

EXAFS confirmation of the structure and stoichiometry of lanthanide-carbonate complexes in solutions

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Background and scientific interest of the study

Trivalent transuranian actinides (Cm^{3+} , Am^{3+}) and radioactive lanthanides (Ln) present in nuclear waste can be dispersed in the environment by nuclear accidents, or by alteration of High Level Waste (HLW) packages. Migration of these RNs in natural systems is controlled by retention processes at the surface of solid phases, but also by RN speciation in solution. This speciation is a function of physico-chemical conditions (pH, temperature) and of the presence of ligands, such as (bi)carbonate, a powerful complexant of actinides and lanthanides [1]. Thus, to correctly predict the fate of these RNs it is essential to develop robust models of actinide and Ln complexation by (bi)carbonate. These models in turn hinge on an accurate description of the molecular structure and stoichiometry of solution complexes.

Because of this environmental importance, our project aimed at unraveling the thermochemical and structural parameters describing Ln and actinide complexation in solution. To this end, EXAFS spectroscopy was used to determine the structure (binding mode of carbonate and stoichiometry of Ln-carbonate complexes in solution. We have used Ln because these cations are good analogues of actinides at the same oxidation states. Furthermore, the K-edge of Ln was selected to avoid complications in the data analysis resulting from the limited k-span available at the L3-edge of mist light lanthanides, and to get rid of multiple-excitation effects. These studies also aimed at providing an insight on the Ln complexation by carbonate over the whole Ln series, from the light ones (La^{3+} , Nd^{3+} and Eu^{3+}) which are the best chemical surrogates for actinides, to heavy ones (Lu^{3+}), for which data were previously collected at the L3 edge.

Scientific and technical outcome

Data collection at the Ln K-edge was possible, but not in fluorescence-yield mode as initially expected. In fact, the counting statistics from the fluorescence detector appeared to be too limited to provide a convenient signal-to noise ratio. In contrast, the use of long (≥ 12 cm) polypropylene liquid cells made it possible to collect the spectra in transmission mode. Although most of the beam ($\geq 90\%$) was absorbed in the cell, the high photon flux, combined with the extreme stability of the BM 29 robust design made it possible to measure X-ray absorption edges of $\Delta\mu x \sim 0.02\text{-}0.03$ in transmission mode.

Examples of EXAFS spectra obtained at the Nd K-edge are plotted in figure 1a. The gain from working at the K-edge of lanthanide is immediately apparent for the fully hydrated Nd (Nd_{aq}). The EXAFS spectrum at the K-edge extends to 15 \AA^{-1} with an exquisite quality, whereas it stops to $\leq 11.5 \text{ \AA}^{-1}$ at the L3 edge. More important, the Fourier Transform of the EXAFS spectra at the L3-edge display the main peak at $R+\Delta R = 2 \text{ \AA}$ resulting from oxygens of the coordination sphere, but also several peaks of appreciable intensity over the $[2.5, 4.5] \text{ \AA}$ range. These side peaks originate from double excitation features which can be only partially removed, thereby affecting the accuracy of EXAFS fits [2]. In contrast, only the main peak at 2 \AA and two small peaks at $2\text{-}3 \text{ \AA}$ are observed on the K-edge FT. The absence of spurious FT at $> 3 \text{ \AA}$ greatly simplifies the spectral analysis of the spectra collected in carbonate solutions.

The spectral data from fully hydrated Nd can be contrasted to that of Nd diluted in a carbonate solution (fig. 1a,b). Clearly, in a carbonate brine, the main FT peak at 2 \AA displays a bump on its high-distance side, and a new peak of appreciable intensity can be observed near 3.5 \AA . Both features can be attributed to carbonate groups forming inner-sphere bidentate complexes with Nd, resulting in a Nd-C distance near 2.9 \AA . In this geometry, Nd, C and the distal O atom (O_{dist}) from the carbonate group are

aligned, resulting in multiple scattering (MS) focusing effect magnifying the EXAFS contribution from O_{dist} . This focusing effect explains the significant amplitude from the next-nearest peak at 3.5 Å. This qualitative explanation has been confirmed by preliminary quantitative modelling using FEFF8-generated phase and amplitude functions. Note that this MS scattering peak has been observed for all samples of Ln in carbonate solutions (La, Nd, Eu: fig. 1c), pointing at the strong similarities of Ln environments, in agreement with thermodynamical predictions. Future, complete modelling will be performed in order to obtain a comprehensive model of Nd, La and Eu coordination by carbonate groups in concentrated alkaline solutions. These spectral analyses will complement laboratory studies of the solubility of LN- carbonate solids, and quantum mechanical (DFT)

References

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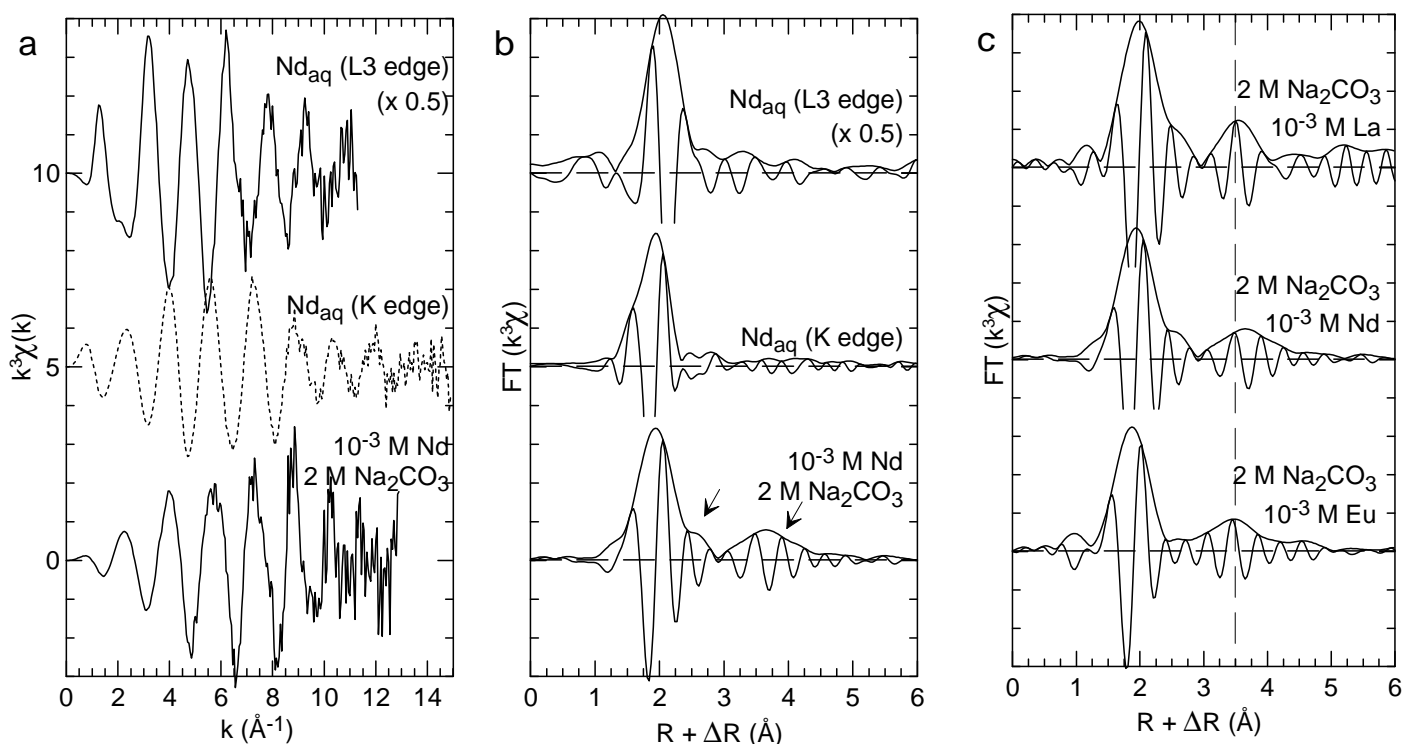


Figure 1 (a). EXAFS spectra at the L3-edge and the K-edge for La_{aq} and La complexed with carbonates in a 2 M Na_2CO_3 brine. The amplitude of L3-edge EXAFS data has been divided by two (b) FT of the EXAFS spectra for La_{aq} and La complexed with carbonates in a 2 M Na_2CO_3 brine. (c) FT for La, Nd and Eu in 2 M carbonate solutions. Note the MS peak near 3.5 Å.