ROBL-CRG	**Experiment title:** Abiotic antimony reduction by Fe(II) systems	**Experiment number**: 20-01-668
Beamline: BM 20	**Date of experiment**: from: Mar 12 to: Mar 16, 2009	**Date of report**: Apr 17 2011
Shifts: 12	**Local contact(s)**: A.C. Scheinost	*Received at ROBL:* Apr 17 2011

Names and affiliations of applicants (* indicates experimentalists):
A. C. Scheinost*[1], R. Kirsch*[1,2],
[1]Institute of Radiochemistry, FZD, Dresden, Germany
[2]Laboratoire de Géophysique interne et Tectonophysique, Université Joseph Fourier, Grenoble, France

EXAFS and XPS investigation of Sb(V) reduction on mackinawite

Reduction of Sb(V) at the surface of nanoparticulate mackinawite was studied using X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) spectroscopy. Two series of experiments, at pH 5 and pH 8 respectively, were conducted where four different Sb concentrations (0.1, 0.3, 0.6, 0.8 mM) were reacted with aqueous suspension of mackinawite under CO_2-free, anoxic conditions. XPS results demonstrate high surface loading and complete reduction of Sb(V) to Sb(III) at pH 5, whereas at pH 8 lower surface loading coupled with incomplete reduction of Sb(V) is observed. Presence of Fe(III)-O and S^0 as oxidation products were identified at the surface of reacted samples at both pH. Sb K-edge EXAFS results indicate that Sb(III) is coordinated by three sulfur atoms at pH 5. At pH 8, however, only a small part of Sb(V) is reduced to Sb(III) which is most likely bound to S atoms, while the remaining Sb(V) atoms are in edge sharing and bidentate corner sharing linkages with $Fe(O,OH)_6$ octahedra which are formed as a reaction product.

Table 1. Fitting parameters for EXAFS spectra.

Sample	Shell	C.N.	Distance (Å)	σ^2
0.3 mM Sb, pH 5	Sb-S	2.97	2.48	0.0039
	Sb-Sb	0.60	3.81	0.0078
0.1 mM Sb, pH 8	Sb-O	3.7	1.98	0.0043
	Sb-S	1.0	2.44	0.0037
	Sb-Fe	1.0	3.12	0.0038[c]
	Sb-Fe	2.0	3.55	0.0038[c]
0.8 mM Sb, pH 8	Sb-O	4.8	1.97	0.0033[c]
	Sb-S	0.2	2.46	0.0033[c]
	Sb-Fe	1.0	3.09	0.0058[c]
	Sb-Fe	2.3	3.55	0.0058[c]

c: correlated, S_0^2 :1.1, fit mode: k^3+k^2

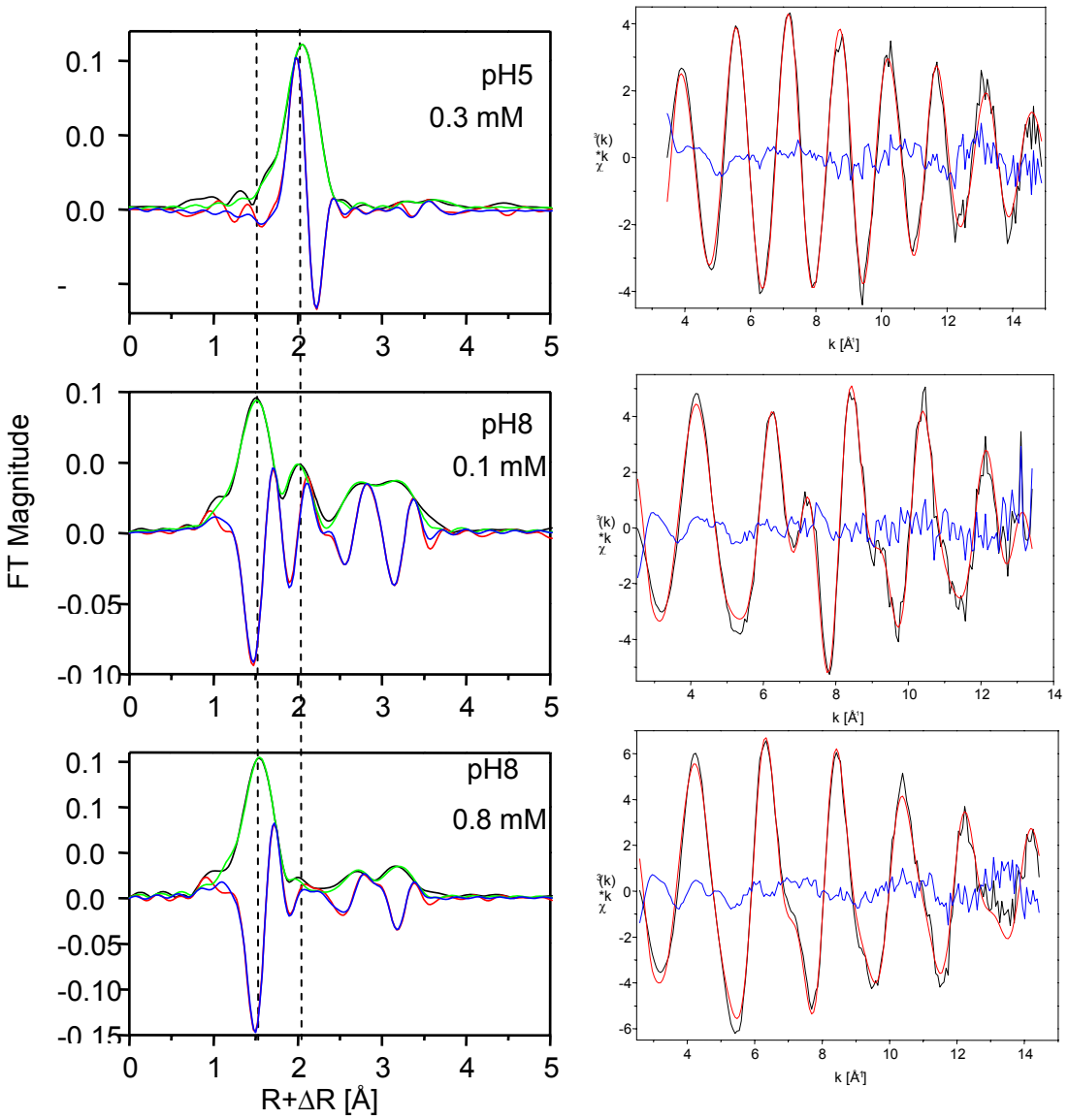
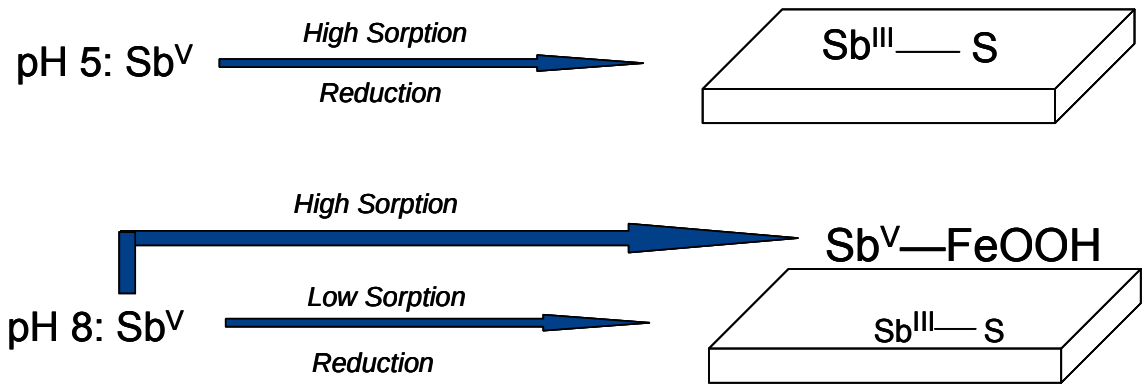


Fig. 1. Fitted Sb K-edge EXAFS spectra and the corresponding Fourier transforms.

The figure below gives a reaction scheme highlighting the more chalcophile nature of Sb(III) versus the more oxyphile nature of Sb(V).



Kirsch R., Banerjee D., Charlet L., and Scheinost A. C. (2011) EXAFS and XPS investigation of Sb(V) reduction on mackinawite. *Environmental Science & Technology*, submitted.