

REPORT ON PROJECT 30-02-683

‘EXAFS investigation of the chemical forms of naturally occurring Zn in soils’

The aim of the project 30-02-683 was to complete an EXAFS investigation of the chemical forms of naturally occurring Zn in soils developed over Zn geochemical anomalies. Studying these natural systems where Zn has been interacting with soil components for thousands to millions years should allow to depict bio-mineralogical processes that can drive Zn speciation on a large-time scale.

Materials and methods

Due to lack of time, only two soil profiles, over the three initially selected, have been studied. Three clayey fractions (0.2-2 μm) from the A-, B- and C-horizon and one bulk (< 2 mm) fraction from the B-horizon were studied for the first soil profile (Ardèche). Because clayey fractions were missing at the moment of the EXAFS experiments, silty fractions (2-20 μm) from the A- and B-horizon and from two specific horizons (containing either phosphate or ferric centimetric nodules) were studied for the second soil profile (Morvan).

In addition, Zn sorbed onto ferrihydrite, onto goethite (FeOOH) and onto birnessite (MnO_2), as well as a Zn-phosphate (hopeite, Zn_3PO_4), were also analyzed as reference compounds.

EXAFS data were recorded at the Zn K-edge (9659 eV) at cryogenic temperature (10K), with a monochromator equipped with two Si(220) crystals. For dilute soil samples and Zn sorption reference compounds, EXAFS data were collected in fluorescence mode using a Ge 13-elements detector. A 3T V filter was used to damp the fluorescence of Fe for soil samples (up to 8 wt% Fe) and for sorption samples onto Fe (hydr)oxides, whereas a 3T Ti filter was used to damp Mn fluorescence for sorption sample onto birnessite. No filter was used to attenuate the Rayleigh scattering. Due to its large amount of Zn, the Zn-phosphate reference compound was analyzed in transmission mode. Between 3 and 10 scans were recorded for each sample, depending on Zn concentration.

Data quality

For all samples studied, glitches above 11.5 \AA^{-1} prevent a long k-range analysis of EXAFS data as it is illustrated in Figure 1 for the 0.2-2 μm fraction of the A-horizon from the first soil profile (Ardèche).

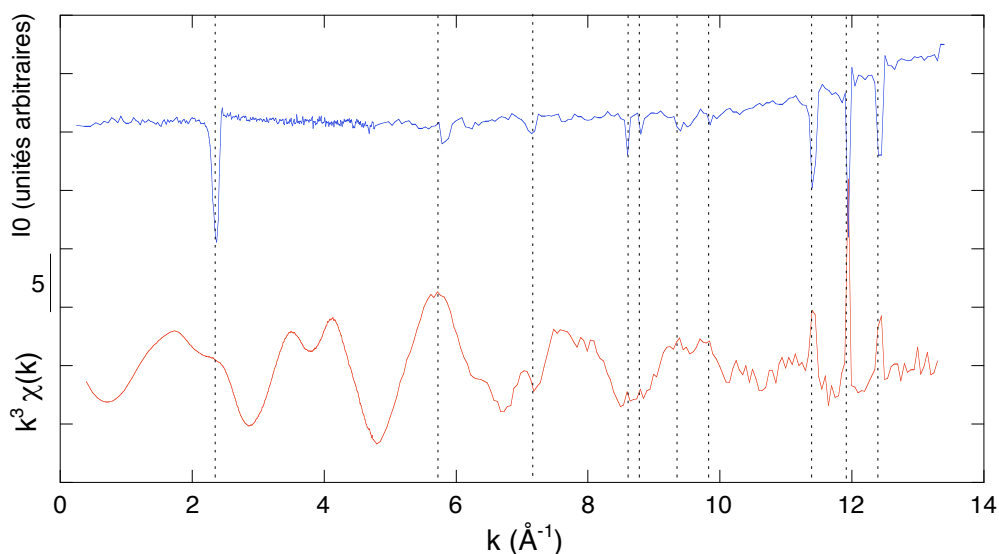


Figure 1 : (top) I_0 signal and (bottom) EXAFS spectra of 0.2-2 μm fraction of A-horizon from Ardèche soil profile.

Preliminary results

First soil profile (Ardèche)

For the first soil profile (Ardèche), the quality of the EXAFS data is good (Figures 2A and 2B). Preliminary comparison between samples studied indicates that Zn speciation is similar in the 0.2-2 μm fractions from A- and B-horizon and in the bulk sample from B-horizon, whereas it seems to differ in the 0.2-2 μm fractions from C-horizon (Figures 2A and 2B). On $k^3\chi(k)$ spectra, this difference can be seen around 4 \AA^{-1} where a beat pattern is observed for A- and B-horizons and not for the C-horizon, and after 7 \AA^{-1} where oscillations of the C-horizon are shifted compared to those of A- and B-horizons (Figure 2A). On RDFs, this difference is evidenced by the occurrence of four peaks around 1.60, 2.70, 3.80 and 5.55 \AA (uncorrected for phase shift) for A- and B-horizons, whereas the C-horizon exhibits only three peaks around 1.45, 3.35 and 5.00 \AA (uncorrected for phase shift) (Figure 2B).

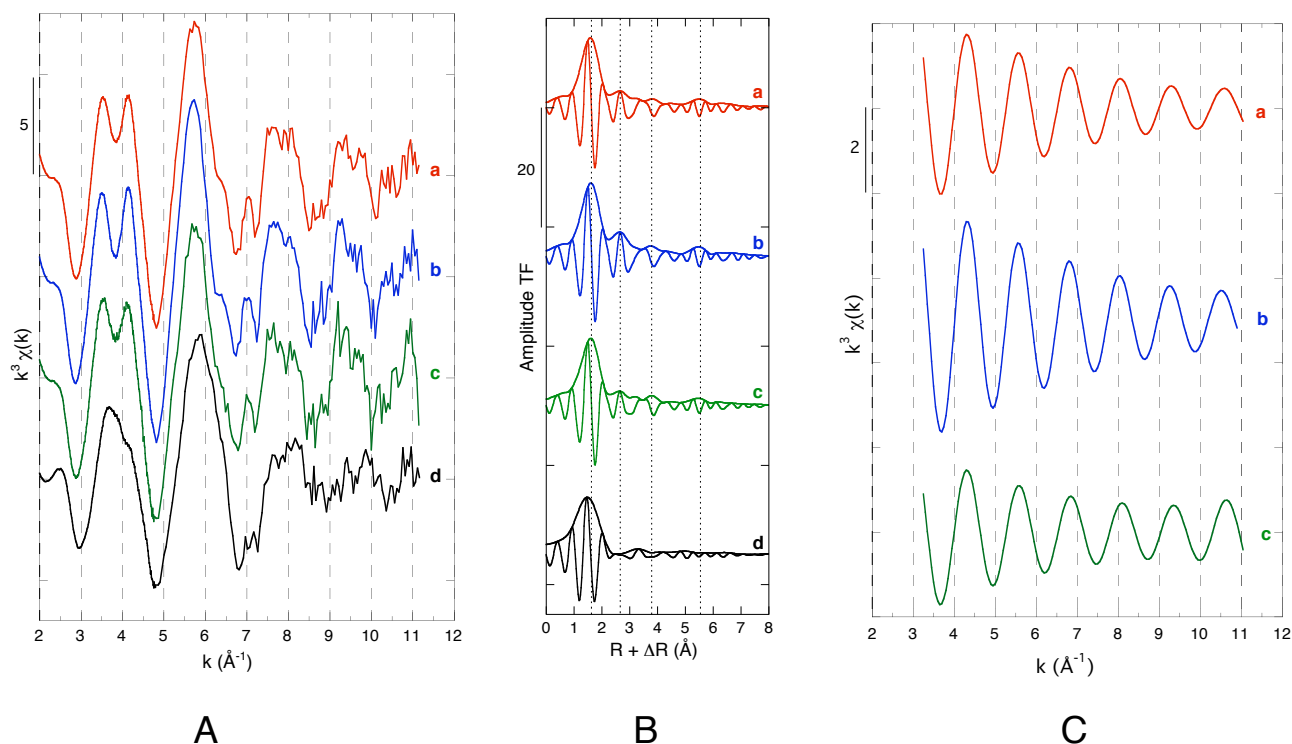


Figure 2A : EXAFS spectra of (a) 0.2-2 μm fraction of A-horizon, (b) 0.2-2 μm fraction of B-horizon, (c) bulk fraction of B-horizon and (d) 0.2-2 μm fraction of C-horizon.

Figure 2B : RDF (uncorrected for phase shift) of (a) 0.2-2 μm fraction of A-horizon, (b) 0.2-2 μm fraction of B-horizon, (c) bulk fraction of B-horizon and (d) 0.2-2 μm fraction of C-horizon.

Figure 2C : Inverse Fourier Transform of second-neighbours of (a) 0.2-2 μm fraction of A-horizon, (b) 0.2-2 μm fraction of B-horizon and (c) bulk fraction of B-horizon.

Detailed analysis of EXAFS data is still in progress, but a preliminary observation can already be drawn. The inverse Fourier transform of the peak related to the second-neighbours shell (around 2.70 \AA , uncorrected for phase shift) on the RDFs of A- and B-horizons (Figure 2B) yields a partial $k^3\chi(k)$ spectra which can be related to “light” elements with a maximum at low k values (Figure 2C).

Further comparisons with model compounds, as well as, changes in EXAFS signal after various chemical treatments (exchangeable Zn, Zn bound to organic matter or to amorphous or crystalline iron oxides, Zn-carbonate and Zn-phosphate), will help to identify actual Zn speciation along this soil profile.

Second soil profile (Côte d'Or)

For the second soil profile (Côte d'Or), the quality of the EXAFS data is quite low (Figures 3A and 3B). This poor signal/noise ratio is related to the fact that the beam displaced on the samples during EXAFS scans with the same order of magnitude (20 μm) than single grains constituting the samples (fraction 2-20 μm). Hand-grinding of the samples in an agate mortar failed at reducing enough the size of single grains so as to avoid such artefact.

Preliminary comparison between samples indicates that Zn speciation is different in the 2-20 μm fractions of E-horizon, Bt-horizon and the two horizons containing Fe or PO_4 nodules (Figures 3A and 3B). This change at the scale of the soil profile can also be observed at the scale of the specific horizon containing Fe nodules where Zn speciation is different between the 2-20 μm fraction and the separate Fe nodules (Figures 4A and 4B).

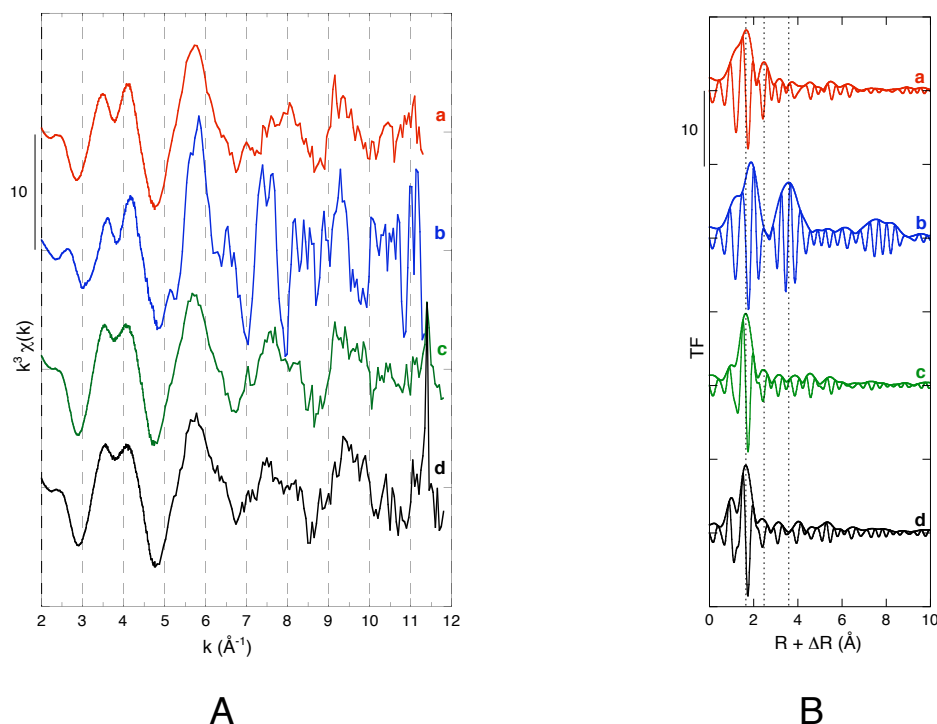


Figure 3 A : EXAFS spectra of (a) 2-20 μm fraction of E-horizon, (b) 2-20 μm fraction of Bt-horizon, (c) 2-20 μm fraction of horizon with Fe nodules and (d) 2-20 μm fraction of horizon with PO_4 nodules.
Figure 3 B : RDF (uncorrected for phase shift) of (a) 2-20 μm fraction of E-horizon, (b) 2-20 μm fraction of Bt-horizon, (c) 2-20 μm fraction of horizon with Fe nodules and (d) 2-20 μm fraction of horizon with PO_4 nodules.

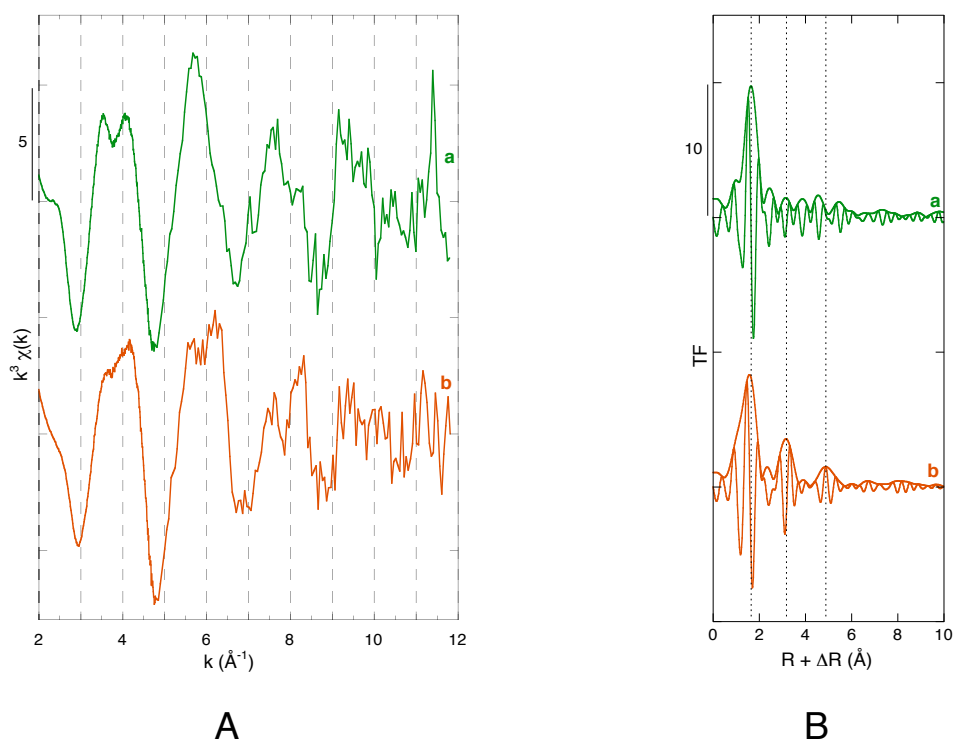


Figure 4A : EXAFS spectra of (a) 2-20 μm fraction of horizon with Fe nodules and (b) separate Fe nodules.
Figure 4B : RDF (uncorrected for phase shift) of (a) 2-20 μm fraction of horizon with Fe nodules and (b) separate Fe nodules.

The $k^3\chi(k)$ spectra of the E-horizon is very similar to those of A- and B-horizons from the first soil profile (Ardèche) (Figure 5A), which suggest a similar speciation for Zn. However, comparison of the RDFs indicates that this similarity is not so obvious and emphasizes the importance of further EXAFS data analysis (Figure 5B).

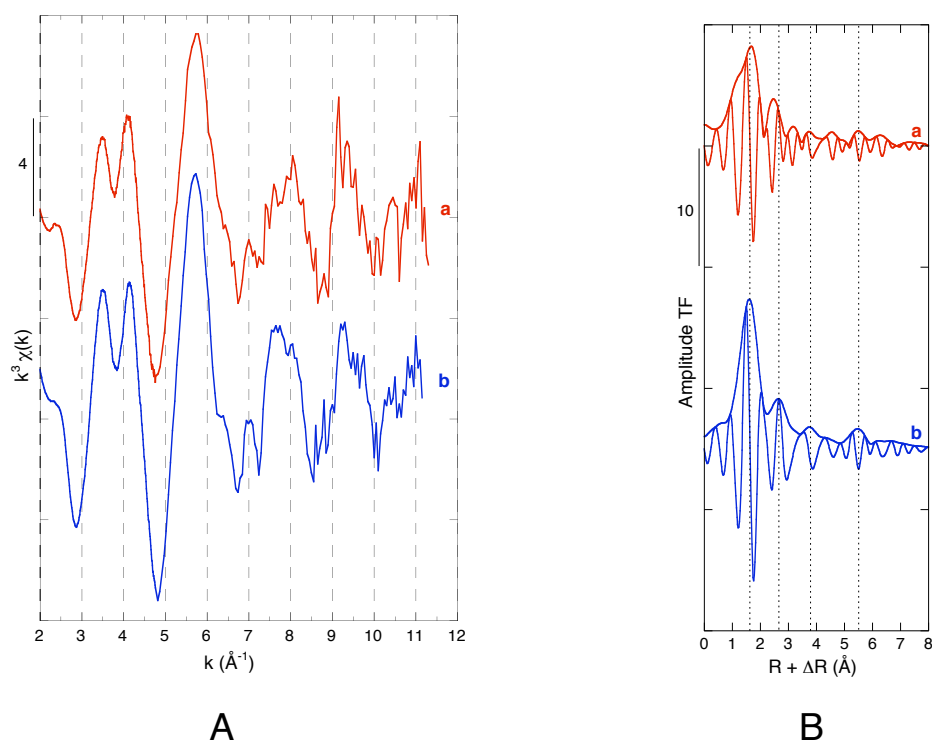


Figure 5A : EXAFS spectra of (a) 2-20 μm fraction of E-horizon and (b) 0.2-2 μm fraction of B-horizon from the first soil profile (Ardèche).

Figure 5B : RDF (uncorrected for phase shift) of (a) 2-20 μm fraction of Bt-horizon and (b) 0.2-2 μm fraction of B-horizon from the first soil profile (Ardèche).

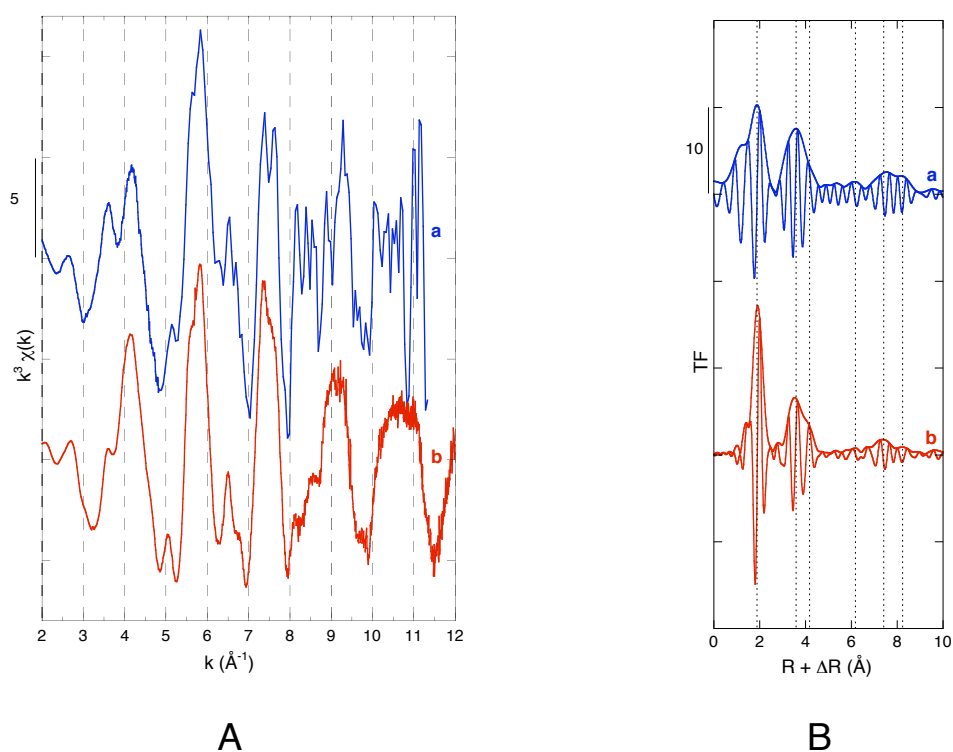


Figure 6A : EXAFS spectra of (a) 2-20 μm fraction of Bt-horizon and (b) sphalerite (ZnS) model compounds (data obtained during CH-531 project in 1998 on ID26).

Figure 6B : RDF (uncorrected for phase shift) of (a) 2-20 μm fraction of Bt-horizon and (b) sphalerite (ZnS) model compounds (data obtained during CH-531 project in 1998 on ID26).

The $k^3\chi(k)$ spectra of the Bt-horizon is very well structured (Figure 3A) and the RDF exhibits a very intense peak around 3.60 Å (uncorrected for phase shift) related to the second-neighbours shell around central Zn (Figure 3B). The first-neighbours peak of this sample is located around 1.90 Å (uncorrected for phase shift), which is too long for Zn-O linkage and indicate rather Zn-S bonds within this sample. Comparison of EXAFS data of this sample with those of reference compounds strongly suggests that Zn occurs as Zn sulfides in the Bt horizon of this soil profile (Figures 6A and 6B).

The $k^3\chi(k)$ spectra and the RDFs of the two horizons containing Fe or PO_4 nodules are very similar which suggest that Zn speciation is the same in these two samples (Figures 3A and 3B).

Actual speciation of Zn in all samples studied, but the Bt-horizon of the second soil profile (Côte d'Or), has not been yet identified. Data analysis is still in progress. Shell-by-shell analysis will be used to depict Zn neighbouring in each sample studied. Experimental EXAFS spectra will be fitted by a linear combination of EXAFS spectra of selected reference compounds to yield quantitative speciation of Zn in all samples investigated.