

Oxidation states of arsenic in micrometer scales in the soil particles under various redox conditions using micro-XRF-XANES

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We have studied speciation of As and Sb in soil environment under various redox conditions [1-4]. In Mitsunobu et al. [4], the oxidation states and host phases of As in soil samples of mine tailing (Ichinokawa mine, Ehime, Japan) and in laboratory systems were determined by X-ray absorption fine structure (XAFS) spectroscopy. HPLC-ICP-MS was also used for speciation of As in soil water. In the natural soil-water system, As was present as a mixture of As(III) and As(V) by normal XAFS analysis. It was also suggested by combining the results of Fe and Mn XAFS analyses and a positive correlation among As and Fe abundances in the soil that the host phases of Sb and As in soil were Fe(III) hydroxide. EXAFS analyses of As are also consistent with this fact. Under reducing conditions, the concentration of As in the soil water increased.

In this study, the host phase of As was confirmed by the 2-D distributions of As and Fe by micro-XRF (Fig. 1) and also the correlation diagram of the counts of As and Fe (Fig. 2). In the latter case, the correlation coefficient (R^2) between Fe and As was 0.634, which was larger than those of any other elements vs. As (e.g., $R^2 = 0.231$ for Mn and As, 0.153 for Zn and As). The results showed that the host phase of As was Fe minerals, which may be Fe oxihydroxides as suggested by the micro-XANES spectra of Fe for the spots shown in Fig. 1. Manganese K-edge XANES shows that Mn is at lower oxidation state, suggesting that Mn oxides no longer exist in the soil horizon.

Arsenic K-edge micro-XANES spectra were recorded as various spots as shown in Fig. 3. The As(III) ratio estimated from the simulation of XANES showed that the ratio is rather constant between 20% to 40%, showing that the reduction of As(V) proceeds equally to any particles within the soil.

References

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- [3] S. Mitsunobu et al., Anal. Chem. **78** (2006) 7040-7043.
- [4] S. Mitsunobu et al., Environ. Sci. Technol. **40** (2006) 7270-7276.

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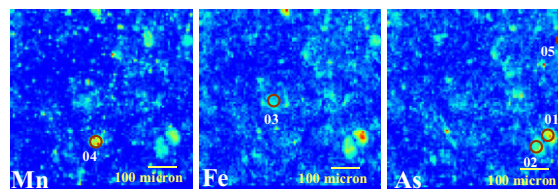


Fig. 1. 2-Distributions on Mn, Fe, As in soil particles.

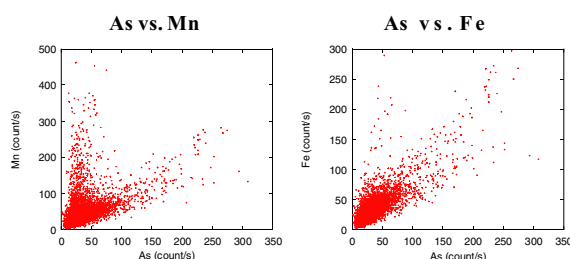


Fig. 2. Correlation of counts of As vs. Mn and Fe in the soil samples.

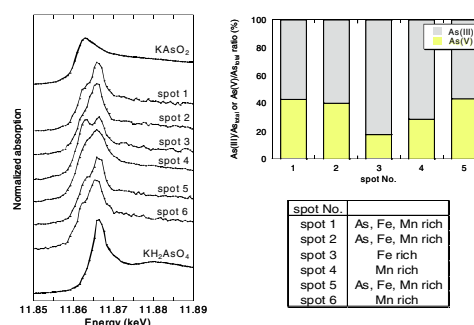


Fig. 3. Arsenic K-edge micro-XANES spectra at various spots indicated in Fig. 1 with the summary of the As(III)/As(V) ratios.

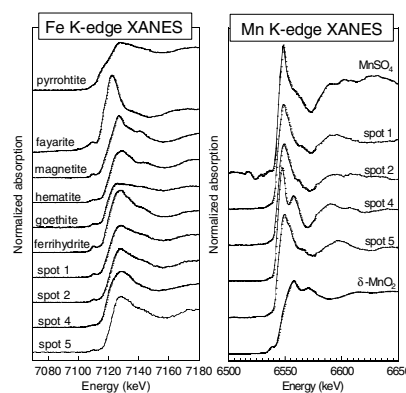


Fig. 4. Iron and Mn K-edge micro-XANES spectra at various spots indicated in Fig. 1.