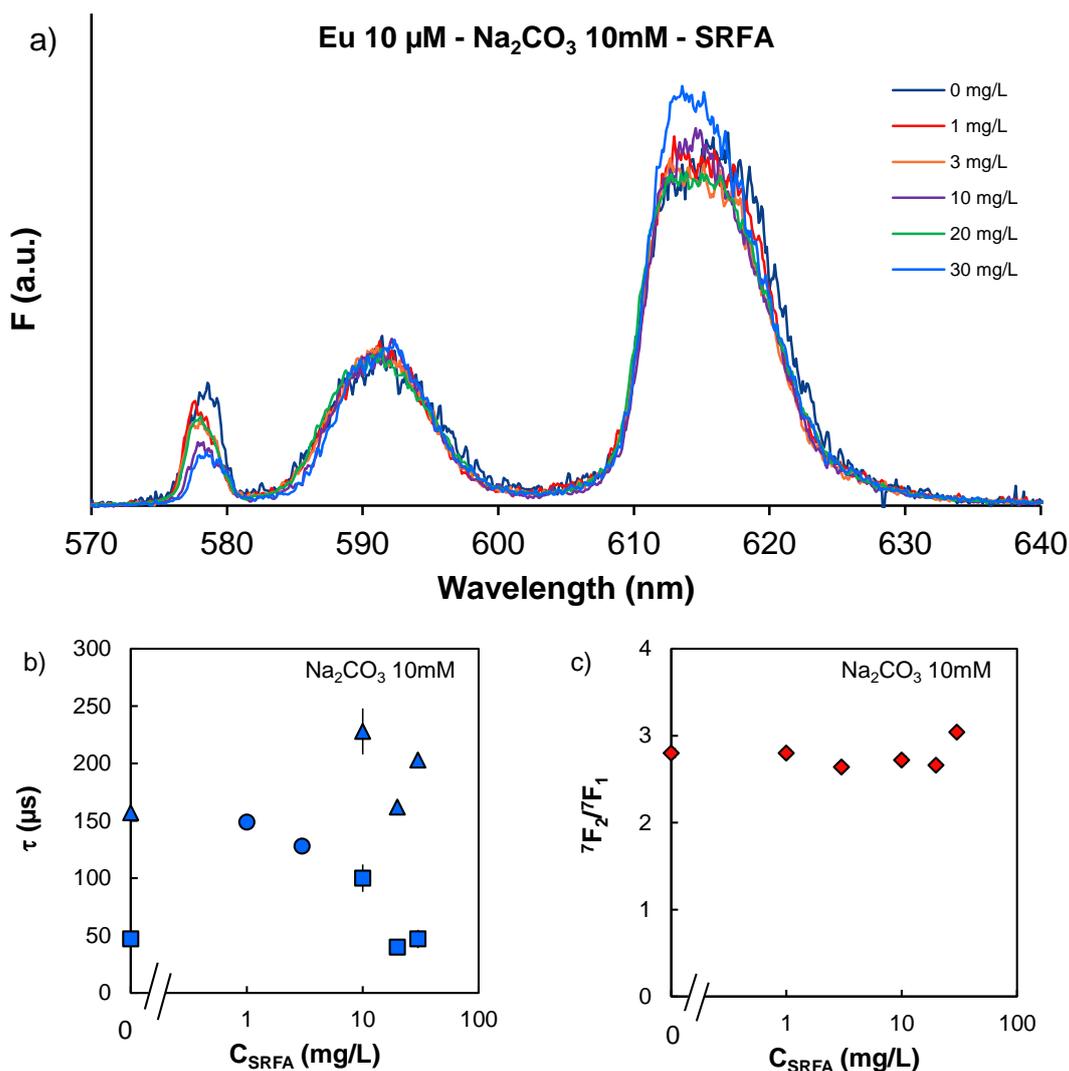
**Figure 5. Speciation of Eu(III)-CO<sub>3</sub>-FA ternary system at varying  $C_{SRFA}$ ,  $[CO_3]_{total} = 1$  mM (a), and  $[CO_3]_{total} = 10$  mM —  $[HCO_3^-] = 8.5$  mM — (b);  $C_{Eu(III)} = 10$   $\mu$ M, pH ca. 7, and  $I = 0.1$  M NaClO<sub>4</sub>; species representing less than 2% are not plotted; thermodynamic constants from Table 1, and NICA-Donnan parameters from Table 2.**

### 3.2.2. Eu-CO<sub>3</sub>-SRFA ternary system with fixed total carbonate 10 mM

The total carbonate concentration was chosen as for the previous experiment: EuCO<sub>3</sub><sup>+</sup> is the major complex in solution at pH ca. 7, but Eu(CO<sub>3</sub>)<sub>2</sub><sup>-</sup> is also present (Figure 5b) and we should evidence the impact of SRFA concentrations on these two complexes.

Spectra for Eu-CO<sub>3</sub>-FA ternary system with fixed total carbonate concentration of 10 mM — i.e. [HCO<sub>3</sub><sup>-</sup>] = 8.5 mM — normalized to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition area are presented in Figure 6a. The evolutions are showing some similarity with the ones for a fixed [CO<sub>3</sub>]<sub>total</sub> = 1 mM (Figure 4a) — [HCO<sub>3</sub><sup>-</sup>] = 0.85 mM. The <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> and <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transitions are also showing a narrowing with C<sub>SRFA</sub>. The <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub> transition relative intensity evolves in the same way, i.e. a decrease with C<sub>SRFA</sub> until 10 mg<sub>SRFA</sub>/L, and then an increase at 20 mg<sub>SRFA</sub>/L, and a final decrease at higher C<sub>SRFA</sub>. The evolution is less clear for the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition: one can only say that the peak increases from 30 mg<sub>SRFA</sub>/L. The <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition is showing a hypsochromic shift with C<sub>SRFA</sub>.

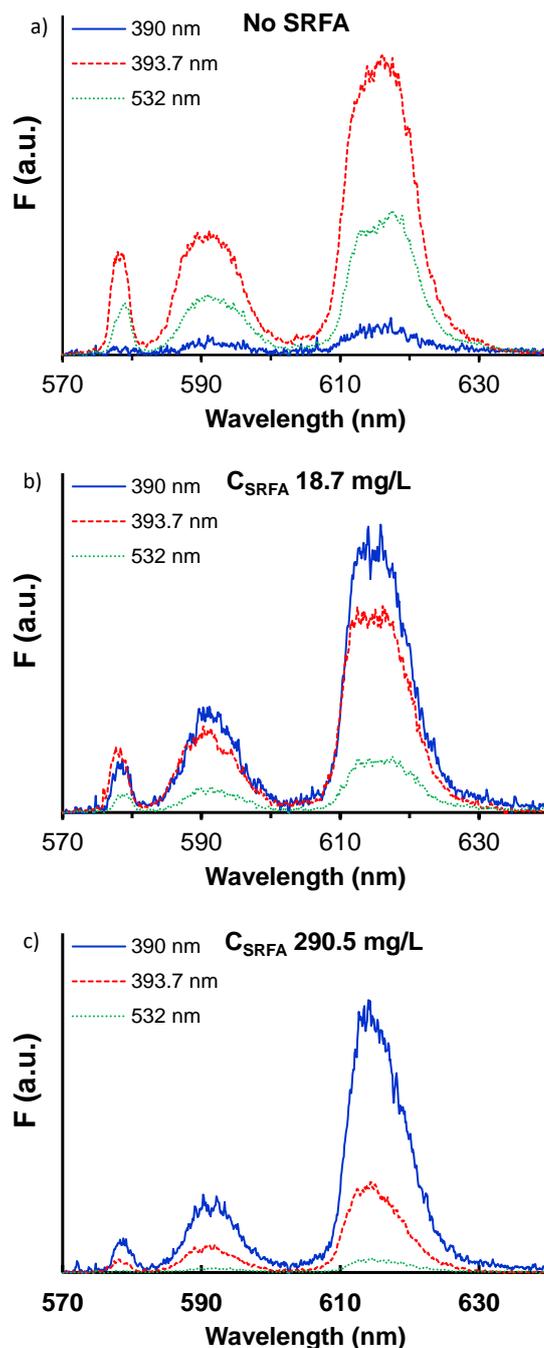
Eu(III) is showing bi-exponential decays for most cases, but it is not possible to fit bi-exponential decays for all C<sub>SRFA</sub> — here for C<sub>SRFA</sub> lower than 3 mg<sub>SRFA</sub>/L — and it is not possible to evidence a real trend with C<sub>SRFA</sub> (Figure 6b). No clear evolutions could be evidenced either for asymmetry ratios (Figure 6c) with C<sub>SRFA</sub> compared to Eu-CO<sub>3</sub>-SRFA ternary system with fixed [CO<sub>3</sub>]<sub>total</sub> of 1 mM — [HCO<sub>3</sub><sup>-</sup>] = 0.85 mM.



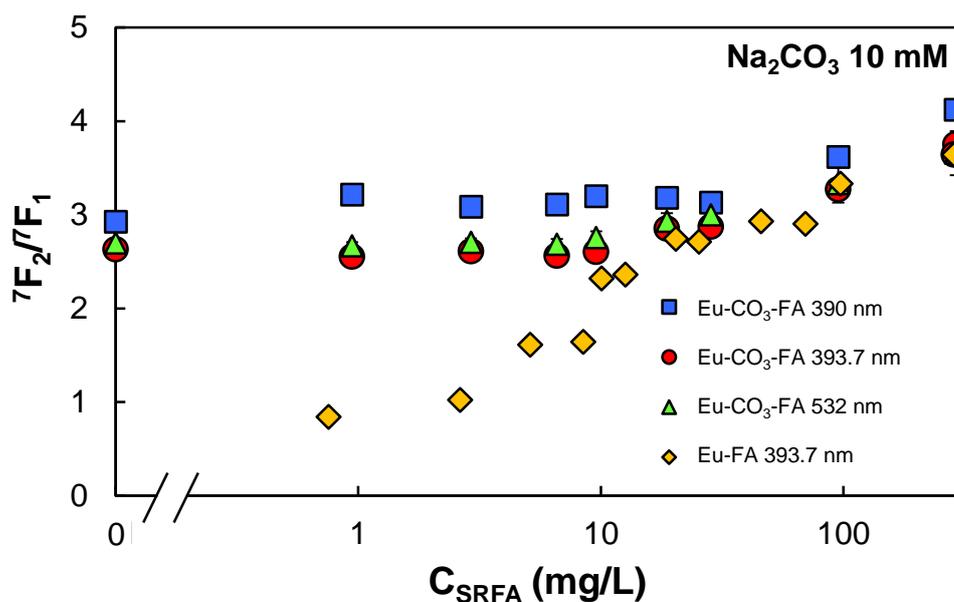
**Figure 6. Spectroscopic data of Eu(III)-CO<sub>3</sub>-SRFA ternary system with fixed [CO<sub>3</sub>]<sub>total</sub> at 10 mM — [HCO<sub>3</sub><sup>-</sup>] = 8.5 mM — vs. SRFA concentrations in mg<sub>SRFA</sub>/L: (a) luminescence spectra normalized to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition area; (b) luminescence decay times, with circles symbols for mono exponential decay times, diamonds (slow component) and squares (fast component) for bi-exponential decay times; (c) Evolution of <sup>7</sup>F<sub>2</sub>/<sup>7</sup>F<sub>1</sub> area ratio; C<sub>Eu(III)</sub> = 10  $\mu\text{M}$ , I = 0.1 M NaClO<sub>4</sub>, pH ca. 7,  $\lambda_{\text{exc}}$  = 393.7 nm, D = 10  $\mu\text{s}$ , W = 300  $\mu\text{s}$ , 600 lines/mm grating.**

### 3.2.3. Selective excitation of the Eu-CO<sub>3</sub>-SRFA ternary system

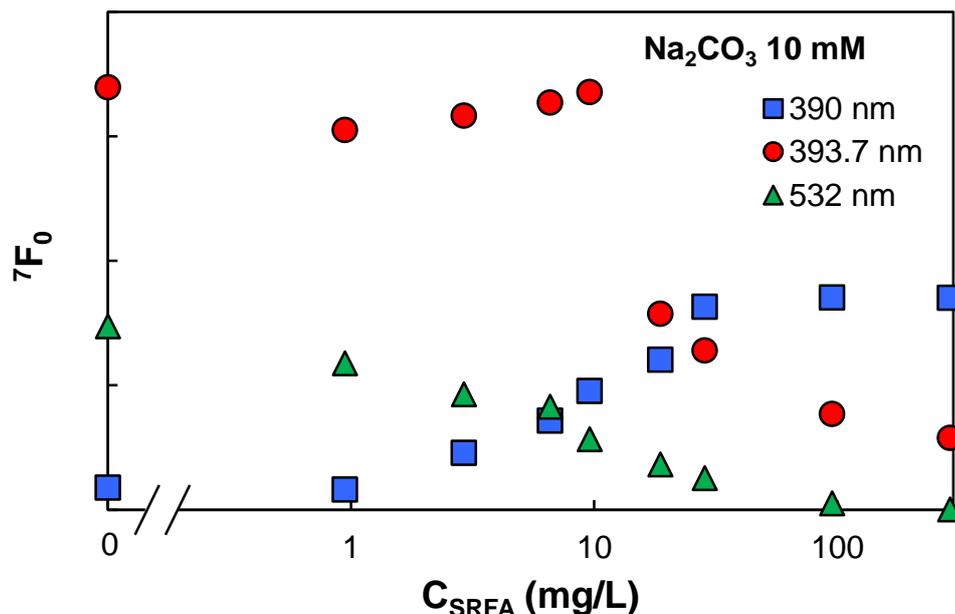
In attempt to quantify Eu-CO<sub>3</sub>-SRFA ternary complexes in the system with fixed [CO<sub>3</sub>]<sub>total</sub> = 10 mM — [HCO<sub>3</sub><sup>-</sup>] = 8.5 mM —, several excitation wavelengths ( $\lambda_{exc}$ ) are used either to excite selectively Eu(III) through the <sup>5</sup>L<sub>6</sub>←<sup>7</sup>F<sub>0</sub> transition ( $\lambda_{exc}$  = 393.7 nm), to take advantage from the antenna effect (Alpha et al., 1990) from the SRFA ( $\lambda_{exc}$  = 390 nm), or to minimize the excitation of the fulvic complex ( $\lambda_{exc}$  = 532 nm) as illustrated in Figure 7. Asymmetry ratios <sup>7</sup>F<sub>2</sub>→<sup>7</sup>F<sub>1</sub> of Eu(III)-CO<sub>3</sub>-SRFA ternary system depending on C<sub>SRFA</sub> for excitation wavelengths  $\lambda_{exc}$  = 390, 393.7, and 532 nm are presented in Figure 8. These evolutions are too weak to be quantified and used as spectral titration curves (Dobbs et al., 1989) as previously done for the Eu-SRFA binary system (Kouhail et al., 2016). However, one can notice that the areas of the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub> transition, for excitation wavelengths of 390 and 532 nm (Figure 9), are significantly changing and can be used as spectral titration curves. The <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub> at  $\lambda_{exc}$  = 532 nm are showing a decrease of signal with C<sub>SRFA</sub>, when the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub> at  $\lambda_{exc}$  = 390 nm are increasing with C<sub>SRFA</sub> due to the formation of organic complexes.



**Figure 7. Eu(III)-CO<sub>3</sub>-SRFA normalized luminescence spectra to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition for excitation wavelengths  $\lambda_{\text{exc}} = 390$  nm (antenna effect through SRFA, plain blue lines),  $\lambda_{\text{exc}} = 393.7$  nm (selective excitation of Eu(III), red dashed lines) and  $\lambda_{\text{exc}} = 532$  nm (minimizing SRFA and Eu(III) excitation, green dotted lines) at varying  $C_{\text{SRFA}}$ ;  $C_{\text{Eu(III)}} = 10 \mu\text{M}$ ,  $[\text{CO}_3]_{\text{total}} = 10 \text{ mM}$  —  $[\text{HCO}_3^-] = 8.5 \text{ mM}$  —, pH ca. 7,  $I = 0.1 \text{ M NaClO}_4$ ,  $D = 10 \mu\text{s}$ ,  $W = 300 \mu\text{s}$ , 600 lines/mm grating.**



**Figure 8. Evolution of asymmetry ratio of Eu(III)-CO<sub>3</sub>-SRFA ternary system depending on C<sub>SRFA</sub> for excitation wavelengths  $\lambda_{exc} = 390$  nm (antenna effect through SRFA, blue squares),  $\lambda_{exc} = 393.7$  nm (selective excitation of Eu(III), red circles) and  $\lambda_{exc} = 532$  nm (minimizing SRFA and Eu(III) excitation, green triangles); C<sub>Eu(III)</sub> = 10  $\mu$ M, [CO<sub>3</sub>]<sub>total</sub> = 10 mM — [HCO<sub>3</sub><sup>-</sup>] = 8.5 mM —, pH ca. 7, and I = 0.1 M NaClO<sub>4</sub>; yellow diamonds represent the evolution of asymmetry ratio of the Eu(III)-SRFA binary system from Kouhail et al. (2016).**

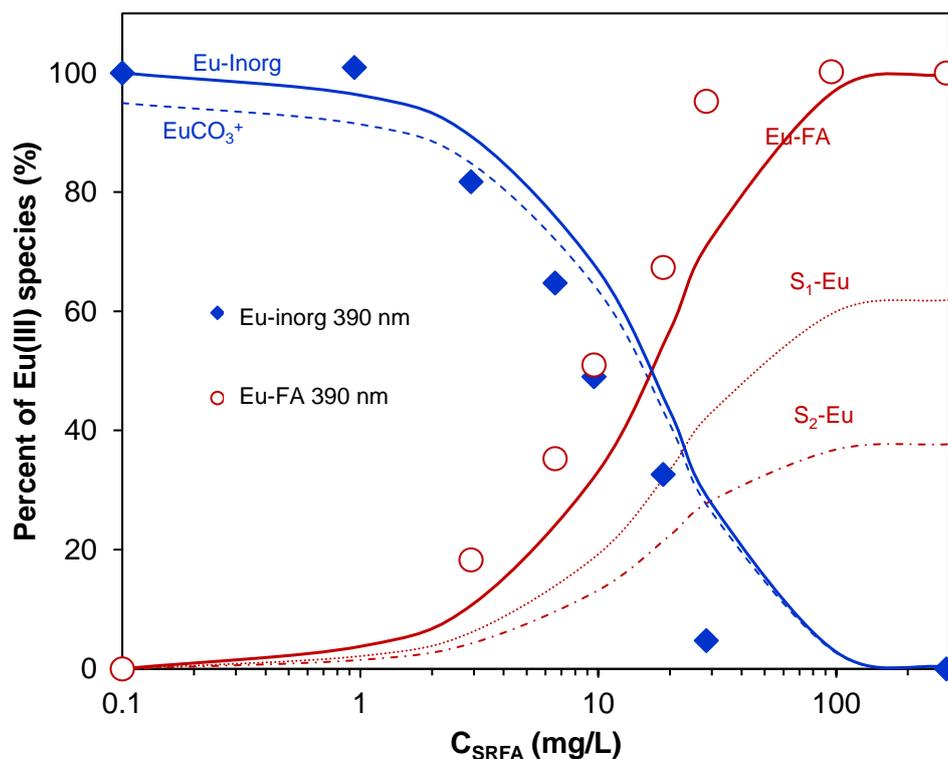


**Figure 9.** Evolution of the  ${}^7F_0$  transition area of Eu(III)-CO<sub>3</sub>-SRFA ternary system depending on C<sub>SRFA</sub> for excitation wavelengths  $\lambda_{\text{exc}} = 390$  nm (antenna effect through SRFA, blue squares),  $\lambda_{\text{exc}} = 393.7$  nm (selective excitation of Eu(III), red circles) and  $\lambda_{\text{exc}} = 532$  nm (minimizing SRFA and Eu(III) excitation, green triangles); C<sub>Eu(III)</sub> = 10  $\mu$ M, [CO<sub>3</sub>]<sub>total</sub> = 10 mM — [HCO<sub>3</sub><sup>-</sup>] = 8.5 mM —, pH ca. 7, and I = 0.1 M NaClO<sub>4</sub>.

#### 4. Discussion

Ternary complexes of europium-carbonate-fulvic acid were evidenced from TRLS experiments. However, asymmetry ratios  ${}^7F_2/{}^7F_1$  present rather small amplitude evolutions, which make the quantification of these ternary complexes difficult. The evolutions of the  ${}^5D_0 \rightarrow {}^7F_0$  transition area in Figure 10 are used as spectral titration curves to calculate proportions of Eu(III) bound to SRFA. One can evidence the presence of an Eu(III)-CO<sub>3</sub>-SRFA ternary complex since the proportions of Eu(III) involved in inorganic complexes and Eu(III) bound to SRFA are not fitting with the ones calculated with

NICA-Donnan parameters from Kouhail et al. (2016). The implementation of  $\log_{10}K$  and  $n$  values for a ternary complex should help better describing this system.

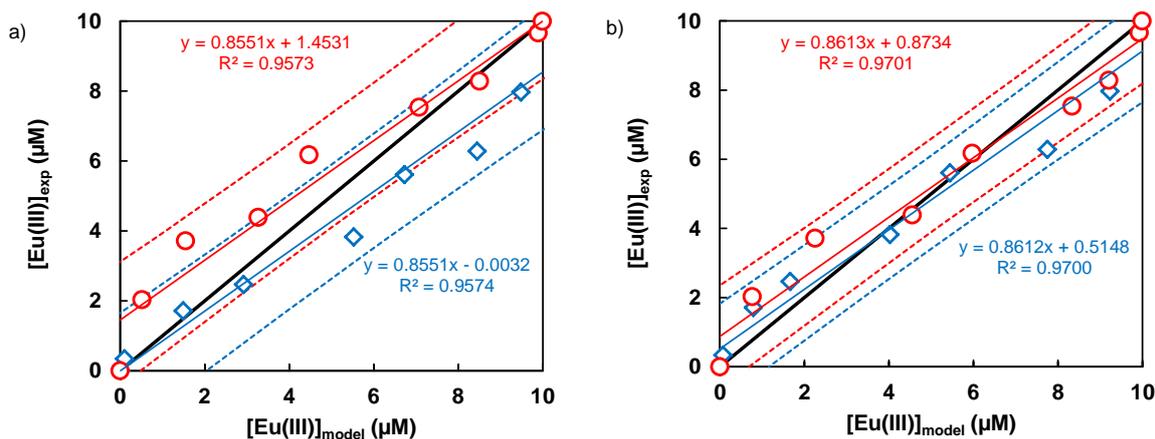


**Figure 10. Speciation of Eu(III) in Eu(III)-CO<sub>3</sub>-SRFA ternary system depending on C<sub>SRFA</sub> using the evolution of the <sup>7</sup>F<sub>0</sub> transition at 390 nm as a spectral titration curve. The lines are the results of NICA-Donnan simulation of the system; C<sub>Eu(III)</sub> = 10 μM, [CO<sub>3</sub>]<sub>total</sub> = 10 mM — [HCO<sub>3</sub><sup>-</sup>] = 8.5 mM —, pH ca. 7, and I = 0.1 M NaClO<sub>4</sub>; thermodynamic constants from Table 1, and NICA-Donnan parameters from Table 2; species representing less than 2% are not plotted.**

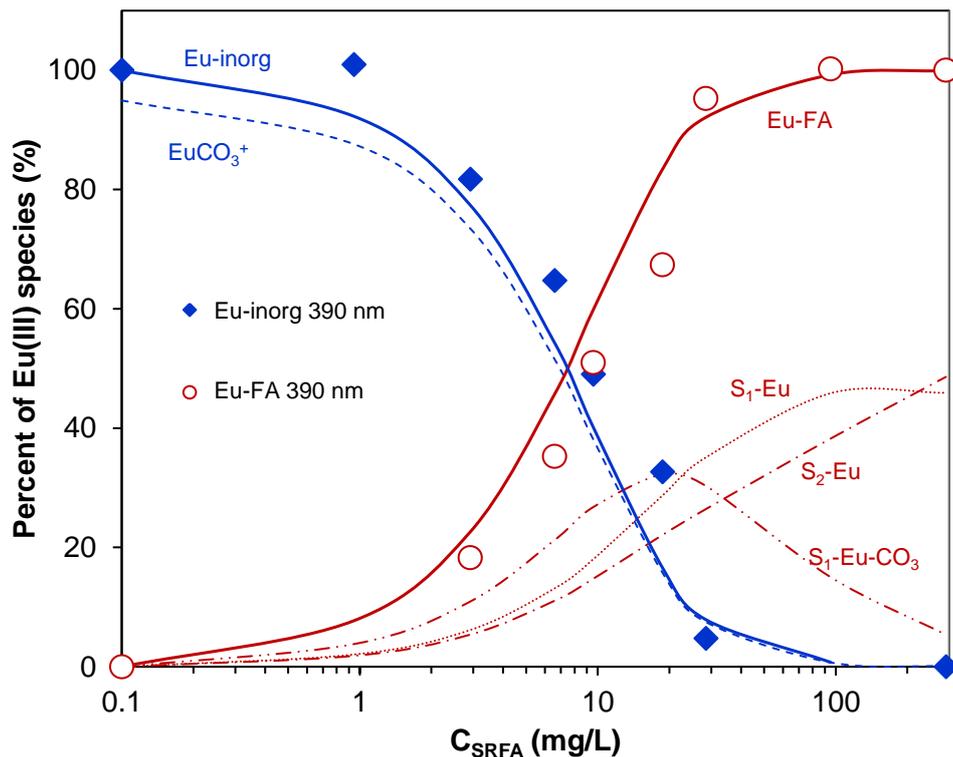
As low affinity (S<sub>1</sub>) and high affinity (S<sub>2</sub>) sites for proton in SRFA are enough to explain the Eu(III)-SRFA binary system (Kouhail et al., 2016), one can assume that only these two types of sites are involved in a potential ternary complex. The data were fitted using ECOSAT with various  $\log_{10}\tilde{K}$  for ternary complexes (Figure S6 of the SI). The best fit of the data is obtained considering only a Eu(III)-CO<sub>3</sub>-SRFA ternary complex on low affinity

sites for proton S1 with  $\log_{10}\tilde{K}_{\text{Eu}^{3+},\text{CO}_3^{2-},1} = 5.6 \pm 0.1$  and  $n_{\text{Eu}^{3+},\text{CO}_3^{2-},1} = 1$  (Figure 11) and the results of the modeling are presented in Figure 12.

The experimental data were too scarce to be fitted using FIT program coupled with ECOSAT. Thus, we cannot provide uncertainties and correlation matrices for the ternary system NICA Donnan parameters. We used ECOSAT instead to calculate the proportion of Eu(III) present in inorganic and organic complexes for various  $\log_{10}\tilde{K}_{\text{Eu}^{3+},\text{CO}_3^{2-},1}$  for ternary complexes plotted vs. the experimental data (Figure S6 of the SI). The associated linear regressions and 95% confidence intervals of the proportions of Eu(III) experimental vs. Eu(III) modeled are also presented in the Figure S6 of the SI. Adding parameters on high affinity sites ( $S_2$ ) for the proton do not help to fit the data, so we only used parameters for low affinity sites ( $S_1$ ). The heterogeneity parameter  $n_{\text{Eu}^{3+},\text{CO}_3^{2-},1}$  does not seem to influence the fits, so we choose to fix it at  $n_{\text{Eu}^{3+},\text{CO}_3^{2-},1} = 1$ . The data were fitted using Eu(III)-CO<sub>3</sub>-SRFA ternary complex on low affinity sites for proton S<sub>1</sub> with  $\log_{10}\tilde{K}_{\text{Eu}^{3+},\text{CO}_3^{2-},1}$  varying from 5 to 6 and fixed  $n_{\text{Eu}^{3+},\text{CO}_3^{2-},1} = 1$ . The best fit of the data is obtained considering a Eu(III)-CO<sub>3</sub>-SRFA ternary complex on low affinity sites for proton S<sub>1</sub> with  $\log_{10}\tilde{K}_{\text{Eu}^{3+},\text{CO}_3^{2-},1} = 5.6$  (Figure S6h of the SI) since the slope of the linear regressions of the proportions of Eu(III) experimental vs. Eu(III) modeled are the closest to one, with the better determination coefficient  $r^2$ .



**Figure 11. Eu(III) concentration measured vs. Eu(III) modeled using the NICA-Donnan model a) without considering Eu(III)-CO<sub>3</sub>-SRFA ternary complexes and b) considering Eu(III)-CO<sub>3</sub>-SRFA ternary complexes with  $\log_{10} \tilde{K}_{\text{Eu}^{3+}, \text{CO}_3^{2-}, 1} = 5.6$  and  $n_{\text{Eu}^{3+}, \text{CO}_3^{2-}, 1} = 1$ . The concentration of Eu(III) in organic complexes (red circles), with associated regression (red plain line and dash-dotted 95% confidence interval); and the concentration of Eu(III) in inorganic complexes (blue diamonds), with associated regression (blue plain line and dashed 95% confidence interval); the solid black line is the 1:1 line.**



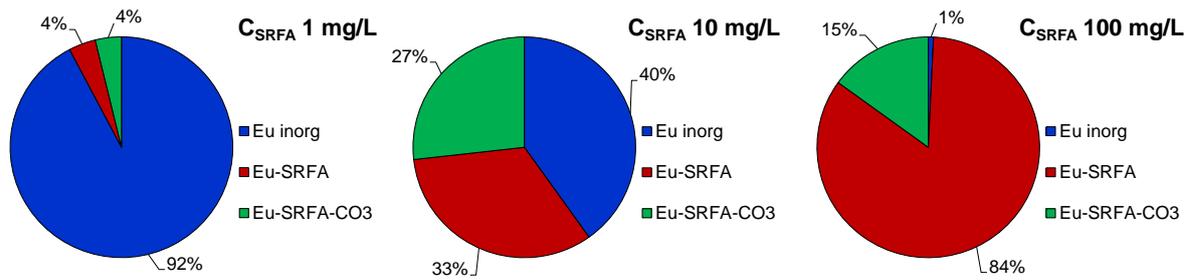
**Figure 12. Speciation of Eu(III) in Eu(III)-CO<sub>3</sub>-SRFA ternary system depending on C<sub>SRFA</sub> using the evolution of the <sup>7</sup>F<sub>0</sub> transition at 390 nm as a spectral titration curve: The diamonds represent the Eu(III) inorganic complexes and the circles represent the Eu(III) fulvic acid complexes; the lines are the results of NICA-Donnan modeling considering Eu(III)-CO<sub>3</sub>-SRFA ternary complex with  $\log_{10} \tilde{K}_{\text{Eu}^{3+}, \text{CO}_3^{2-}, 1} = 5.6$  and  $n_{\text{Eu}^{3+}, \text{CO}_3^{2-}, 1} = 1$  on S<sub>1</sub>; C<sub>Eu(III)</sub> = 10 μM, [CO<sub>3</sub>]<sub>total</sub> = 10 mM — [HCO<sub>3</sub><sup>-</sup>] = 8.5 mM —, pH ca. 7, and I = 0.1 M NaClO<sub>4</sub>; thermodynamic constants from Table 1, and NICA-Donnan parameters from Table 2.**

From TRLS spectra, decay times, and with the help of NICA-Donnan calculations, we are able to propose the formation of EuCO<sub>3</sub>S<sub>1</sub> ternary complexes in aqueous media relevant of environmental conditions. In view of the restricted pH span of our study due to EuOHCO<sub>3</sub>(s) precipitation, a study of the solubility of these ternary phases with TRLS and various other spectroscopic techniques should help improving the understanding of

these complex systems. Antoniou et al. (2011) studied the formation and solubility of  $\text{LnOHCO}_3$  phases — namely Nd(III) and Sm(III) — under high enough concentrations of lanthanides to obtained data — TGA, ATR-FTIR, Raman, and eventually TRLS — of the phases themselves at 100 mg of solid in 50 mL, or *approx.* 9 mmol<sub>Sm</sub>/kg<sub>w</sub> for 500 mg<sub>AH</sub>/L. They noted a decrease in the crystallite size for Nd(III) and an increase for Sm(III), and a slight decrease in solubility of  $\text{SmOHCO}_3(\text{cr})$ . Under our conditions, i.e.  $C_{\text{Eu(III)}} = 10 \mu\text{M}$ , no change in the TRLS signal are observed at the highest  $C_{\text{SRFA}}$  with time. It should mean that if a solid phase is forming, then its crystallite size is very small and the phase does not precipitate with SRFA. This could be reminiscent of the observation of small iron polynuclear species observed by Weber et al. (2006a).

The NICA-Donnan parameters for the Eu-SRFA system were used to understand the  $\text{Eu-CO}_3$ -SRFA ternary system. The formation of these mixed complexes seems to be confirmed, but their prevalence appears to be less important than expected by previous studies on actinides (Morgenstern et al., 2000; Panak et al., 1996).

A simulation of the speciation of this system by the NICA-Donnan model — with the NICA-Donnan parameters from Kouhail et al. (2016) — shows that the proportions of Eu complexed to SRFA are not in agreement with those computed by the model if a ternary complex is not taken into account. Considering a  $\log_{10} \tilde{K}_{\text{Eu}^{3+}, \text{CO}_3^{2-}, 1} = 5.6$  with  $n_{\text{Eu}^{3+}, \text{CO}_3^{2-}, 1} = 1$  — i.e., a homogeneous distribution in binding sites — on low affinity sites for the proton, for a ternary complex helps better describing this system. These complexes can represent as much as 27% of the europium speciation for a  $C_{\text{SRFA}}$  of 10 mg/L and a total carbonate concentration of 10 mM ( $[\text{HCO}_3^-] = 8.5 \text{ mM}$ , Figure 13) so they need to be considered within the framework of the NICA-Donnan modeling of natural carbonated waters.



**Figure 13. Speciation of Eu(III) for  $C_{SRFA}$  of 1, 10 and 100 mg/L using the NICA-Donnan model considering Eu(III)-CO<sub>3</sub>-SRFA ternary complexes with  $\log_{10}\tilde{K}_{Eu^{3+},CO_3^{2-},1} = 5.6$  and  $n_{Eu^{3+},CO_3^{2-},1} = 1$  on S1;  $C_{Eu(III) tot} = 10 \mu M$ ,  $[CO_3]_{total} = 10 mM$  —  $[HCO_3^-] = 8.5 mM$  —, pH ca. 7, and  $I = 0.1 M NaClO_4$ . The percentage of Eu(III) inorganic complexes are represented in blue, Eu binary fulvic complexes (S1-Eu, S2-Eu, and Eu<sub>Donnan</sub>) are in red, and S1-Eu-CO<sub>3</sub> ternary complex is in green.**

## 5. Conclusions

Our purpose was to study the possible formation of europium-fulvic acid-carbonate ternary complexes by time-resolved luminescence spectroscopy for various concentrations of carbonates and fulvic acid. These complexes were supposed to be significant under mildly basic carbonated natural waters but were not implemented in the NICA-Donnan modeling of natural organic matter complexation of Eu(III).

From the evolutions of shapes and maxima of the  $^5D_0 \rightarrow ^7F_0$ ,  $^5D_0 \rightarrow ^7F_1$  and  $^5D_0 \rightarrow ^7F_2$  transitions of Eu(III), we have evidenced that other species are present in addition to the  $Eu(CO_3)_n^{(3-2n)+}$  complexes and to the Eu-SRFA species that we have previously evidenced (Kouhail et al., 2016). We have used selective ( $\lambda_{exc} = 393.8 nm$ ) and indirect ( $\lambda_{exc} = 390$  and  $532 nm$ ) excitation of the Eu-CO<sub>3</sub>-SRFA system to build complexation isotherms that can be used in the framework of the NICA-Donnan model. We have implemented in the

model  $\log_{10}\tilde{K}_{\text{Eu}^{3+},\text{CO}_3^{2-},1} = 5.6$  and  $n_{\text{Eu}^{3+},\text{CO}_3^{2-},1} = 1$  for a Eu-CO<sub>3</sub>-SRFA ternary complex on low affinity for proton sites that helps better describing the system. These ternary complexes represent a significant proportion of the Eu(III) complexes in solution and should be consider in future studies.

## Supplementary material

Supplementary data, six figures and ten tables, associated with this article can be found, in the online version.

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