ROBL-CRG	**Experiment title:** Sorption and redox reaction of Sn^{II} and Sn^{IV} at the magnetite/water interface in presence and absence of organic ligands	**Experiment number**: 20-01-708
Beamline: BM 20	**Date of experiment**: from: 07-11-2010 to: 11-11-2010	**Date of report**: 19-03-2011
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Report:

Tin is a widespread contaminant in the environment due to its use in antifouling paints, PVC plastics and pesticides. Furthermore, the fission product [126]Sn is of substantial concern for nuclear waste disposal because of a rather long half-life (10^5 years). In contrast to its significance, the geochemistry of tin is not well understood, especially at neutral pH and low ionic strength. For tin concentrations lower than 10^{-7} M, Sn^{II} is assumed to be soluble, whereas Sn^0 and Sn^{IV} precipitates at favorable pH and Eh conditions. Hydrolysis products of Sn are controversially discussed, pointing to a large variety of possible hydrolysis species including polynuclear species similar e.g. to the early actinides. Currently, there exist only few data on the sorption of Sn^{II} and Sn^{IV} to relevant minerals in soils and sediments, showing both strong pH dependence and pH-independence of sorption – corresponding to the uncertainty of tin aqueous species. Finally, the redox equilibria between Sn^{II} and Sn^{IV} are under debate, hence the currently predicted prevalence of Sn^{IV} even under reducing conditions may be questioned. Therefore, significant research gaps exists in terms of tin aqueous speciation, sorption and redox, making predictions about the environmental behaviour and fate of tin, including ecotoxicity, rather uncertain. This is particularly true for anoxic conditions, which are of relevance for marine sediments (antifouling paints) as well as radwaste repositories ([126]Sn).

As part of a wider investigation to be completed in the next two years, we have studied the local structure and oxidation state in the Sn(II)/magnetite/water system under varying pH, and under cryostatic conditions to maintain O_2-free conditions (see Figure). The XANES edge position, the oxygen coordination number of 6 and the Sn-O distance of 2.05 Å are all in line

with Sn(IV), hence complete oxidation of Sn(II) took place within 24 h reaction time. Beyond the coordination sphere, two Sn-Fe paths could be fitted, indicative of edge-sharing and corner-sharing linkages between Sn(IV) ocathedra and Fe octahedra, suggesting inner-sphere complexation at the magnetite surface. With decreasing pH, the Sn-Fe distances become shorter and coordination numbers increase.
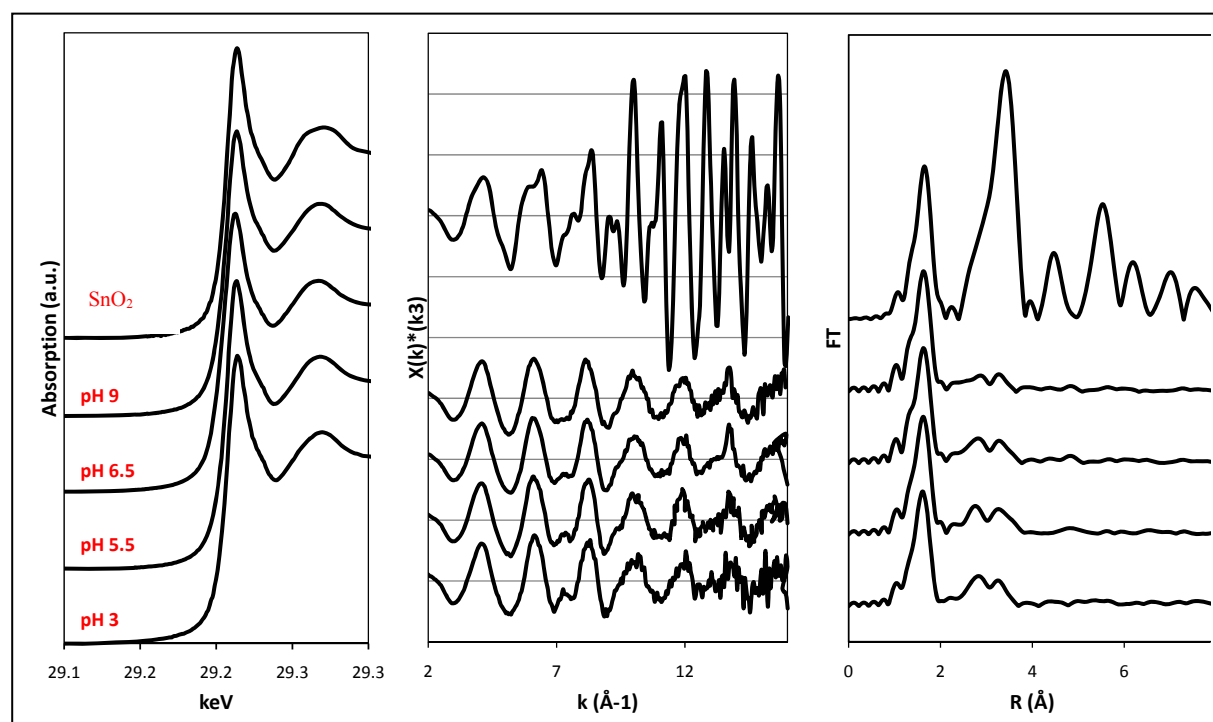

Figure 1. Sn K-edge XANES (left), EXAFS (middle), and Fourier transform (right) spectra of pH series of Sn-sorbed magnetite.

Table 1. EXAFS curve fit results of SnO_2 and Sn-sobed magnetite

Sample		Residual	Path	CN	Distance R	σ^2	E^0 shift	Area under XAFS paths
SnO₂		5.661	Sn - O	6	2.05	0.0026	10.1	49
			Sn - Sn	2.3	3.19	0.0022	10.1	40
			Sn - Sn	8.4	3.72	0.0022	10.1	100
Sn-sorbed magnetite	**pH 3**	8.102	Sn - O	6.1	2.05	0.0041	9.9	100
			Sn - Fe	1.2	3.14	0.0037	9.9	21
			Sn - Fe	3.4	3.58	0.0076	9.9	24
	pH 5.5	8.981	Sn - O	6.1	2.05	0.0040	9.7	100
			Sn - Fe	0.9	3.15	0.0012	9.7	26
			Sn - Fe	1.7	3.60	0.0025	9.7	26
	pH 6.5	9.040	Sn - O	5.9	2.05	0.0040	9.8	100
			Sn - Fe	0.9	3.16	0.0016	9.8	24
			Sn - Fe	1.6	3.60	0.0033	9.8	22
	pH 9	8.511	Sn - O	6.1	2.05	0.0038	9.9	100
			Sn - Fe	0.6	3.17	0.0018	9.9	15
			Sn - Fe	1.2	3.62	0.0038	9.9	14