 ROBL-CRG	Experiment title: Sorption and redox reaction of SnII and SnIV at the magnetite/water interface in presence and absence of organic ligands	Experiment number: 20-01-708
Beamline: BM 20	Date of experiment: from: 23-02-2011 to: 26-02-2011	Date of report: 28-01-2013
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Report:

In this report we are going to show the interfacial redox of Sn(II) on magnetite as a function of time. The samples, therefore, were prepared by varying reaction time at fixed pH 6.5 under anoxic condition. XAS spectra were collected in fluorescence mode, maintaining a sample temperature of 10-15 K in a closed-cycle He cryostat.

As shown in fig. 1 and table 1, the XANES spectra of the magnetite reaction products show already for the shortest reaction time an edge energy in line with that of Sn(IV) (29207 eV), reported in the previous report, suggesting complete oxidation within 30 min. This is further confirmed by the EXAFS-derived coordination of about 6 O at 2.05 Å, while the Sn(II) aquo complex has about 3 O at a larger distance of 2.21 Å. Longer distance shells are fitted with Sn-Fe paths of about 3.15 and 3.59 Å. Although the FT peak at about 3.2 Å, corresponding to the longer Sn-Fe shell at about 3.59 Å, varies in intensity with time, no clear trend is observed from the fit data. Furthermore, the EXAFS spectra show no statistically significant trend with time. Therefore, not only the Sn oxidation state, but also the local structure remains the same over time.

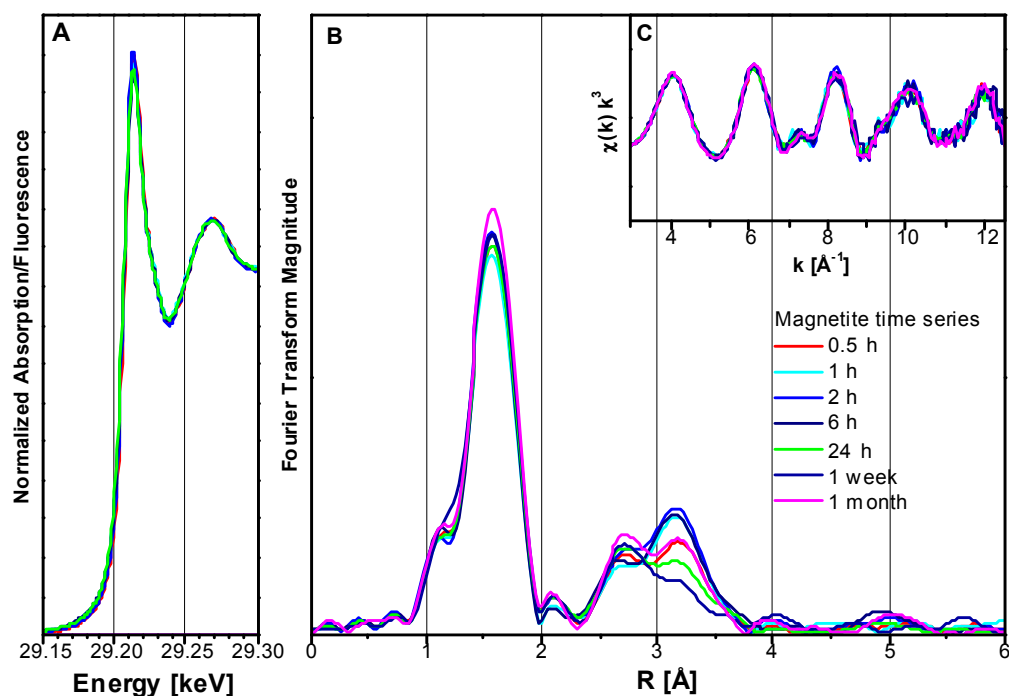


Figure 1 Sn-XAS spectra of Sn(II)-sorbed magnetite as a function of time (colored lines, pH=6.5±0.05). A: XANES, B: EXAFS Fourier Transform Magnitude, C: k³-weighted EXAFS spectra.

Table 1 Fitting data of time series samples of Sn-sorbed magnetite (pH 6.5±0.05)

Time	E ⁰ /eV	Path	CN	R/Å	σ ² /Å ²	Path	CN	R/Å	σ ² /Å ²	E ⁰ shift /eV	%R ¹
0.5 h ²	29207.7	Sn-O	6.3	2.05	0.0040	Sn-Fe Sn-Fe	1.2 2.4	3.15 3.60	0.0046 0.0046	4.5	5.8
1 h	29207.2	Sn-O	6.3	2.05	0.0044	Sn-Fe Sn-Fe	1.1 3.4	3.15 3.60	0.0054 0.0054	4.1	6.1
2 h	29207.3	Sn-O	6.4	2.05	0.0040	Sn-Fe Sn-Fe	1.2 3.3	3.15 3.59	0.0049 0.0049	4.1	6.6
6 h	29207.1	Sn-O	6.3	2.05	0.0039	Sn-Fe Sn-Fe	1.2 3.4	3.13 3.59	0.0053 0.0053	4.1	8.3
24 h	29207.1	Sn-O	6.3	2.05	0.0041	Sn-Fe Sn-Fe	1.4 1.8	3.15 3.60	0.0043 0.0043	4.4	6.4
1 w ³	29207.4	Sn-O	6.8	2.05	0.0045	Sn-Fe Sn-Fe	1.5 1.3	3.14 3.59	0.0049 0.0049	4.6	4.9
1 m ⁴	29207.6	Sn-O	6.5	2.05	0.0036	Sn-Fe Sn-Fe	1.2 2.0	3.14 3.58	0.0033 0.0033	4.6	5.3

¹% Residual, ² hour, ³ week, ⁴ month