

ROBL-CRG

**Experiment title:**

Lutetium L3 and europium L2-edge EXAFS measurements of Lu(III)/Eu(III)-sorbed iron compounds

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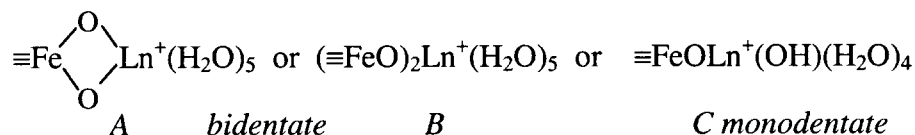
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**Report: EXAFS and TRLFS study of lanthanides(III) sorbed onto Hydrous Ferric Oxide (HFO)**

The purpose of this study is to characterize trivalent lanthanide (Ln(III)) species sorbed onto hydrous ferric oxide (HFO) by combining wet-chemical sorption data with spectroscopic investigations. Both extended x-ray absorption spectroscopy (EXAFS) and time resolved-fluorescence spectroscopy (TRLFS) experiments were performed. Eu(III) fluorescence in the visible range  ${}^5D_0 \rightarrow {}^7F_x$  was used for the determination of the number of coordinated water molecules from the fluorescent lifetime. TRLFS is not possible for Lu(III), due to its full 4f shell. EXAFS transmission experiments on HFO:Lu(III) sorbed samples were performed at ROBL and at beamline A1, HASYLAB. Lutetium was used to avoid the spectral interference with the Fe K edge, which is a problem for investigations of HFO:Eu samples at the Eu L3 edge. Using the Eu L2 edge avoids this interference. However, the L2 transition has only one-half the intensity and a high residual Fe absorption, thereby limiting the measurable Eu(III) sample loadings. The transferability of TRLFS results from HFO:Eu(III) to HFO:Lu(III) and EXAFS results on HFO:Lu(III) to HFO:Eu(III) is justified because wet-chemical sorption behavior of both these Ln(III) onto HFO is the same.

A Eu(III)-lifetime of 195  $\mu$ s was obtained from TRLFS on a HFO:Eu solid sample, prepared at pH 5.6. This increase in lifetime over that for the Eu(III) aquo species indicates that five water molecules (and/or hydroxyl groups) are in the first Eu(III) coordination sphere [1].

Sorption studies indicate a change in the sorbed species with increasing pH. At low pH, formation of a monodentate species according to the reaction  $\equiv\text{Fe}-\text{OH} + \text{Ln}^{3+}(\text{H}_2\text{O})_{8,9} \rightarrow \equiv\text{Fe}-\text{O}-\text{Ln}^{2+}(\text{H}_2\text{O})_5$  is proposed, where  $\equiv\text{Fe}$  represents an iron atom on the HFO surface. At pH values above  $\sim 5.5$ , a change in the surface species formed is observed. The following three structures for the sorbed species are possible:



EXAFS structural parameters for the Lu coordination in HFO:Lu(III) samples prepared at varying pH allow characterization of the monodentate species formed at low pH and differentiation between species at higher pH, the monodentate deprotonated species (C) and the two possible bidentate species: A, with Lu(III) bonding *via* iron oxide polyhedral edges, and B, with geminal corner-sharing bonding.

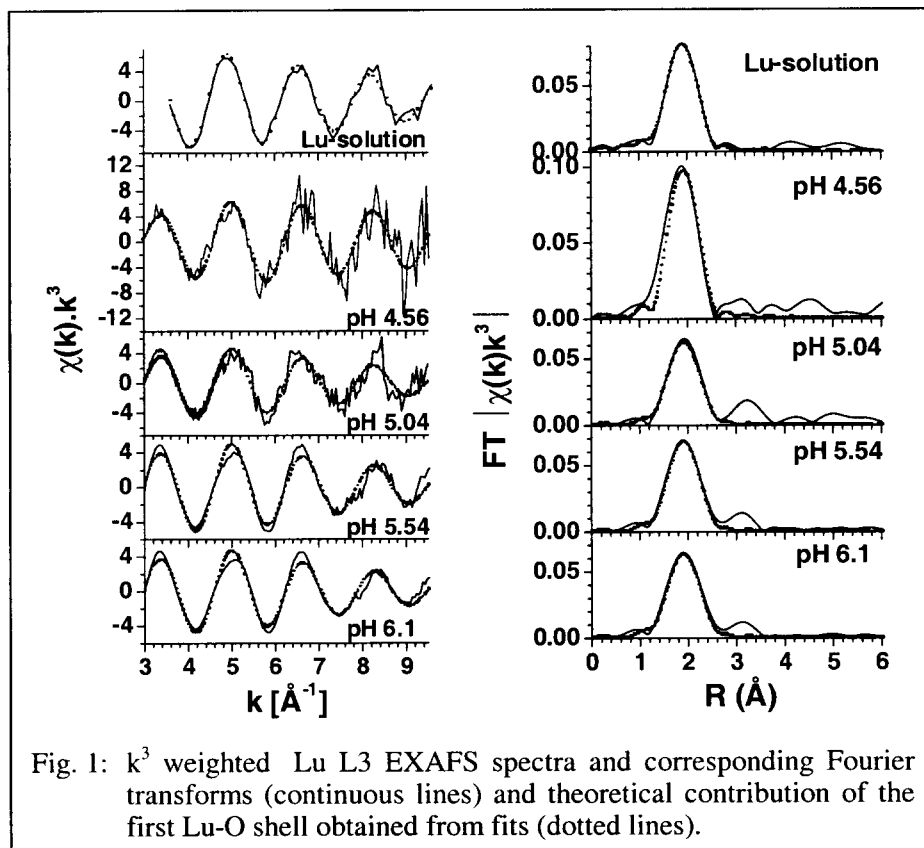


Fig. 1:  $k^3$  weighted Lu L3 EXAFS spectra and corresponding Fourier transforms (continuous lines) and theoretical contribution of the first Lu-O shell obtained from fits (dotted lines).

coordination upon binding to the HFO surface is evident. Within experimental error, the coordination number for all HFO:Lu(III) sorption samples is the same, 6-8. As expected,  $N$  is less for the sorption samples than for the aquo species. The only change in the metrical parameters observed with pH is in the relative mean square displacement or EXAFS Debye-Waller factor,  $\sigma^2$ . The fit results show that the larger relative intensity for the sample prepared at pH 4.56 results from a smaller  $\sigma^2$ , even smaller than that for the aquo species. The static disorder in this sample is thus lower. The proximity of the HFO surface has an effect of lowering the mean square displacement of water molecules coordinated to Lu(III). The presence of a second peak above pH 5 at  $\sim 3.1$  Å is attributed to a Lu-Fe distance. This indicates that a species different from the one at pH 4.56 is formed. If the surface species *C* were formed, then a Lu-Fe interaction should not be observed, due to both the long length expected for this interaction and to dynamic atomic displacements. In contrast, the Lu-Fe distance expected for species *A* and *B* is shorter and the species has a more rigid structure so that this distance should be observed. The EXAFS results exclude the formation of the surface species *C*. Fit results for Fe coordination numbers in the second shell will provide evidence for the presence of either species *A* or *B*.

**Table 1:** Results of the fit for the first shell Lu-O.  $S_0^2$  was held constant at 1 and the underlined  $\Delta E_0$  were kept constant at the value obtained for the pH 6.1 sample; all three samples were measured during the same run.

Sample	pH	N	R [Å]	$\sigma^2 \cdot 10^{-3}$ [Å <sup>2</sup> ]	$\Delta E_0$ [eV]	Residual
Reference: Lu-solution		8 - 9	2.31	8	4.4	17.5
HFO:Lu	4.56	7 - 8	2.31	4	<u>6.9</u>	45.1
HFO:Lu	5.04	6 - 7	2.31	9	7.4	31.8
HFO:Lu	5.54	7 - 8	2.30	9	<u>6.9</u>	24.9
HFO:Lu	6.1	7 - 8	2.30	10	6.9	22.7

[1] W. De W. Horrocks and D.R. Sudnick, J. Am. Chem. Soc. 101, 334 (1979)

[2] A.L. Ankudinov, B. Ravel, J.J. Rehr and S.D. Conradson, Phys. Rev. B, 7565 (1998)