

The beamtime has been used very effectively to collect Mn, Ni and Zn-EXAFS data on synthetic and natural lithiophorite. We have shown by a detailed analysis of the three first Mn shells contributions, and in particular of multiple-scattering effects, that Mn<sup>3+</sup> and Mn<sup>4+</sup> are orderly distributed in the phyllosmanganate layer. This was totally unknown, and even unexpected, and allowed us to reconcile data obtained by chemistry, XRD and EXAFS. Zn was shown to be incorporated in the brucitic (Al(OH)<sub>3</sub>) layer, whereas Ni substitutes for Mn in the phyllosmanganate layer.

The results from our experiments have been reported in an article, which is submitted to *Geochimica et Cosmochimica Acta*. Its abstract is copied below.

### **Natural speciation of Mn, Ni and Zn at the micrometer scale in a clayey paddy soil using X-ray fluorescence, absorption, and diffraction**

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#### **ABSTRACT**

Knowledge of the solid-phase speciation of trace elements in the environment is important to understand their sequestration mechanisms, and to manage, predict and remediate contaminated soils and sediments. The speciation of Mn (0.19 g/kg), Ni (46 mg/kg) and Zn (42 mg/kg) in the argillic horizon (120 cm depth, pH = 5.6) of an Ultisol from a paddy soil in northern Taiwan was investigated by a combination of advanced X-ray synchrotron techniques. Microchemical associations were imaged by synchrotron-based X-ray microfluorescence, host minerals were identified by standard and micrometer-resolved X-ray diffraction, and the local coordination environment of Mn, Ni, and Zn was probed using extended X-ray absorption fine structure (EXAFS) spectroscopy on powdered samples, and polarized EXAFS spectroscopy on a highly textured self-supporting clay film from the <2 μm fraction of the soil. Manganese was found to be concentrated in Fe-Mn soft mottles (44.4 g/kg) and speciated as turbostratic hexagonal birnessite and lithiophorite having Mn<sup>3+</sup>/Mn<sup>4+</sup> atomic ratio of about 20 % and 50 %, respectively. Quantitative analysis of high order scattering paths of the EXAFS spectrum for natural and synthetic (Al<sub>0.67</sub>Li<sub>0.32</sub>)(Mn<sub>0.68</sub><sup>4+</sup>Mn<sub>0.32</sub><sup>3+</sup>)O<sub>2</sub>(OH)<sub>2</sub> lithiophorite revealed that Mn<sup>3+</sup> and Mn<sup>4+</sup> are ordered in the  $\left[ (\text{Mn}_{0.68}^{4+}\text{Mn}_{0.32}^{3+})\text{O}_2 \right]^{0.32-}$  layer. A structural model for their distribution pattern is proposed, in which Mn<sup>4+</sup> and Mn<sup>3+</sup> are ordered similarly to Al and Li in the  $\left[ (\text{Al}_{0.67}^{3+}\text{Li}_{0.32}^+)\text{(OH)}_2 \right]^{0.32+}$  layer, with Mn<sup>3+</sup> cations being surrounded by six Mn<sup>4+</sup>, and Mn<sup>4+</sup> cations by three Mn<sup>3+</sup> and three Mn<sup>4+</sup>. The suggested similarity of cation ordering in the manganese and aluminium layers of lithiophorite likely increases its overall stability in providing a more homogeneous balance of the excess and deficit of charges in each layer. Ni

( $r = 0.70 \text{ \AA}$ ) is taken up quantitatively by the soil lithiophorite, and substituted for Mn ( $r(\text{Mn}^{4+}) = 0.54 \text{ \AA}$ ,  $r(\text{Mn}^{3+}) = 0.65 \text{ \AA}$ ) in the manganese layer. In contrast to Ni, Zn ( $r = 0.74 \text{ \AA}$ ) fills vacant sites from the dioctahedral gibbsitic layer of natural lithiophorite, in a similar manner as lithium ( $r = 0.74 \text{ \AA}$ ) in synthetic lithiophorite. The partitioning of the two trace metals between the two layers of lithiophorite is determined essentially by steric effect and the general preference for slightly smaller site in the case of nickel, whose size is intermediate between those of  $\text{Mn}^{3+}$  and  $\text{Li}^+$ . In contrast with nickel, which is detected where there is lithiophorite, zinc is not specifically associated with this mineral, and the Zn-lithiophorite association found in Fe-Mn mottles is not representative of the bulk soil. The combined use of X-ray diffraction, and powder and polarized EXAFS spectroscopy revealed that Zn is predominantly bound to hydroxy-Al layers sandwiched between 2:1 vermiculite layers in the fine soil matrix. Although zinc is associated with two distinct mineral phases in Fe-Mn mottles and in the clayey matrix, its molecular-scale speciation is the same since it fills the vacant sites of a gibbsitic layer in both minerals, the difference being that the aluminous layer is intercalated between  $\text{MnO}_2$  layers in lithiophorite and between hydrous silicate layers in phyllosilicate. The incorporation of Zn in the gibbsitic layer of the two minerals helps increase their stability by providing positive charge to balance the negative charge from the 2:1 phyllosilicate layer and from the  $\left[ (\text{Mn}_{0.68}^{4+} \text{Mn}_{0.32}^{3+}) \text{O}_2 \right]^{0.32-}$  layer of lithiophorite. The coordination chemistry of zinc described in this study is believed to be the main sequestration mechanism of zinc in acidic to near-neutral aluminium-rich clayey soils.