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Oxidation of antimony (III) in soil using X-ray absorption fine structure

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1 Introduction

The chemical state of elements in the sediment and soil has been used as a good indicator to estimate the redox state which considered as an important research topic in geochemistry and environmental chemistry. Antimony(Sb) is one of those elements which responds sensitively to redox state and exists multiple valence states in the sediment and soil. Studies on Sb chemical states show that the toxicity of Sb(III) is much more poisonous than Sb(V) (Gurnani et al., 1994). In addition, previous reports about the chemical behaviour of Sb showed that despite being emitted mostly as Sb(III) into environment, antimony exists mainly as Sb(V) in soil samples. However, the mechanism of the oxidation of Sb(III) in soil is still unknown.

The purpose of this study is to observe the oxidation process of Sb(III) in soil using X-ray absorption fine structure (XAFS) spectra and hopefully determine the element which cause the oxidation reaction.

2 Experiment

We used andosol which are widely distributed throughout Japan in this research. Sb oxidation reaction experiment was performed by doping with Sb into andosol for a concentration of Sb-1000 ppm. Soil samples were sealed immediately in polystyrene bags for XAFS measurement after adjusting the water content to 30%. Measurement was carried out once immediately after doping with Sb (reaction time(RT) = 0) representing the beginning of the oxidation reaction and measured again several times (RT = 1d, 3d, 5d, 14d).

Sb K-edge XAFS spectra was collected in fluorescence mode using a Lytle detector at the beamline AR-NW10A of Photon Factory Advanced Ring. Mn K-edge XAFS measurements were also carried out in fluorescence mode using a Lytle detector at the beamline BL-12C of Photon Factory. Both the XANES region and EXAFS region were recorded. XAFS analysis was conducted using REX2000 software provided by Rigaku Corp (version 2.5.5). The scattering parameters were obtained by FEFF 7 package (Ankudinov and Rehr, 1997).

3 Results and Discussion

Sb K-edge XANES spectra of andosol are shown in Fig. 1. The XANES spectra of reference compounds Sb_2O_3 and $K[Sb(OH)_6]$ show that Sb(III) has a lower absorption edge energy of 30,493.7 eV and a relatively less pronounced white line in comparison with Sb(V). Result of the first measurement (RT = 0) is almost the same as the spectra of Sb_2O_3. However, spectra get much closer to $K[Sb(OH)_6]$ after 2 weeks of reaction time. Based on the speciation fitting result estimated by REX2000 of RT = 14d, about 71.2% of Sb are in pentavalent form. On the other hand, Sb K-edge XANES spectra of reaction time 1d – 5d are all close to the spectra of trivalent oxide. The speciation fitting results for Sb(V) of RT = 1d, 3d, 5d are 7.6%, 19.4%, 30.6%, respectively. Oorts et al. (2008) pointed out that Sb_2O_3 could be almost oxidized in two days after entering the soil. However, results in our experiment show that the speed of Sb(III) oxidation reaction in andosol was rather slow. This may be due to the relatively high Sb(III) concentration in our research (1000ppm) in comparison with the concentration of 510ppm of theirs, and a silt-loam soil was used in their report, so the differences in soil types should also be considered.

Fig. 2 gives the Mn K-edge XANES spectra results (RT = 0, 14d) during the process of the Sb(III) oxidation reaction. As we can see, absorption edge energy is closer to quadrivalent compounds at the beginning of the experiment and then change to a lower value after 2 weeks

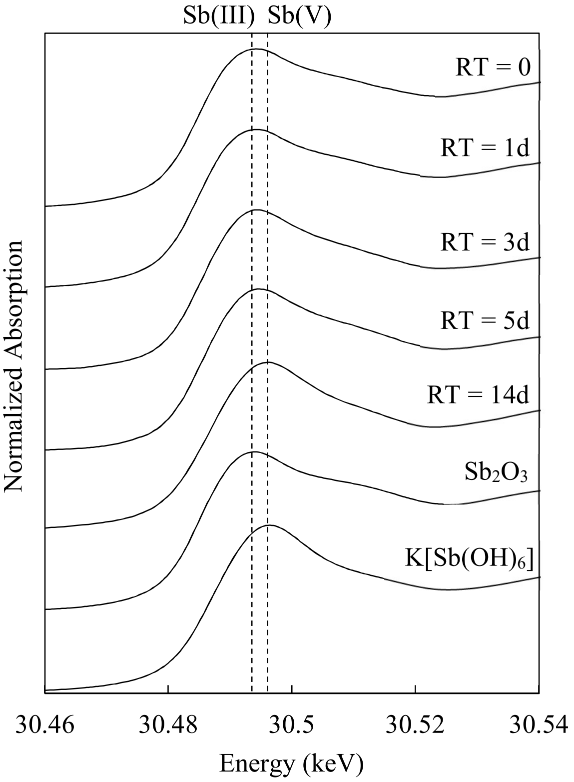

Fig. 1. Sb K-edge XANES spectra change over time in andsol. From top: reaction time(RT) = 0, 1d, 3d, 5d, 14d.

and the spectrum characteristics become more like the divalent reference compounds. This indicates the chemical form of Mn has been changed in the redox reaction with Sb(III).

EXAFS spectra and fit results of Sb in andosol during the oxidation reaction are shown in Fig. 3 and Table 1. Spectra of RT = 0 are clearly different from the RT = 14d by their small peaks of first Sb-O bond in the EXAFS Fourier transforms at about 1.6 Å before correcting for phase shift and the coordination number is close to three (Table 1). On the other hand, second measurement shows larger peak and the coordination number is close to six. Both first shell Sb-O bonds and distances of the two measurements are almost the same which at around 1.99 Å. Shell Sb-Sb bond of the fist measurement (RT = 0) shows a distance of 3.6 Å. However, Sb-Sb bond disappeared after 2 weeks of the oxidation reaction of Sb(III) which indicates that Sb_2O_3 compound have been all converted into other forms and possibly adsorbed in andosol. These results confirm again that Sb(III) has been oxidized to Sb(V) during 2 weeks of the reaction and show that the oxidation states of Sb can also be discriminated based on the coordination numbers of the first shell Sb-O bond.

By using X-ray absorption fine structure spectra, we successfully observed the process of the oxidation of antimony (III) in the soil and can assume that Mn(IV) may plays an important role in the reaction according to the significantly XANES spectra change during the reaction.

References
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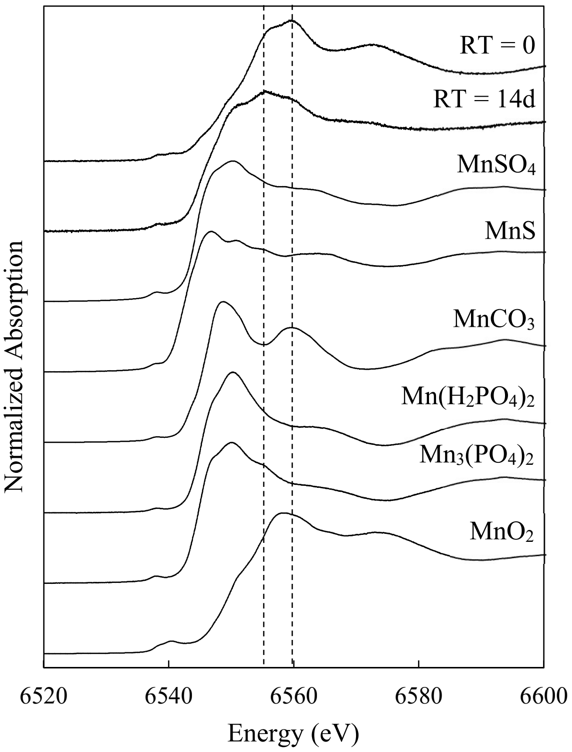

Fig. 2. Mn K-edge XANES spectra change over time in andsol. From top: RT = 0, 14d.

Table 1
EXAFS results during the oxidation reaction of Sb(III) in andosol.

RT	Shell	CN	R(Å)	ΔE_0 (eV)	σ^2
RT=0	Sb-O	3.2±0.3	1.988±0.010	16.0±2.9	0.003[a]
	Sb-Sb	4.5±1.1	3.588±0.012		0.003[a]
RT=14d	Sb-O	5.7±0.5	1.993±0.012	13.1±3.1	0.003[a]

[a] Fixed during fit; CN: coordination number.

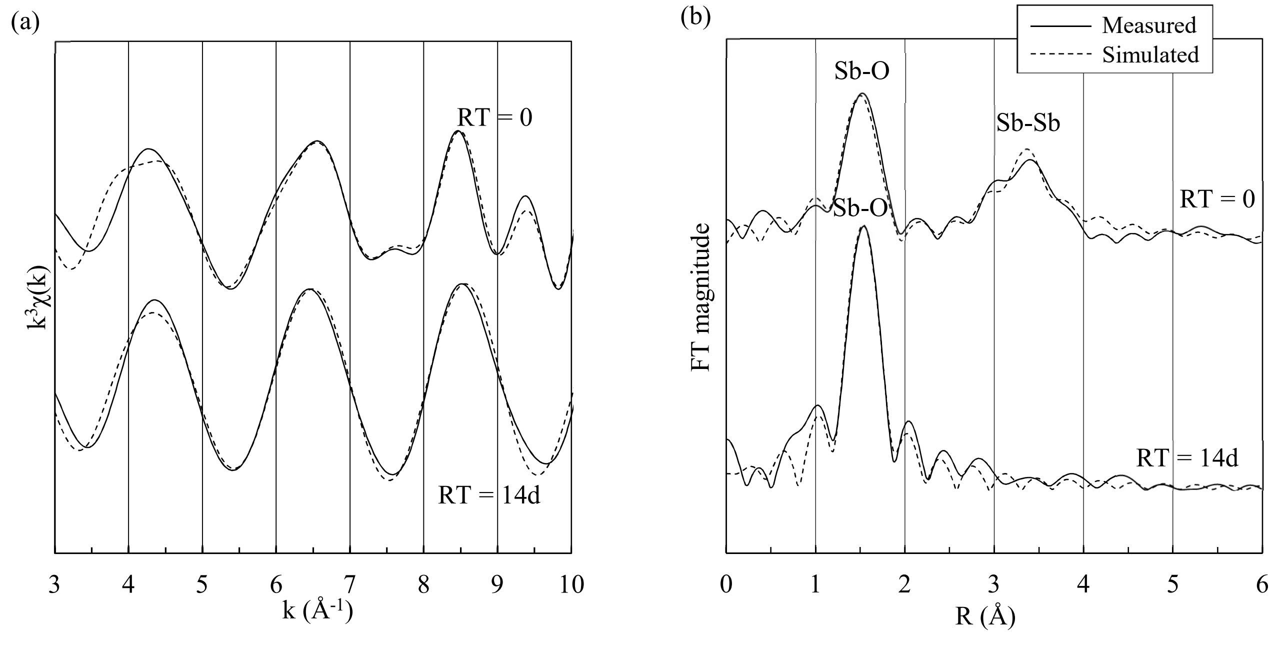

Fig. 3. Fourier transformed k^3-weighted EXAFS spectra of Sb before and after the oxidation reaction in andosol in k space (a) and R space (b).