

REPORT ON PROJECT 30-02-787

Molecular-level control on Zn isotopic fractionation upon sorption onto Fe and Mn oxides

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The aim of the project 30-02-787 was to use EXAFS data to control, at the molecular level, the quality of sorption samples prepared for Zn isotopic analyses. These spectroscopic data will especially help to rule out the occurrence of trace amounts of hydroxides, oxides or surface precipitates possibly forming during sorption experiments at pH above 7 and/or with high Zn loadings and which could not be evidenced by X-ray diffraction techniques.

Materials and methods

Several Zn-sorbed ferrihydrite and goethite samples were prepared following pH-dependant sorption isotherms. During these experiments 9 identical Zn stock solution were reacted with the same amount of Fe (hydr)oxide (ferrihydrite or goethite) under constant stirring at various pH (4, 5, 6, 6.5, 7, 7.5 and 8) during 24 hours. After each experiment, solutions were ultra-filtered for chemical and isotopic measurements and solids were air-dried and separated in two parts. The first one was dissolved in concentrated HNO_3 for chemical and isotopic measurements. The second one was conserved for spectroscopic analyses.

The fraction of Zn sorbed onto Fe (hydr)oxides was estimated by comparing the concentration of Zn in the solution at the end of each sorption experiment with that in the initial solution. Results are shown on Figure 1, where the fraction of Zn sorbed onto Fe (hydr)oxides is depicted against pH of the reacting solution. According to these results, the Zn-sorbed ferrihydrite and goethite samples reacted at pH 5, 7 and 8 were selected for EXAFS analyses.

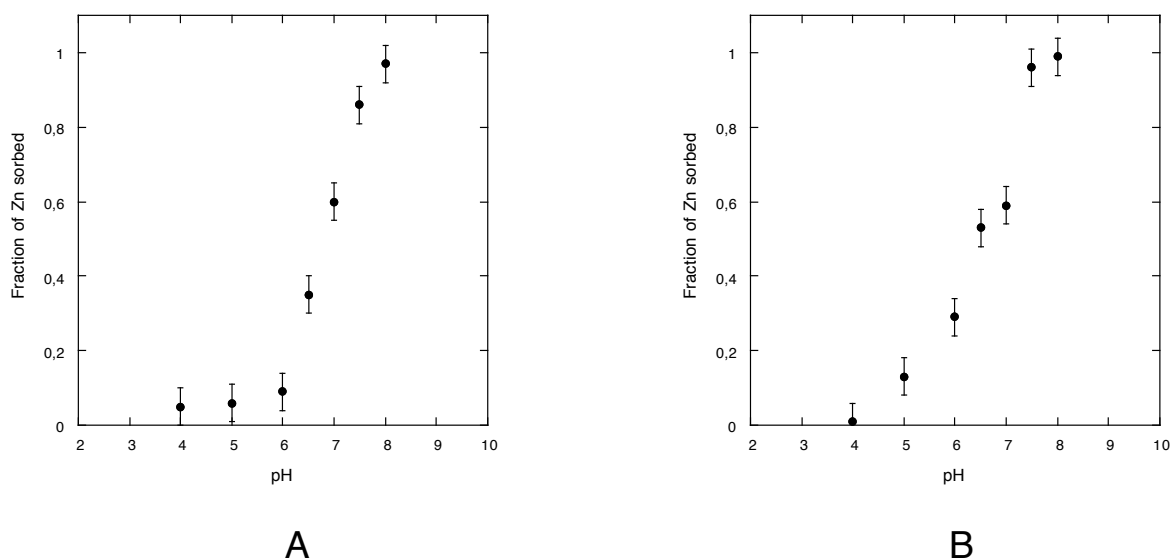


Figure 1: Results of pH-dependant sorption isotherms for Zn sorbed onto ferrihydrite (A) and goethite (B).

Results

Because chemical analyses indicate that Zn-sorbed Fe (hydr)oxides obtained at pH 8 have a much higher Zn loadings than the ones synthesized at pH 4 and 6, these samples are the most concerned by possible precipitation of unwanted Zn species during sorption experiments. As a consequence, only spectroscopic results obtained on these Zn-sorbed Fe (hydr)oxides at pH 8 will be discussed in this report. These spectroscopic results are presented in Figure 2.

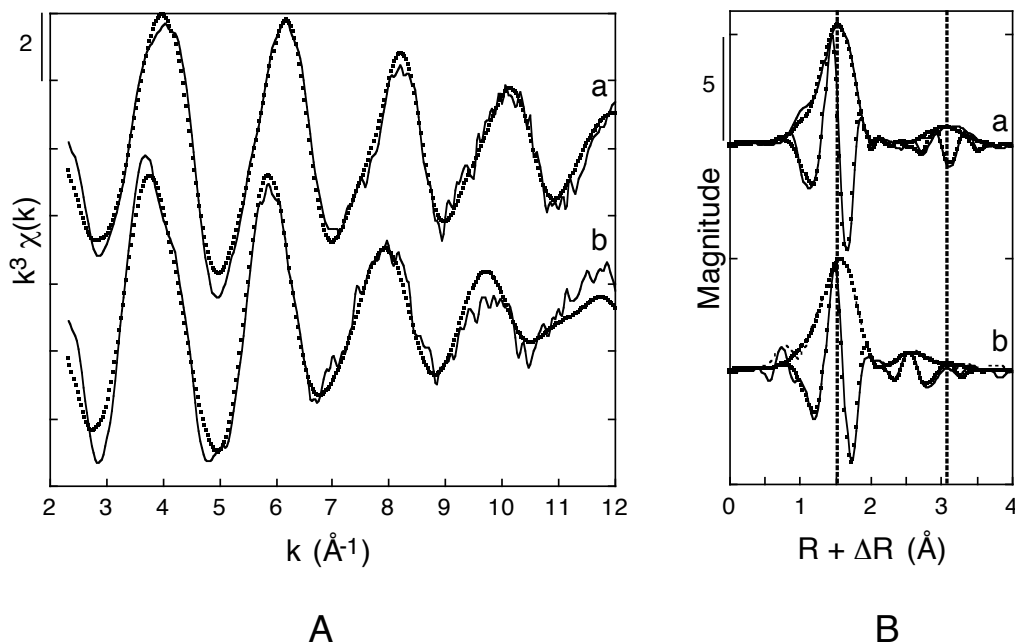


Figure 2 : Experimental (plain lines) and calculated (dotted lines) EXAFS spectra (A) and RDFs (B) of the Zn-sorbed ferrihydrite (a) and goethite (b) at pH 8 for 24 hours.

The first result is that studied samples are ‘‘sorption’’ samples, as indicated by the low second-neighbour signal visible on the RDFs of both samples (Figure 2B). This first point allows to rule out the possible occurrence of surface precipitates, which is very important for the interpretation of isotopic data.

The second result is that Zn surface complexes onto ferrihydrite and goethite are different. This point is illustrated by the difference in the frequency of the oscillations of the EXAFS spectra of both Zn sorbed Fe (hydr)oxides (Figure 2A), which is reflected in the different position of the first-neighbor peaks on their RDFs (Figure 2B). The lower frequency of the EXAFS spectrum of Zn-sorbed ferrihydrite and smaller R value of its first-neighbor peak suggests a shorter Zn-O distance than in the Zn-sorbed goethite sample. In addition, the much longer R value of the second-neighbor peak on the RDF of the Zn-sorbed ferrihydrite compared to the Zn-sorbed goethite also point out to different Zn surface complexes for both samples (Figure 2B).

	First shell (Zn-O)			Second shell (Zn-Fe/Zn)			
	$R(\text{\AA})^{(1)}$	$N^{(2)}$	$\sigma(\text{\AA})$	$R(\text{\AA})^{(1)}$	$N^{(2)}$	$\sigma(\text{\AA})$	$\Delta E_0(\text{eV})$
Zn-sorbed ferrihydrite	1.97	3.2	0.07	3.47	1.0	0.10	6.2
Zn-sorbed goethite	2.05	4.6	0.09 ⁽³⁾	3.07	0.9	0.09 ⁽³⁾	5.9
				3.26	0.8	0.09 ⁽³⁾	5.9

⁽¹⁾ Accuracy on distances is $\pm 0.02 \text{ \AA}$ and $\pm 0.04 \text{ \AA}$ for first and second neighbours, respectively.

⁽²⁾ Accuracy on N is $\pm 30 \%$. ⁽²⁾ Linked parameter.

Table 1 : Results of the shell-by-shell analysis of the partial EXAFS pectra of the Zn-sorbed ferrihydrite and goethite obtained after back-transformation of the first- and second-neighbour shells of their RDFs.

These observations are confirmed by the results of the shell-by-shell analysis of the partial EXAFS spectra of both Fe (hydr)oxides obtained after back-transformation of the first- and second-neighbor peaks of their RDFs. This shell-by-shell analysis was performed with the Zn-O phase-shift and amplitude functions extracted from the franklinite (ZnFe_2O_4 ; Hill et al., 1979) and the smithsonite (ZnCO_3 ; Effenberger et al., 1981) structures for the first-neighbor contribution of tetrahedral and octahedral Zn, respectively. The second-neighbor contribution of both tetrahedral and octahedral Zn was adjusted with the Zn-Fe phase-shift and amplitude functions extracted from the franklinite structure.

Results of this shell-by-shell analysis are presented in Figure 3 and Table 1. The best fits were obtained with 3.2 Zn-O at 1.97 Å and 1 Zn-Fe at 3.47 Å for the Zn-sorbed ferrihydrite and about 4.6 Zn-O at 2.07 Å and 1 Zn-Fe at 3.07 Å and 1 Zn-Fe at 3.26 Å for Zn sorbed onto goethite.

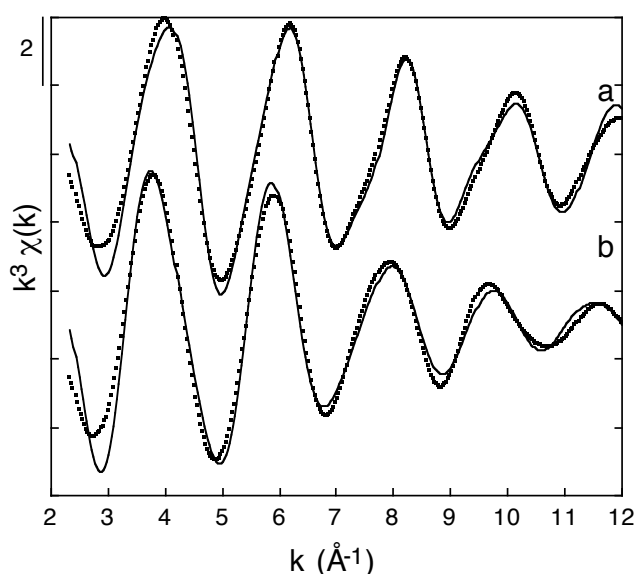


Figure 3 : Experimental (plain lines) and calculated (dotted lines) partial EXAFS spectra of the Zn-sorbed ferrihydrite (a) and goethite (b) obtained after back-transformation of the first- and second-neighbour shells of their RDFs.

For the Zn-sorbed ferrihydrite, the short Zn-O distance is in agreement with tetrahedral Zn surface complexes, whereas the much longer Zn-O distance for the Zn-sorbed goethite is compatible with octahedral surface complexes. In addition, the long Zn-Fe distance found for the second-neighbours of the Zn-sorbed ferrihydrite indicates a Zn-Fe association with corner-sharing complexes, whereas the Zn-Fe distance found for the Zn-sorbed goethite is more compatible with Zn-Fe edge-sharing complexes.

All these results are in agreement with past studies on Zn sorption onto HFO (Schlegel et al., 1997 and Juillot et al., 2003) and goethite (Waychunas et al., 2002; Juillot et al., 2003), which confirm that all the Zn-sorbed Fe (hydr)oxides synthesized can be confidently used for studying the effect of sorption processes on the isotopic fractionation of Zn between aqueous and sorbed Zn species.

References

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