XAFS Study on the Comparison of Soil-water Distribution of Antimony with that of Arsenic under Various Redox Conditions

Antimony (Sb) is the 9th most exploited metal worldwide being mined each year. It is heavily used (> 10^5 tons annually worldwide) in non-metal products such as antimony trioxide (Sb_2O_3), primarily in flame retardants, but it is also used as a catalyst in the production of plastics, a fining of glassware, and a pigment in paints and lacquers [1]. Antimony compounds are considered to be pollutants of priority interest by the United States Environmental Protection Agency and the European Union. However, the geochemical and environmental behaviors of Sb are largely unknown. Antimony belongs to group 15 in the periodic table below arsenic (As), and the most frequently observed species are Sb(III) and Sb(V) in the environment. The behavior and toxicity of Sb in the environment depend on its oxidation state as is similar to that of As. The toxicity of Sb(III) compounds is 10 times higher than that of Sb(V) species [1]. Therefore, Sb analysis in environmental samples requires quantitative measurement of Sb(III) and Sb(V). The aim of this study is the speciation of Sb and As in both solid and water phases to understand the reaction of Sb in soil-water environment and to compare the Sb behavior with As examined in mine tailings in a natural system and in a soil-water system synthesized in laboratory [2].

Natural soil and soil water samples containing Sb and As were collected around the Ichinokawa mine pithead, Ehime, Japan, which was formerly one of the largest Sb mine (stibnite: Sb_2S_3) in the world. To observe the Sb and As species under various redox conditions, the soil and soil water samples were collected at four different depths. It was found that the Eh (redox potential expressed in voltage) value decreased with the depth. In laboratory experiments, soil containing Sb and As was incubated for 7 days at 25°C to observe their oxidation states under various redox conditions by changing the total amount of water in the soil. The Eh value decreased with the increase of the water amount. Antimony *K*-edge XAFS spectra were measured at beamline **BL01B1** in SPring-8 in fluorescence mode, while *K*-edge XAFS spectra of As, Fe, and Mn at beamline BL12C in KEK-PF. The oxidation states of Sb and As in soil water were determined by high performance liquid chromatography (HPLC)-ICP-MS.

In both Ichinokawa and laboratory experiment systems, Sb XANES analysis shows that Sb in the soil was dominantly present as Sb(V) and slight Sb(III) was observed in soil under reducing condition or at lower Eh (Fig. 1(a)). On the other hand, most of As was as As(III) (reduced species) under reducing condition (Fig. 1(b)). These results show that Sb(V) is stable form in the environment and that Sb is oxidized under more oxic condition than As. Local structure of Sb and As were examined by EXAFS to obtain direct information on the host phases of Sb and As in the soil. All radial structure functions (RSFs) for Sb and As were quite similar within soil profiles. The RSF of

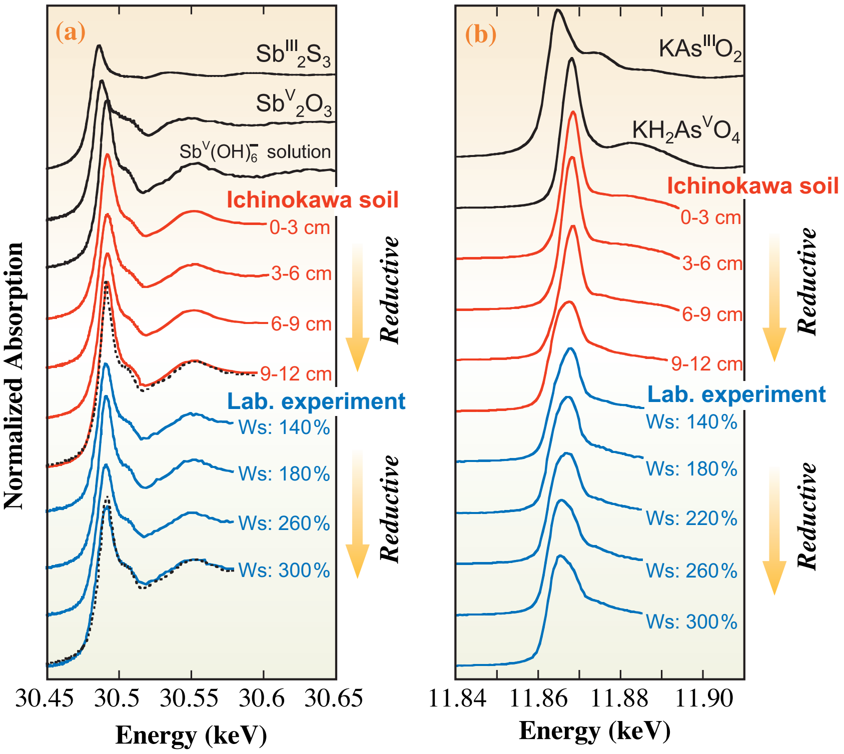

Fig. 1. **(a)** Normalized Sb *K*-edge XANES spectra of the reference materials (Sb_2S_3, Sb_2O_3, and $Sb(OH)_6^-$ solution), Sb in soil samples in the laboratory experiments, and in the Ichinokawa soil samples. Some spectra were overlapped with the spectrum of $Sb(OH)_6^-$ shown by dotted curves for comparison. **(b)** Normalized As *K*-edge XANES spectra of the reference materials ($KAsO_2$ and KH_2AsO_4), As in solid samples in the laboratory experiments, and in the Ichinokawa soil samples.

Sb(V) adsorbed on Fe hydroxide (ferrihydrite) has second prominent peak near 2.85 Å in addition to Sb-O shell near 1.5 Å (Fig. 2(a)). These features in RSFs and EXAFS spectra are similar to all the soil samples for Sb and As (Fig. 2), suggesting that Sb and As in the soil is mainly associated with Fe(III) hydroxide at all the depths [2].

Under reducing condition, concentration of As in the soil water increased with Fe and Mn concentrations in both Ichinokawa and laboratory experiment systems. These results suggest that As release from soil depends on (i) the reductive dissolution of Fe(III) hydroxide, host-phase of As in soil, and (ii) the reduction of As(V) to As(III), since As(III) is more mobile than As(V) [3,4]. On the other hand, Sb abundance in soil water decreased under reducing condition and Sb in the soil water was predominantly in the oxidized form, Sb(V), opposite to findings of As. In addition, Fe XANES analysis shows that Fe(III) hydroxide in the soil keeps its potential as adsorbent and host-phase for Sb even under reducing condition, which suggests that the decline of Sb abundance in reducing soil water may be due to a change of Sb species. It is reported that the solubility of Sb(III) is much lower than that of Sb(V) [5], and the Sb(III) was also slightly observed in both soil and soil water phases under reducing condition in present study. Therefore, it is considered that Sb reduced to Sb(III) was precipitated on the mineral surface due to its low solubility and that the precipitates containing Sb(III) like Sb_2O_3 cause the fixation of Sb to solid phase under reducing condition. These findings suggest that the different behavior of Sb and As under reducing condition is one of important factors controlling the partition behavior of Sb and As in soil-water systems.

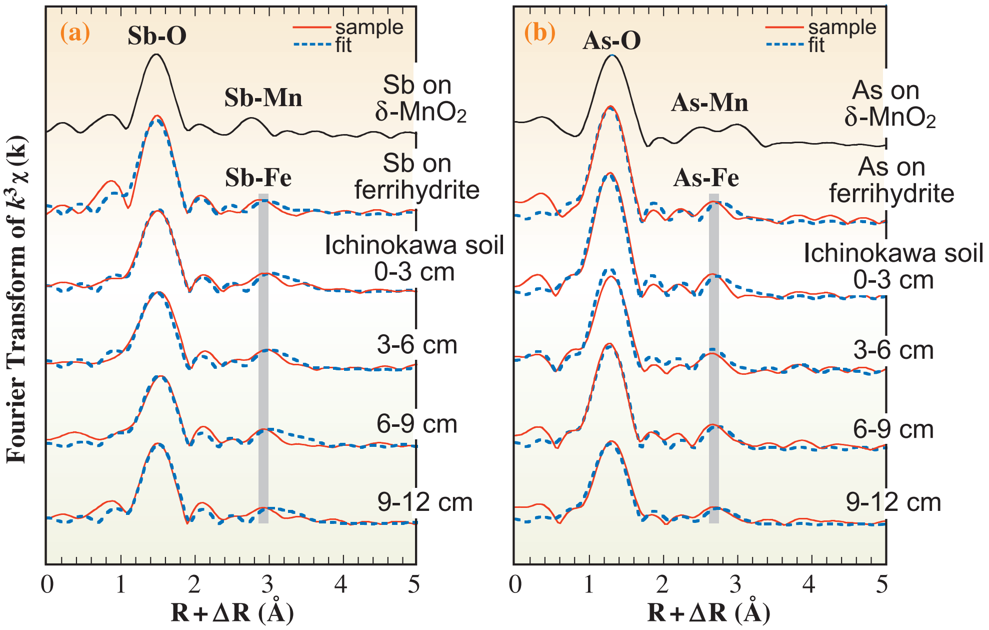

Fig. 2. Fourier-transformed EXAFS spectra of Sb **(a)** and As **(b)** in the Ichinokawa soil samples and model compounds (Sb and As adsorbed on ferrihydrite and δ-MnO_2 in **(a)** and **(b)**, respectively).

Satoshi Mitsunobu* and Yoshio Takahashi

Department of Earth and Planetary Systems Science,
Hiroshima University

*E-mail: mitsunobu@hiroshima-u.ac.jp

References

[1] M. Krachler *et al.*: Trends Anal. Chem. **13** (2001) 79.
[2] *S. Mitsunobu, T. Harada and Y. Takahashi: Environ. Sci. Technol. 40 (2006) 7270.*
[3] P.L. Smedley and D.G. Kinniburgh: Appl. Geochem. **17** (2002) 517.
[4] Y. Takahashi *et al.*: Environ. Sci. Technol. **38** (2004) 1038.
[5] M. Filella *et al.*: Earth-Sci. Rev. **57** (2002) 125.