Mixed Lanthanide-CO_3-Fulvic Complex: Spectroscopic Evidence

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The formation of mixed complexes between lanthanides and actinides(III), complexing inorganic anions, and humic substances is still not completely settled, particularly, the competition, or mixed complex formation, with CO_3^{2-} [5,6]. To propose answers on this topic, time-resolved laser-induced luminescence spectroscopy (TRLS) experiments in the system Eu(III)-CO_3-FA at pH 7 are done, using Suwannee River fulvic acid (SRFA). Starting from former characterization of the Eu-SRFA system [1], the evolution of both the fluorescence spectra and lifetimes of Eu(III) at pH 7 and varying concentrations of carbonate and FA are obtained. With the use of an optic parametric oscillator, several excitation wavelengths (λ_{exc}) were used either to excite selectively Eu(III) through the $^5L_6$<$^7F_0$ transition (λ_{exc} = 394.7 nm), to take advantage of the antenna effect from the SRFA (λ_{exc} = 390 nm), or to minimize the excitation of the fulvic complex (λ_{exc} = 532 nm).

The evolutions of the Eu(III) luminescence spectra from the $^5D_0$>$^7F_{0,2}$ transitions are showing modifications of the assymmetry ratio (area ratio of $^5D_0$>$^7F_2$ transition to the $^5D_0$>$^7F_1$ transition) that indicates the presence of several species in addition to the $EuCO_3^+$ and Eu-FA complexes. The occurence of bi-exponential decay times, with a faster than Eu^{3+} component, is typical of the occurrence of fulvic complex [8] even in the presence of carbonates.

The analyses of the undirect excitation of the Eu-CO_3-SRFA systems are used to build the complexation isotherms varying both SRFA or total carbonate concentrations in the framework of the NICA-Donnan modeling of the Eu(III)-SRFA system [1,2]. In view of the restricted pH span, no strict attribution to the different possible types of sites can be done. Different complex formation are considered and discussed.

[5] Morgenstern *et al.* Radiochim. Acta **88**, 7-16. [6] Pourret *et al.* J. Colloid Interface Sci. **305**, 25-31. [7] Kouhail *et al.* (accepted) Environ. Sci. Technol. [8] Reiller & Brevet, Spectrochim. Acta A **75**, 629-636 [9] Kinniburgh *et al.* (1999) Colloids Surf. A **151**, 147-166.