

## Mechanism of antimony immobilization in contaminated soil under reducing condition

Antimony (Sb) is the ninth most mined metal worldwide. It is frequently used in a variety of industrial products such as flame retardants, catalysts in the synthesis of plastics, and alloys for ammunition. In general, the natural abundance of Sb in soils and sediments is low (less than 1 mg/kg) and it ranges from  $10^{-3}$  to  $10^{-6}$  mg/L in fresh water [1]. However, elevated concentrations of Sb have been detected in soils near mining and smelter areas and at shooting ranges [2,3]. However, the geochemical and environmental behaviors of Sb in natural aquifers are still largely unknown, while Sb and its compounds have recently been considered as pollutants of priority interest [2 and references therein].

The oxidation states of Sb observed in the environment are Sb(III) and Sb(V). It is considered that the geochemical fate and toxicity of Sb depend on the oxidation state; Sb(III) compounds are more toxic than Sb(V) compounds [1]. Recent studies have shown that the Sb concentration in pore water decreases under reducing conditions in contaminated soil, where the reductive dissolution of Fe(III) hydroxides (the host phase of Sb in soil) took place in soil (ex. [3]). However, the mechanism of this Sb immobilization in reductive soil is still unclear. Accordingly, to understand the chemical processes associate with Sb behavior, we have characterized Sb and Fe species in soil collected under reducing conditions at the microscale by micro-X-ray absorption fine structure ( $\mu$ -XAFS) and electron probe microanalyzer (EPMA) techniques. In particular, the spatial distributions of Sb oxidation states within a soil particle were examined, since the oxidation state is an important factor controlling the mobility and solubility of Sb.

Natural soil samples in mine tailings were collected near the Ichinokawa mine pithead in Ehime, Japan. The redox condition of the soil was highly reductive (Eh = -107, pH 7.7; gray zone in Fig. 1), and Sb was accumulated in the soil. For  $\mu$ -XAFS and EPMA, we prepared a thin section of the soil sample. Antimony K-edge  $\mu$ -XANES experiments were performed at beamline BL37XU, a third-generation synchrotron facility. The incident beam was monochromatized with a Si(111) double-crystal monochromator and focused to 0.9 (V)  $\mu\text{m} \times 1.3$  (H)  $\mu\text{m}$ .

The chemical maps for Sb, Fe, and Si of two soil grains based on EPMA (Fig. 2) showed that Sb was accumulated into Fe oxides secondarily deposited on the rim of silicate minerals in grains A-B. Quantitative analyses indicated that the rims in grains A and B

contain 4–15 wt.%  $\text{Sb}_2\text{O}_5$ , suggesting that Sb was highly concentrated in these parts. Figure 3(a) shows the normalized Sb K-edge XANES spectra of Sb hot spots in the rims of grains A and B. As presented in Figs. 3(b) and 3(c), the XANES spectra were measured at seven hot spots for each grain, including interior and surface points. The absorption edge of Sb shifted to lower energy at the surface (hot spots A5–7 and B4–7). These findings suggest that Sb(III) exists at the surface parts in both grains A and B. This partial Sb reduction to Sb(III) on the surface of the soil grain was also supported by XANES theoretical fittings (Figs. 3(d) and 3(e)). Previous studies reported that Sb(III) is adsorbed at the surface of Fe(III) hydroxides (the host phase of Sb in this soil) by inner-sphere surface complexation of the soil at pH 7.7 and it is adsorbed more strongly on the solid phase than Sb(V) [4]. Hence, Sb(III) has a higher affinity to the solid phase than Sb(V). In addition, the solubility of Sb(III) species in the soil is much lower (more than  $10^5$  times) than that of Sb(V) species, because Sb(III) forms neutral (or no anionic) hydroxide species,  $\text{Sb}(\text{OH})_3^0$ , in this pH range.

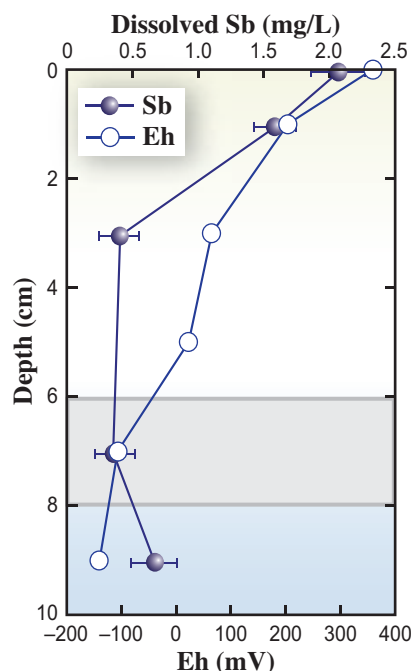


Fig. 1. Depth profile of Sb concentration and Eh (indicator of redox condition) in Ichinokawa soil. The gray box shows the depth of soil investigated in this study.

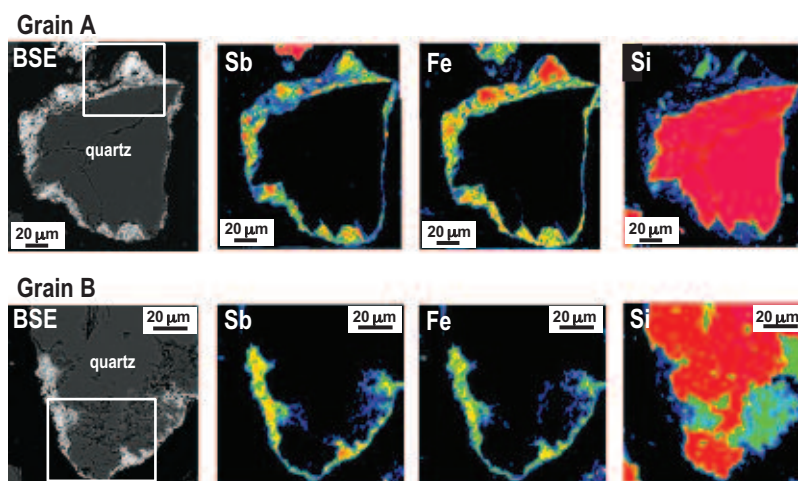


Fig. 2. Backscattered electron photomicrographs (BSEs) and element distribution maps for Sb, Fe, and Si of three soil particles (grains A-B) in Ichinokawa soil. The white frames in BSEs of grains A and B correspond to the images enlarged in Figs. 3(b) and 3(c), respectively.

These results suggest that the reduction to Sb(III) in the system can be a significant factor for Sb distribution for the solid phase observed under reducing conditions, considering both adsorbed and

precipitated species. This study emphasized the importance of speciation in environmental samples in understanding the fate of Sb in the aquatic environment.

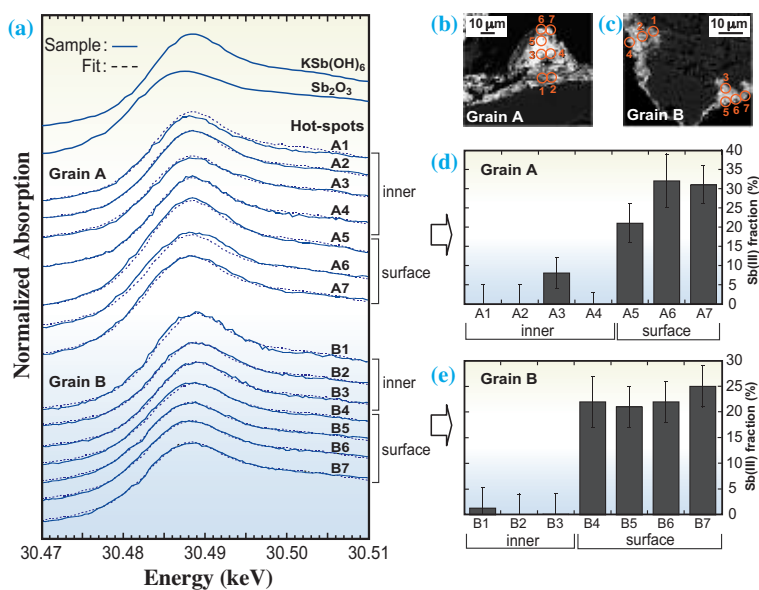


Fig. 3. (a) Normalized Sb K-edge  $\mu$ -XANES spectra (solid lines) of the reference materials ( $\text{Sb}_2\text{O}_3$  and  $\text{KSb}(\text{OH})_6$ ) and the points of interest (Sb hot spots) in grains A and B. Dashed lines overlapped on solid lines indicate the linear combination fits. Spectra of hot spots are shown in (a) according to “inner” or “surface” areas in each grain. (b) and (c) BSE images in grains A and B, respectively. The letters next to the orange circles indicate spots measured in (a). (d) and (e) Sb(III) fractions estimated by the simulation of Sb  $\mu$ -XANES in spots of grains A and B, respectively.

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## References

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