Speciation and Quantification of Inorganic and Organic Phosphorus Forms in Environmental Samples by P *L*-edge XANES

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Introduction

Phosphorus (P) is important in agriculture and the environment. Imbalances in soil and environmental P pools cause significant depressions in agricultural crop yields and the pollution of freshwater. Besides wet chemical fractionation of bonding types and ^{31}P NMR, synchrotron-based P-XANES is a new analytical approach to investigate P species. Most relevant investigations studies used X-ray absorption at the P *K*-edge [1], but P *L*-edge also appears to be a promising complementary approach for environmental samples.

Science

Our long-term objective is to develop P *L*-edge XANES as a method for the speciation and quantification of P in environmental samples. We measured mixtures of reference standards with varying ratios of individual chemical compounds to find out the limits of the application of spectra deconvolution by linear combination fits. Subsequently, P *L*-edge XANES will be applied to various environmental chemistry problems such as transformation of Ca-P from bones into microbial P compounds by fungi, P speciation in ashes from renewable energy production and P forms in manure, composts, altering wetlands, etc.

Materials and Methods

As a first step, we did spiking experiments with organic (sodium phytate, adenosine mono-, di-, and triphosphate, phospholipids) and inorganic (Ca-phosphate, Mg-phosphate, and Fe/Al-phosphate) P compounds. The experimental approach is similar to work done at the DCM-beamline in Madison, WI in March 2007 (P *K*-edge XANES). We used the same samples/sample holders to achieve direct comparability of P *K*- and *L*-edge spectra. Second, we investigated thermally treated bone materials that were inoculated with beneficial microorganisms. The P *L*-edge XANES spectra were recorded on beamline 11ID-2 (VLS-PGM) at the Canadian Light Source.

Discussion

Figure 1 compares the *L*-edge and *K*-edge XANES spectra of organic P reference compounds. Obviously the P *L*-edge spectra were much more distinguishing than the P *K*-edge spectra. Therefore, quantitative analysis by linear combination fitting may result in more reliable results using *L*-edge spectra.

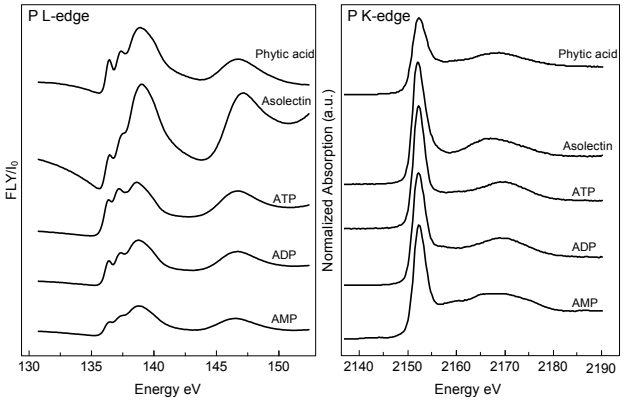

Figure 1. P *L*-edge (left) and *K*-edge (right) XANES spectra of some organic phosphates.

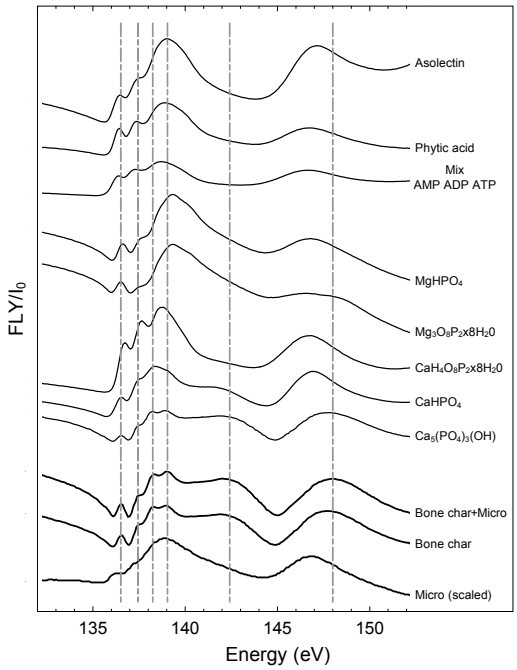

Figure 2. P *L*-edge XANES spectra of a bone char sample (Bone char), a bone char sample after treatment with beneficial microorganisms (Bone char+Micro) and of the microorganisms washed off the bone char after a growth period (Micro) compared to various reference compounds for organic and inorganic P.

Discussion

The spectrum of bone char more closely resembles the spectra of Ca-phosphates than the spectrum of $Mg_3O_8P_2 \cdot 8H_2O$. Especially the feature at 148 eV in the bone char was observed only in $Ca_5(PO_4)_3(OH)$. Growth of the microorganisms at the bone char dissolved some of the phosphates as visualized by electron micrographs. This means the microorganisms must have incorporated inorganic P into organic P of their metabolites. The spectrum of the microorganisms manually separated from their bone char growth medium was more similar to the spectrum of asolectin (a reference compound for phospholipids) than to the spectrum of nucleotide phosphates (a mix of AMP ADP ATP). Particularly, the small features at 136.5 and 137.5 eV and the energy position of the most prominent feature at 139 eV distinguished this spectrum from that of the AMP ADP ATP-mix. It follows that the organic P in the microorganisms represents P-lipids to a larger extent than nucleotid phosphates. This agrees with average ratios nucleotide-P to lipid-P ratios of 1:2 to 1:5 in soils [2], and 1:420 in soil microbial biomass [3].

Conclusion

To the best of our knowledge these results demonstrate for the first time that the microbial utilization of inorganic P sources could be shown by P *L*-edge XANES. Thus, P *L*-edge XANES offers an additional possibility to investigate P enriched environmental samples. Complementary new information about the abundance of various organic P forms could be gained that cannot obtained by P *K*-edge XANES.

References

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