Application of XANES for the Determination of Oxidation States of Co and Pb in Natural Ferromanganese Nodules

Yoshio Takahashi,* Akira Usui,† Kazu Okumura,†† Tomoya Uruga,†††
Masaharu Nomura,†††† Mio Murakami, and Hiroshi Shimizu
Department of Earth and Planetary Systems Science, Graduate School of Science,
Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526
†*Institute for Marine Resources and Environment, Geological Survey of Japan, AIST, Higashi, Tsukuba, Ibaraki 305-8567*
††*Department of Applied Chemistry, Faculty of Engineering, Tottori University, Koyama-chi Minami, Tottori 680-8552*
†††*SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), Kouto, Mikazuki-cho, Sayo-gun, Hyogo 679-5198*
††††*Photon Factory, Institute of Materials Structure Science, KEK, Oho, Tsukuba, Ibaraki 305-0801*

(Received October 17, 2001; CL-011017)

Cobalt K-edge and Pb L_{III}-edge XANES spectra were obtained by fluorescent XANES using solid state detector (SSD) for Co and Pb in natural rocks, ferromanganese nodules. The XANES spectra suggest that Co(III) and Pb(II) are their main oxidation states in ferromanganese nodules. Based on the results, enrichment mechanisms of Co and Pb in ferromanganese nodules were discussed.

Ferromanganese nodule is the chemical deposit on the deep-sea floor, which has a major economic potential for metals such as Ni, Cu, and Co due to their enrichment in ferromanganese nodules.[1] In order to clarify their enrichment mechanisms, speciation of the elements enriched in ferromanganese nodules is indispensable. For this purpose, X-ray absorption near-edge structure (XANES) is a promising technique to clarify the chemical-states, especially oxidation-states, of various elements. High sensitivity of fluorescence XANES coupled with Ge solid state detectors (SSD) enables us to obtain information for the speciation of trace elements (<100 ppm) in natural materials, such as rocks and soils. In this paper, XANES was applied to investigate oxidation-states of Co and Pb in ferromanganese nodules. These elements are usually enriched in hydrogenetic ferromanganese nodules, but there have been some proposed mechanisms for their enrichment.[1–3] There have been few studies to reveal the chemical-state of these elements except for a study done by X-ray photoelectron spectroscopy (XPS).[3] However, the XPS spectra of Co and Pb from ferromanganese nodules are not very clear to show their oxidation-states explicitly. Fluorescence XANES is the best method because of its high sensitivity to investigate more clearly the oxidation-states of Co and Pb in ferromanganese nodules. In addition, characterization by XANES provides Co and Pb species in the bulk of ferromanganese nodule (μm order). XPS signals are confined to Co or Pb species at the solid surface less than 100 Å when electron kinetic energy ranges between 100 and 1000 eV employed in the XPS study for ferromanganese nodule.[3,4] It is probable that Co and Pb species suggested by the XPS study were different from those in the bulk of the nodules.

Ferromanganese nodule sample (D535) was recovered at the South Pacific Ocean (13°00.6'S, 159°17.6'W, 5222 m depth).[5] Major and minor elements were measured by ICP-AES and ICP-MS after decomposition. Fe/Mn ratio (wt%) at a layer we studied for XANES in D535 was 0.59, which is consistent with the fact that D535 is hydrogenetic origin.[5,6] Abundances of Co and Pb at the layer were 0.48% and 0.071%, respectively. These abundances are within the range of these elements found in other hydrogenetic-type ferromanganese nodules that are relatively enriched in Co and Pb.[5,7]

XANES spectra were obtained at the beamline 12C in KEK-PF for Co K-edge where a Si(111) double-crystal monochromater and a bent cylindrical mirror were employed to obtain monochromatic X-ray.[8] The energy resolution (ΔE) is better than 2 eV around the energy of Co K-edge. Lead L_{III}-edge XANES was measured at the beamline BL01B1 in SPring-8 with a Si(111) double-crystal monochromater with two mirrors, where ΔE is better than 3 eV at Pb L_{III}-edge.[9] The measurements were carried out at room temperature in ambient air condition. The energy calibration was conducted for Co K-edge and Pb L_{III}-edge with CoO and PbO_2, respectively. Shift of absorption edge of CoO or PbO_2 was not observed during the experiments. In order to obtain their XANES spectra, fluorescence measurement with 19 elements solid-state detector (SSD) was indispensable due to their low abundances. In order to reduce the signal from fluorescent X-ray of Mn and Fe, matrix elements of ferromanganese nodule, a vanadium filter ($\mu t = 3$ or 6) was always inserted between the sample and the SSD for Co K-edge XANES measurement, while a chromium filter ($\mu t = 6$ or 9) for Pb L_{III}-edge XANES. Dead time correction was made for the SSD counting.[10] For the natural ferromanganese nodules, a chip of the air-dried sample was used for the measurement. However, thin section or powdered sample showed similar spectra to that of a chip sample.

Figure 1 shows the XANES spectra of Co in ferromanganese nodules. The XANES spectra of reference materials (CoO and Co_2O_3), showed a chemical shift, which is often observed in XANES spectra, that is, the peak edge is shifted to higher energy for

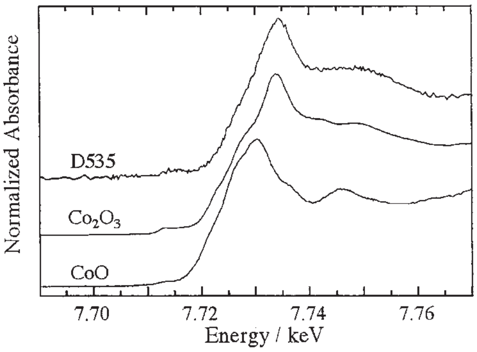

Figure 1. Cobalt K-edge XANES spectra for CoO, Co_2O_3, and ferromanganese nodule (D535).

Co of larger oxidation-state. This relation is often utilized to estimate the oxidation state of Co.[11,12] The Co incorporated in ferromanganese nodules showed a quite similar XANES spectrum to that of Co_2O_3, showing that the oxidation-state of Co in the ferromanganese nodule is trivalent. Since it is estimated that Co is dissolved as divalent ion in seawater,[13] the present result shows that Co is oxidized during sorption on the ferromanganese nodules. Similar oxidation process was considered to occur for Ce in ferromanganese nodules. Our recent studies based on XANES showed that the enrichment of Ce in ferromanganese nodules compared with other rare earth elements is due to the oxidation of Ce at the MnO_2 surfaces.[6] It is suggested that the oxidation from Ce(III) (=dominant valence for dissolved Ce species in seawater) to Ce(IV) during sorption process by MnO_2 promotes the following sorption of Ce(III), since Ce(III) is always lacking at the MnO_2 surface by the oxidation. It is estimated that this oxidative sorption induces the enrichment of Ce in ferromanganese nodule. The Co K-edge XANES suggested that the enrichment of Co in ferromanganese nodule is also caused by the oxidative sorption on the ferromanganese nodule as is similar to the case of Ce.[1–4]

Figure 2 shows the XANES spectra of Pb L_{III}-edge in D535 and reference samples of PbO (orthorhombic), Pb_3O_4, and PbO_2. Absence of Pb(IV) species in D535 is indicated by the features in XANES spectra due to the electron transition for Pb(II) or Pb(IV) species.[14–16] For Pb(IV) species (PbO_2) having electronic configuration $(5d)^{10}(6s)^0$, pre-edge at 13.052 keV is distinct due to the electron transition from 2p to 6s, as is clearly found from the first derivative of absorbance (Figure 3). Such transition is not observed for Pb(II) species having $(5d)^{10}(6S)^2$ configuration, while pre-edge at 13.056 keV was observed as a shoulder for PbO spectrum due to the electron transition from 2p to an energy level produced by the hybridization of Pb 6s, 6p, and 6d orbitals.[14] The fact that 2p → 6s transition was not observed in D535 suggests that contribution of Pb(IV) is not important as Pb species in D535, but Pb(II) is dominant. In seawater, divalent species are dominant for dissolved Pb species.[13] It has been speculated that the oxidation of Pb(II) to Pb(IV) is the main mechanism for Pb enrichment in ferromanganese nodules.[1,17] However, the present results imply that the oxidative sorption, which is supposed to be the mechanism for Co and Ce enrichment, is not valid as a main factor for Pb enrichment in ferromanganese nodules.

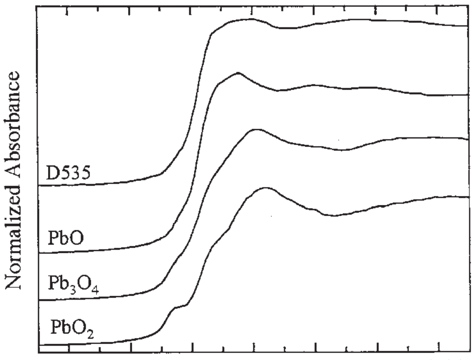

Figure 2. Lead L_{III}-edge XANES spectra for PbO, Pb_3O_4, PbO_2, and ferromanganese codule (D535).

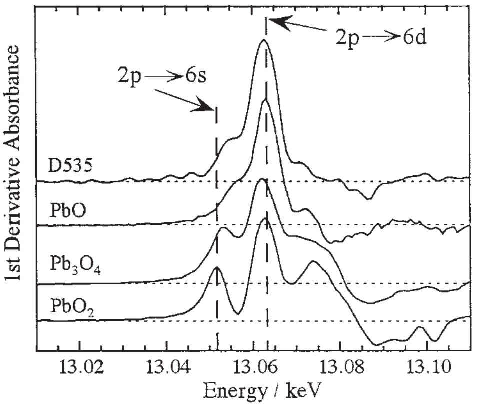

Figure 3. First derivative of Pb L_{III}-edge XANES spectra for PbO_2,Pb_3O_4, PbO, and ferromanganese nodule (D535). The peaks corresponding to electron transition from 2p to 6s for Pb(IV) species and from 2p to 6d for all Pb species are shown.

The direct observation of Co(III) and Pb(II) by the spectroscopic method like XANES is worthy of note, since such information helps us to understand the enrichment mechanism of Co or Pb in ferromanganese nodules. More details on the geochemical interpretation of our results with other XANES results on ferromanganese nodules will be given elsewhere.

This research is supported by a grant-in-aid for scientific research from the Ministry of Education, Science, Sports, and Culture of Japan. This work has been performed with the approval of KEK (Proposal No. 200G267) and JASRI (Proposal No. 2000B0276).

References and Notes

1 P. Halbach, D. Puteanuts, and R. Giovanoli, in "The Manganese Nodule Belt of the Pacific Ocean," ed. by P. Halbach, G. Friendrich, and U. von Stackelberg, Enke, Stuttgart (1988), p 151.
2 N. Takematsu, "Mangan Dankai (Manganese nodule)," Koseisha Kouseikaku, Tokyo (1998) (in Japanese).
3 a) J. W. Murray and J. G. Dillard, *Geochim. Cosmochim. Acta*, **43**, 781 (1979). b) D. L. Crowther, J. G. Dillard, and J. W. Murray, *Geochim. Cosmochim. Acta*, **47**, 1399 (1983).
4 M. P. Seah and W. A. Dench, *Surf. Interface Anal.*, **1**, 2 (1979).
5 A. Usui, "Marine geology, geophysics, and manganese nodule deposits in the Penrhyn Basin, South Pacific," Geological Survey of Japan, Cruise Report No. 23 (1994).
6 Y. Takahashi, H. Shimizu, A. Usui, H. Kagi, and M. Nomura, *Geochim. Cosmochim. Acta*, **64**, 2929 (2000).
7 A. Kochinsky and P. Halbach, *Geochim. Cosmochim. Acta*, **59**, 5113 (1995).
8 M. Nomura and A. Koyama, KEK Report 95-15 (1996).
9 T. Uruga, H. Tanida, Y. Yoneda, K. Takeshita, S. Emura, M. Takahashi, M. Harada, Y. Nishihata, Y. Kubozono, T. Tanaka, T. Yamamoto, H. Maeda, O. Kamishima, Y. Takabayashi, Y. Nakata, H. Kimura, S. Goto, and T. Ishikawa, *J. Synchrotron Rad.*, **6**, 143 (1999).
10 M. Nomura, *J. Synchrotron Rad.*, **5**, 851 (1998).
11 L. Barbey, N. Nguyen, V. Caignaert, F. Studer, and B. Raveau, *J. Solid State Chem.*, **112**, 148 (1994).
12 A. Iida, in "Microscopic X-ray Fluorescence Analysis," ed. by K. H. A. Janssens, F. C. V. Adams, and A. Rindby, John Wiley & Sons, Chichester (2000), Chap. 5, p 117.
13 K. W. Bruland, in "Chemical Oceanography," ed. by J. P. Riley and G. Skirrow, Academic Press, London (1983), p 157.
14 K. J. Rao and J. Wong, *J. Chem. Phys.*, **81**, 4832 (1984).
15 Y. G. Choi, K. H. Kim, V. A. Chernov, and J. Heo, *J. Non-Cryst. Solids*, **246**, 128 (1999).
16 J. R. Bargar, G. E. Brown, Jr., and G. A. Parks, *Geochim. Cosmochim. Acta*, **61**, 2617 (1997).
17 S. Tsunogai and S. Noriki, in "Kaiyo Kagaku," ed. by M. Nishimura, Sangyo Tosho, Tokyo (1983), p 82.