Phosphorus K-edge XANES speciation in soils formed on serpentine landscapes

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1 Introduction

Soils in serpentinic landscapes or serpentinite-derived soils suffer from low Ca content and an abundance of Mg, Fe and heavy metals such as Ni and Cr. Due to the abundance of Fe minerals, P in serpentinite-derived soils occurs chiefly as the one associated with Fe (oxy)hydroxides. It is often reported that the most dominant P pool in serpentinite-derived soils was found in the fraction of dithionite-citrate-bicarbonate and NaOH extracts, indicating that P is strongly-adsorbed and occluded with Fe minerals, respectively. Because of unique soil properties, therefore, P availability and dynamics in serpentinic landscapes differ from those in ordinal (non serpentinite-derived) soils, which may be attributable in some extent to a stark contrast to vegetation on serpentinic landscapes (e.g., metal hyper-accumulating plants). Although very few studies have studied P speciation in serpentinite-derived soils, such information is fundamental to understand P availability and dynamics in serpentinic landscapes. We investigated P K-edge XANES spectroscopy to determine possible P species and hosting minerals in the soil formed on serpentinic landscapes.

2 Experiment

Soils were collected from a serpentinic landscape (ultramafic geology) in Mie Prefecture and air-dried for the P K-edge XANES analysis. The study was conducted using the beamline BL11B equipped with Si(111) monochromator in a fluorescence mode at ambient temperature under a vacuumed condition. The XANES spectra were collected with a step wise in 0.1 eV increments with 1 s/point from 2130 to 2190 eV and in 0.5 eV increments with 1 s/point from 2190 to 2220 eV. Multiple scans across the P K-edge were averaged. Known reference P compounds such as hydroxyapatite were also measured and their XANES spectra were compared with those of soil samples.

3 Results and Discussion

Figure 1 showed selected XANES reference spectra that are representative of soil P species. Calcium phosphate references including hydroxyapatite were characterized by a well-defined shoulder on the high energy side. Compared to these P compounds, organic phosphate references including Ca-phytate and lecithin exhibited featureless spectra (data not shown). References of phosphate associated with Al and Fe minerals were characterized by an intense white-line peak in a narrow energy range. Struvite and P adsorbed on ferrihydrite exhibited a pre-edge between -5 and -2 eV, which can be a distinctive features to differentiate them from phosphate associated with Al minerals.

The XANES spectrum of soil sample was characterized by an intense white-line peak in a narrow energy range, which corresponded to the spectral features exhibited in P associated Al and Fe minerals [1]. The XANES spectra of soil samples had a pre-edge that can be superimposed with that of phosphate adsorbed on ferrihydrite (data not shown). The soils were enriched with Fe minerals, and such soil chemical constraints together with XANES spectra support that the primary hosting phase of phosphate is likely Fe minerals. This was also supported by the result of linear combination fitting using known P references.
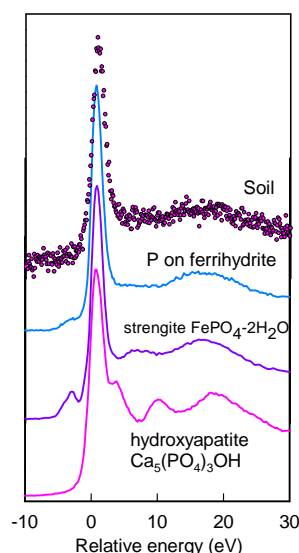

Fig. 1: P K-edge XANES spectra of soil and references

References

[1] Beauchemin *et al*., J. Environ. Qual. **32**, 1809 (2003).

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