ESRF	**Experiment title:** Sorption of trivalent lanthanides (Ln(III)), onto hydrous ferric oxide (HFO) and evolution of the sorbed species upon HFO aging	**Experiment number**: ME-240
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Report:

Low temperature XAFS investigation on the lutetium binding changes during the 2line-ferrihydrite alteration process

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The time dependent changes of Lu(III) speciation, initially sorbed onto two-line ferrihydrite (2LFh) at pH 5.9, during tempering (70°C) and leading to stable crystalline transformation products is studied at the Lu L3 absorption edge. Lu(III) is used as a analogue for the trivalent actinides. Samples are tempered for 0, 84, 155 and 238 hours. Complementary microscopic studies (AFM, SEM), XRD and FTIR spectroscopy confirm transformation of Lu(III):2LFh (pH 6) to both goethite and hematite, with a predominance of hematite. XRD investigation of a transformation series at pH 8 shows that the cell volume of hematite product increases slightly, suggesting the incorporation of Lu(III) in the structure. The EXAFS results aim at determining the fate of the Lu(III) during transformation.

Fig. 1 shows the experimental and the best fit results and their corresponding FT's. The initial sorption sample (temper time = 0) is fit using two coordination shells, an oxygen and an iron shell. The fit yields (Table 1) seven oxygen atoms (O') at a mean bond distance of 2.31Å and a Lu-Fe' distance of 3.41Å. This is in good agreement with previous results[1].

The other samples are fit to structural models including the two possible end products (hematite-like and goethite-like models), with an isotropic expansion of 4% of interatomic distances to simulate Lu(III) incorporation into iron position of the crystal-lattice. The coordination numbers are kept constant at expected values during the fits. Results of the best fit are listed in Table 1. The fit to the 238h tempered sample data is only possible using the hematite-like model. It requires inclusion of a Lu-Fe distance near 3.9Å (Fe4). This

[1] **Dardenne, K.; Schaefer, T.; Denecke, M.A.; Rothe, J.; Kim, J.I. *Radiochim. Acta* 2001, *89*, 469 - 479**

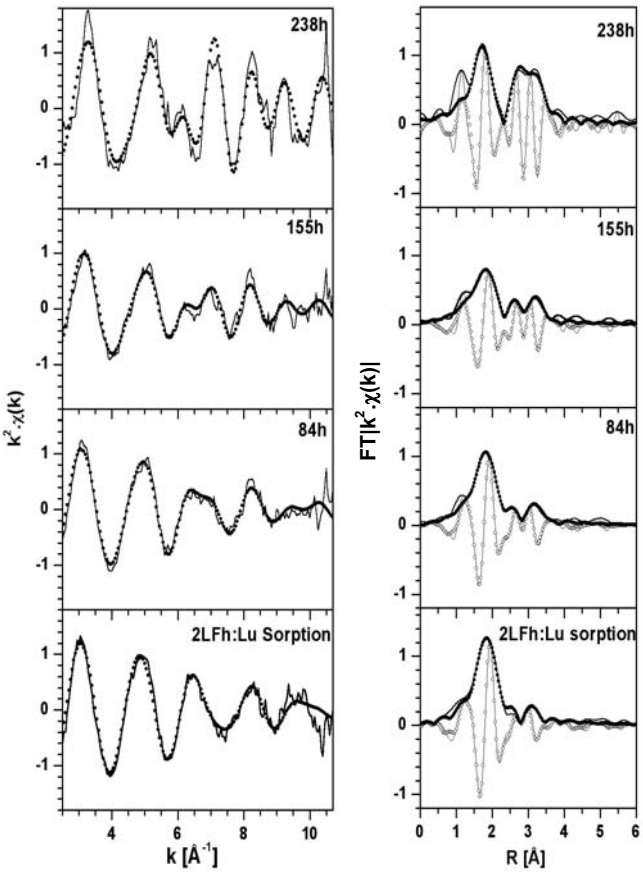

Fig. 1 *Left: k^2-weighted Lu L3 edge EXAFS (lines) and best fit results. (dots). Right: corresponding FT.*

distance is absent in the goethite-like cluster. No good fit is possible using solely the goethite-like cluster model. If Lu(III) is incorporated into goethite, its EXAFS contribution is completely masked by Lu(III) in hematite.

Data from the 84 and 155h tempered samples is modeled with a combination of the temper time = 0 and 238h species. The first coordination shell bond lengths and coordination numbers are fixed to the values obtained for samples with temper times 0 and 238h and scaled with a ratio factor, rf. The rf is the proportion of the Lu(III) incorporated into hematite species (temper time = 238h). Results of the fits are also given Table 1. EXAFS for both 84h and 155h tempered samples is very well modeled with this combination of species. This shows that both species, Lu(III) sorbed onto 2LFh and Lu(III) incorporated into hematite crystal structure, coexist in the intermediate temper time samples.

Table 1: *Coordination number (*N*), interatomic distance (*R*), relative ionization energy shift (*ΔE_0*), mean-square-displacement (*σ^2*) and relative amount Lu incorporated into hematite (*rf*) obtained from fits to the EXAFS shown in Fig. 1.*

Sample **Temper time (h)**	**Neighbor**	**N****	**R** **[Å]**	**ΔE_0** **[eV]**	**σ^2** **[10^{-3} Å^2]**	**rf**
0	O'	7.2	2.31	7.64	7.44	0
	Fe'	1*	3.41	4.8	5.10	
84h	O	1.54	2.19	6.79	7.46	0.26
	O'	5.20	2.31	6.79	7.37	
	Fe1 + Fe2	1.02	3.17	0.80	15.03	
	Fe3 + Fe'	1.51	3.42	0.80	5.60	
	Fe4	1.54	3.93	0.80	10.7	
155h	O	3.98	2.19	6.79	14.68	0.66
	O'	2.61	2.31	6.79	5.23	
	Fe1 + Fe2	2.65	3.12	0.01	13.14	
	Fe3 + Fe'	2.32	3.42	0.01	5.60	
	Fe4	3.98	3.89	0.01	17.2	
238h	O	6*	2.19	6.74	7.22	1.00
	Fe1 + Fe2	4*	3.08	0.01	10.17	
	Fe3	3*	3.41	0.01	2.12	
	Fe4	6*	3.88	0.01	12.1	

* fixed at this value **N(O')=(1-rf)*7.2, N(O)=rf*6 and, N(Fe3+Fe')=(1-rf)*1+ rf*3

These results corroborate XRD results on a transformation series at pH 8 that Lu(III) sorbed onto 2LFh is incorporated into the transformation product hematite crystal lattice, as opposed to being occluded or remaining a sorbed species on the surface.