

## Antimony Interaction with an Abiotic Reducer in Aquatic Environment: Green Rust Compounds

Antimony (Sb) is toxic and its compounds are considered pollutants of priority interest by the United States Environmental Protection Agency and European Union. Sb belongs to group 15 of the periodic table and can exist in multiple oxidation states. The Sb oxidation states frequently observed in the natural environment are Sb(III) and Sb(V). The characteristics of Sb in the environment such as solubility and sorption behavior on natural solids depend on its oxidation state. Moreover, the toxicity of Sb also depends on its oxidation states; Sb(III) compounds have 10 times higher acute toxicity than Sb(V) [1]. Thus, it is essential to determine the oxidation state of Sb in environmental samples to estimate and evaluate its fate. Recently, Sb compounds has been widely used (100 000 tons annually worldwide) for many industrial materials (e.g., flame retardants and catalysts for plastic production, fining agents for glassware, and pigments in paints). However, the geochemical and environmental behaviors of Sb in natural soils and sediments remain largely unknown.

Fe(II)-Fe(III) layered double hydroxides, called green rust (GR), have a brucite-like structure (Fig. 1), which also alternated with interlayer anions (e.g.,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{Cl}^-$ ) and water molecules [2]. GR compounds are formed by a number of abiotic and biotic processes under circumneutral to alkaline conditions in a suboxic environment (Fe(II)/Fe(III) transition zone). Recently, in samples taken from hydromorphic soil and groundwater, GR has been identified as a natural mineral [3]. A number of studies of GR interaction with inorganic and organic contaminants have shown that GR can reduce many contaminants including chromate, selenate, uranyl, nitrate, and halogenated ethanes (e.g., [4]). Owing to

its high reactivity and rapid reduction rate, GR has been newly considered as a remarkable solid in nature. GR may affect the fate and transport of environmental toxins including Sb. To our knowledge, there have been no studies yet of the interaction of Sb with GR, and little is known about the sorption mechanism and reduction potential of any GRs for Sb. Thus, the objectives of the present study are to investigate the interaction of Sb with GR using a atomic-scale speciation method, XAFS. On the other hand, GR is a "metastable" mineral that gradually transforms to other Fe hydroxides such as magnetite ( $\text{Fe}_2\text{O}_3$ ) and lepidocrocite ( $\gamma\text{-FeOOH}$ ). Moreover, the presence of some anions in GR kinetically slows down the rate of transformation, indicating that GR is stabilized by anions. Since Sb(V) dominantly occurs as a monovalent hydroxide anion,  $\text{Sb}(\text{OH})_6^-$ , at  $\text{pH} > 2.5$ , Sb(V) may have a similar special effect on other anions. Therefore, we also investigate the stabilization effect of Sb on GR transformation.

We studied the interaction of Sb with GR by batch sorption experiment with various initial concentrations of Sb(V). The GR for the experiment was synthesized by the air oxidation of ferrous sulfate solution at neutral pH. The batch experiment was carried out in an anoxic glovebox purged with  $\text{N}_2$  gas. After shaking for 24 h at  $25^\circ\text{C}$  at pHs of  $8.0 \pm 0.2$ , solid samples were collected

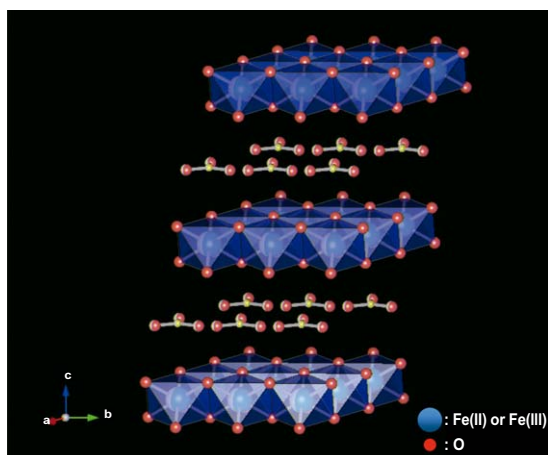


Fig. 1. Structure of green rust. Sulfate, carbonate, and chloride anions generally alternate in the interlayer.

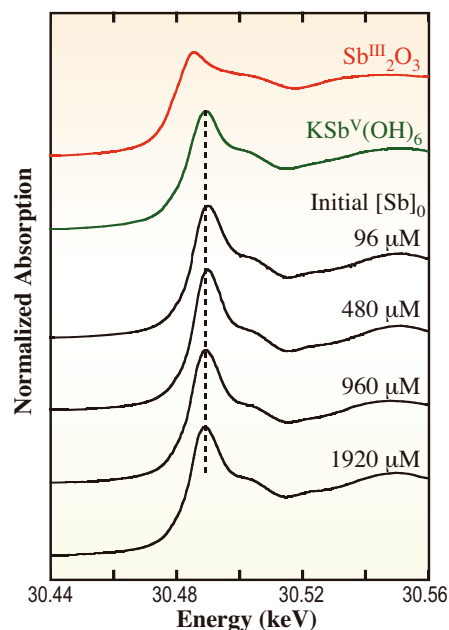


Fig. 2. Normalized Sb *K*-edge XANES spectra of the reference materials ( $\text{Sb}_2\text{O}_3$  and  $\text{KSb}(\text{OH})_6$ ) and collected solids in which Sb is adsorbed at various initial concentrations. A dotted line is drawn to indicate the absorption maximum of Sb(V),  $\text{KSb}(\text{OH})_6$ .

by filtration for further analyses. Antimony and iron (Fe) *K*-edge XAFS spectra were measured at beamline BL01B1 in the fluorescence mode to determine the oxidation states of Sb and Fe, surface complexes of Sb on the solids, and mineral species of the solids.

The normalized Sb *K*-edge XANES profiles (Fig. 2) show that the adsorption edge of the solid samples were similar to that of  $\text{KSb}^{\text{V}}(\text{OH})_6^-$ , indicating that Sb in the samples was predominantly Sb(V). This suggests that GR does not work as a strong reductant in the natural environment. The local structure of Sb in solids was examined by EXAFS to obtain information on the surface complexes of Sb adsorbed on GR. In the Fourier transformation (FT, Fig. 3), two backscattering peaks were consistently observed at 1.5 and 2.8 Å (phase-shift-uncorrected), respectively, at all initial Sb concentration. The simulation results showed that the first peak in FT was due to the Sb-O coordination (coordination number, nearly 6; bond distance, 1.98 Å). The second peak was fitted with one Fe atom at a distance of 3.07 Å. These findings clearly indicates that Sb(V) is adsorbed on GR with an edge-sharing inner-sphere complex. In addition to the speciation of sorbed species, the mineral phase in the Sb(V)-GR system was also characterized using Fe *K*-edge XANES (Fig. 4). A simulation of Fe XANES using reference materials was conducted to determine the GR abundance in the solid samples. Sulfate GR is transformed into  $\text{Fe}(\text{OH})_2$  and magnetite even under an anoxic condition for a relatively short time. At all initial Sb concentrations, the abundance of GR was significantly larger than that of the control

(=system without Sb(V)). Moreover, the GR abundance increased with increasing initial Sb concentration. Therefore, these findings suggest that Sb has a stabilizing effect on GR transformation and that the stability of GR depends on the Sb concentration in the range used in the present study. The present study first demonstrates that GR can be stabilized in the presence of Sb. A similar effect on GR has been reported in other oxyanions (i.e., phosphate, arsenate, and silicate) adsorbed to GR with the formation of an inner-sphere complex. Thus, it is suggested that the inner-sphere complex of Sb in GR (confirmed by EXAFS analysis) strongly contributes to the stabilization of “metastable” GR by Sb [5].

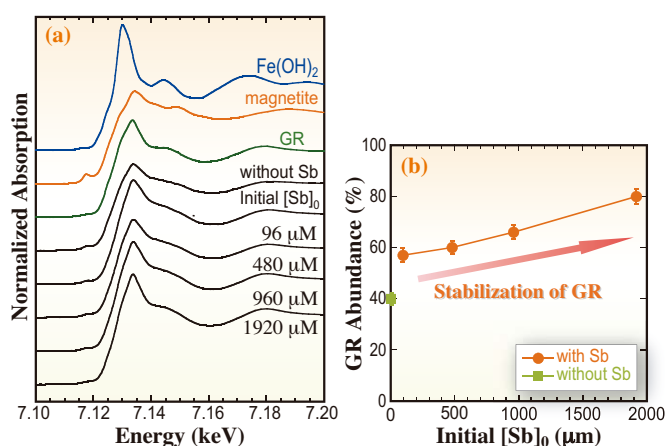


Fig. 4. (a) Normalized Fe *K*-edge XANES spectra of the reference materials, collected solids in Sb-GR systems, and control (system without Sb). (b) GR abundances of collected solids from Sb-GR system and control samples obtained by simulation of Fe *K*-edge XANES.

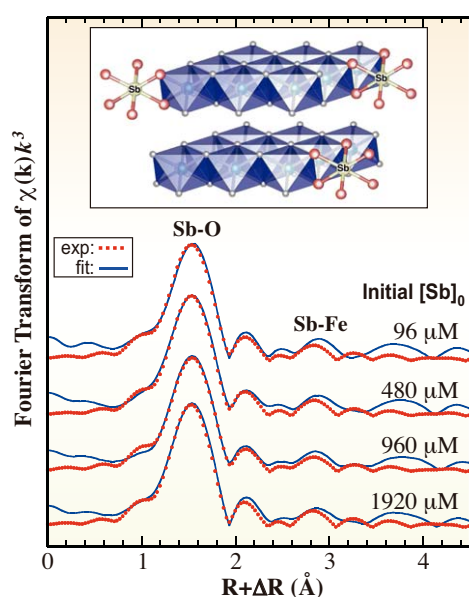


Fig. 3. Fourier-transformed EXAFS spectra of solid samples collected in Sb(V)-GR system (lower) and schematic figure of binding structure of Sb in GR proposed on the basis of results of EXAFS analysis (upper).

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## References

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