12C/2009G676

Co(II) oxidation by biogenic Mn oxide

Kazuya TANAKA*[1], Yukinori TANI[2], Toshihiko OHNUKI[1]
[1]Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
[2]Institute for Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan

Introduction

Cobalt-60 is one of the important radionuclides contained in radioactive wastes. Release of radionuclides from radioactive wastes has been one of the major concerns on disposals of radioactive wastes. Cobalt has divalent and trivalent states in surface environments. Oxidation state of Co affects solubility, complexation and sorption properties on surfaces of minerals. In this study, we investigated the oxidation of Co by Mn oxide produced by a Mn-oxidizing microorganism. The oxidation state of Co sorbed on the biogenic Mn oxide was investigated using XANES.

Methods

We used *Acremonium* sp. strain KR21-2 as a model of Mn-oxidizing microorganisms. Strain KR21-2 was incubated in HAY liquid medium with 1 mM $MnSO_4$ and pH 7.0 on a reciprocal shaker (~ 100 strokes/min) at 25°C for 4 days [1]. The initial Co concentrations in the HAY media were adjusted to be 20 and 40 μM by addition of $CoCl_2$ solution. The Co sorbed biogenic Mn oxide after incubation was collected on a 0.2 μm membrane filter for Co K-edge XANES analysis.

Cobalt K-edge XANES spectra for the biogenic Mn oxide samples were collected at beamline 12C at Photon Factory. CoO, Co_2O_3, CoOOH and Co^{2+} solution were measured as reference materials. The powders of CoO, Co_2O_3 and CoOOH were diluted with boron nitride to be 1wt% Co for XANES measurements in transmission mode. 0.1 M Co^{2+} solution was prepared by dissolution of $CoCl_2 \cdot 6H_2O$ in Milli-Q water. Spectra of the Co^{2+} solution and biogenic Mn oxide samples were collected in fluorescence mode. The fluorescence yield of each sample was monitored using a 19-element Ge solid-state detector (SSD). All the measurements were carried out at room temperature.

Results and discussion

Cobalt K-edge XANES spectra are shown in Fig. 1. The peak tops of Co^{2+} solution and CoO are located around 7729 eV, whereas the trivalent species of Co_2O_3 and CoOOH indicate the peak tops around 7734 eV. The difference of peak top energies between the divalent and trivalent species is about 5 eV [2], which is enough to determine oxidation state of Co sorbed on the biogenic Mn oxide. The biogenic Mn oxide samples show the peak tops around 7734 eV, similarly to the trivalent species. The analysis of the XANES spectra clearly demonstrates

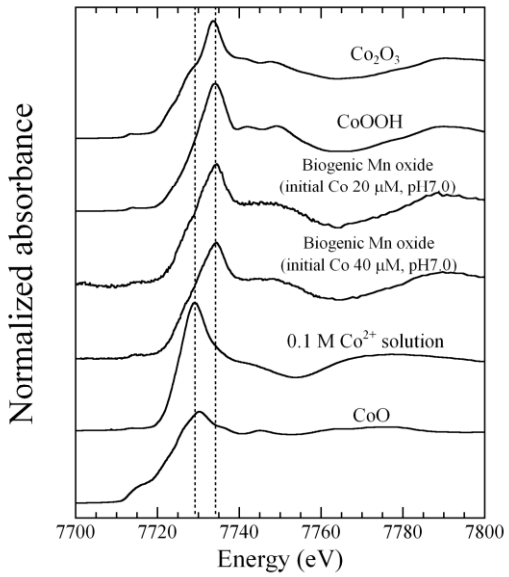

Fig. 1. Cobalt K-edge XANES spectra of the biogenic Mn oxides and reference materials. The two dotted lines indicate the positions of peak top energy for Co^{2+} solution and CoOOH.

that Co(II) was sorbed and then oxidized to Co(III) on the biogenic Mn oxide.

Previous works reported that oxidation state of Co in natural Mn oxides was trivalent [2,3]. The results of this study are consistent with those of the previous works. It is widely accepted that Mn(II)-oxidizing microorganisms play an important role in the formation of natural Mn oxide deposits [4]. However, the oxidation of Co by biogenic Mn oxide has not been studied using a direct way such as XANES. The results of this study can be a starting point for further research on oxidation of Co by biogenic Mn oxide.

References

[1] N. Miyata et al., FEMS Microbiol. Ecol. 47, 101 (2004).
[2] A. Manceau et al., Geochim. Cosmochim. Acta 51, 105 (1987).
[3] Y. Takahashi et al., Geochim. Cosmochim. Acta 71, 984 (2007).
[4] B. Tebo et al., Annu. Rev. Earth Planet. Sci. 32, 287 (2004)

* tanaka.kazuya24@jaea.go.jp