

## **EXAFS signature of structural Zn at trace levels in natural and synthetic trioctahedral 2:1 phyllosilicates**

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### **ABSTRACT**

EXAFS spectroscopy has been used to determine the medium-range structural environment (within a radius of  $\approx 7$  Å) of trace levels of Zn<sup>2+</sup> ions within the octahedral sheets of trioctahedral 2:1 phyllosilicates. EXAFS signatures of trace quantities (800–4000 ppm) of Zn in natural and synthetic trioctahedral 2:1 phyllosilicates (talcs and biotite) were analyzed using *ab initio* FEFF calculations (FEFF 8.10 code) in which various second-neighbor atomic configurations around a Zn-containing octahedral site were examined. Comparison of the results of these model calculations with observed Zn *K*-edge EXAFS spectra provides constraints on the distribution of Zn within the octahedral sheet. Zn was found to be randomly distributed within the octahedral sheets of the synthetic talc containing 4000 ppm Zn. In the natural biotite containing 800 ppm Zn, the distribution of Zn could not be determined because of significant Fe content, which precluded unambiguous FEFF analysis. Finally, FEFF analysis of single-scattering and multiple-scattering contributions to the EXAFS data of the Zn-dilute talc sample, followed by comparison with EXAFS data from a natural dioctahedral illite sample containing 140 ppm Zn, allowed unambiguous identification of spectral features characteristic of Zn<sup>2+</sup> ions incorporated within the octahedral sheets of trioctahedral phyllosilicates. These results indicate that EXAFS spectroscopy can be used to distinguish between incorporation of trace levels of Zn<sup>2+</sup> ions within the octahedral sheet of di- or trioctahedral phyllosilicates. They also provide a strong basis for determining the speciation of Zn at trace concentration levels in natural phyllosilicates from Zn-contaminated soils and sediments using Zn *K*-edge EXAFS spectroscopy. Because the crystal chemistry of other potentially toxic first-row divalent transition elements (i.e., Co<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup>) is similar to that of Zn<sup>2+</sup>, this FEFF-based EXAFS approach could be used to (1) complement existing FTIR and polarized-EXAFS approaches in assessing the distribution of these elements within the octahedral sheets of di- and trioctahedral phyllosilicates and (2) better determine the speciation of these elements in contaminated soils and sediments.

**Keywords:** Zinc, phyllosilicates, EXAFS, FEFF, trace levels