Oxidation States of Antimony and Arsenic in Marine Ferromanganese Oxides Related to Their Fractionation in Oxic Marine Environment

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Oxidation states of Sb and As in marine ferromanganese oxides determined by X-ray absorption near-edge structure showed that both As and Sb are pentavalent in the ferromanganese oxides. The concentration ratios of As/Sb in the ferromanganese oxides are similar to those in seawater. There results are consistent with the fact that As and Sb behave similarly, especially under oxic conditions as suggested from other studies in soil–water and river–sediment systems.

Antimony (Sb) belonging to group 15 in the periodic table below As is one of environmentally concerned elements in recent years due to its acute and chronic toxicities.[1,2] The element is often contained in industrial materials and considered as a pollutant especially in advanced countries. Therefore, environmental behavior of Sb is of great importance in environmental geochemistry, but much less knowledge is available for its chemical processes in nature compared with that of As. For both elements, biogeochemical processes are important, especially for the formation of their reduced (As^{III} and Sb^{III}) and methylated species.[3,4] However, inorganic processes like sorption on Fe–Mn oxides can be also an important factor controlling their behavior in oxic marine environment,[5,6] which is a main topic in this manuscript. Many past studies have suggested that the behavior of Sb depends to great extent on its oxidation state, showing that Sb^{III} is much less soluble than Sb^{V}.[1,2,7,8] However, the oxidation state of Sb in ocean has been determined only in water phase,[1,9] while its speciation in solid phase has not been clarified owing to its low abundance in natural samples, which results in poor knowledge on the geochemical behavior of Sb. In this study, oxidation states of Sb and As in solid phases were investigated by X-ray absorption near-edge structure (XANES) analysis for marine ferromanganese oxides.

Oxidation states of trace elements incorporated in natural ferromanganese oxides can be determined by fluorescence XANES as was reported for Ce, Co, and Pb due to the high sensitivity of the method.[10,11] In this study, we measured Sb K-edge (30.486 keV) XANES in fluorescence mode rather than Sb L_{III}-edge, since the latter measured in fluorescence mode is subject to serious interferences from K lines of K and Ca contained at 0.1–5 wt % level in marine ferromanganese oxides. By employing relatively high-energy X-ray around Sb K-edge, we have successfully obtained Sb K-edge XANES for the first time for natural samples except for contaminated soil samples.[8,12]

Hydrogenetic marine ferromanganese nodules were obtained from two sites in Pacific Ocean; D535 was collected at the South Pacific Ocean (13.0°S, 159.2°W, 5222-m depth) and AD14 around Marshall Island (14.1°N, 167.2°W, 1617-m depth).[11,13] The samples were air-dried and powdered by agate mortar. Since ferromanganese oxides were formed under oxic condition, preparation in air is acceptable as done in other studies.[13,14] Average major element compositions in the deposits were (Mn, Fe) = (27.9 wt %, 16.4 wt %) and (29.5 wt %, 16.7 wt %) for D535 and AD14, respectively, as reported previously.[11] Concentrations of As and Sb were measured in this study by ICP-MS after acid decomposition by the method reported previously.[11,13]

The powdered samples were packed into polyethylene bags for XANES analysis. Arsenic K-edge XANES was measured at beam line 12C in KEK-PF (Tsukuba, Japan) with a Si(111) double-crystal monochromator, while Sb K-edge XANES at BL01B1 in SPring-8 (Hyogo, Japan) with a Si(311) double-crystal monochromator. All the spectra were collected in the fluorescence mode using a 19-element Ge solid-state detector at room temperature under ambient air condition. More details can be found in previous reports.[8]

As shown in As K-edge XANES spectra with their first derivatives (Figure 1), the spectra of reference materials (KH_2AsO_4 and $KAsO_2$) showed a clear chemical shift, that is, the peak edge is shifted to higher energy for As^{V} species. XANES spectra and their first derivatives of As incorporated in the ferromanganese oxides (D535 and AD14) were quite similar to those of KH_2AsO_4, showing that As in the ferromanganese oxides exists as As^{V}. By simulating the spectra of ferromanganese oxides with those of the reference materials by the method reported in the previous study,[8] the As^{V} fraction among total As was estimated to be 100% and more than 86% for D535 and AD14, respectively. There is only one study reporting the As^{V}/As^{III} ratio in marine ferromanganese oxides, also showing that As^{V} fraction is more than 85%.[14] The predominance of As^{V} is consistent with the previous studies that As^{V} has larger affinity for Fe and Mn oxides than As^{III} often observed for As behavior in various water–rock systems.[8,15,16]

Antimony K-edge XANES spectra also showed a clear chemical shift depending on the oxidation state between the two reference materials, Sb_2O_3 and $Sb(OH)_6^-$ solution (Figure 2). The Sb incorporated in the ferromanganese oxides showed XANES spectra almost identical to that of $Sb(OH)_6^-$ solution indicating that Sb in the ferromanganese oxides exists as Sb^{V}. Although there have been various studies on the oxidation states of Sb dissolved in seawater showing that Sb^{V} is predominant species,[1] the present results are new information on the Sb species in solid phase in marine environment. Unlike As, it has been indicated that trivalent species, Sb^{III}, has much lower solubility than that of pentavalent species.[1,2,8] Therefore, one may think that Sb^{III} can be main species in the solid phase, but it was not the case for Sb in ferromanganese oxides.

Under oxic condition, it has been suggested that solid–water

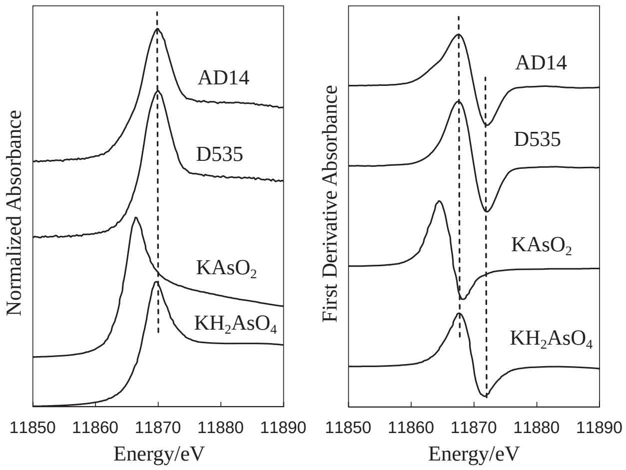

Figure 1. Arsenic K-edge XANES spectra for KH_2AsO_4, $KAsO_2$, and marine ferromanganese oxides (D535 and AD14) and the first derivatives of the spectra.

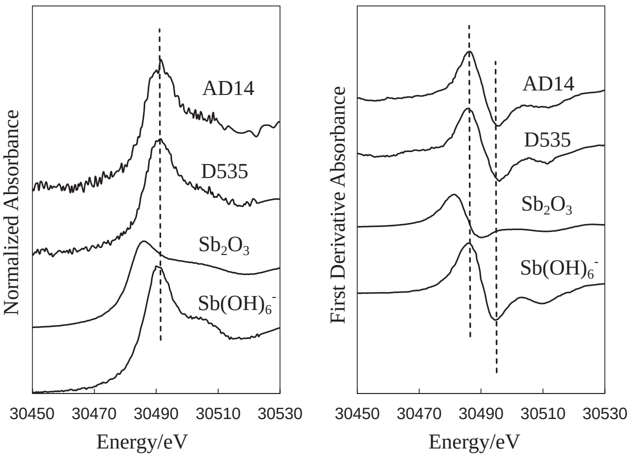

Figure 2. Antimony K-edge XANES spectra for Sb_2O_3, $Sb(OH)_6{}^-$, and marine ferromanganese oxides (D535 and AD14) and the first derivatives of the spectra.

distribution ratio of Sb is similar to that of As in a soil–water system[8] and also in the scavenging processes in a sediment–water system.[17] However, the distribution into water becomes much smaller for Sb under reducing conditions where Sb^{III} forms in the solid phase.[1,2,8] In contrast, As is leached to water to greater degree under reducing conditions by the formation of As^{III} in solid phase.[8,15,16] The concentration ratios of Sb and As in D535 and AD14 were 9.6 and 9.4, respectively, which are similar to the ratios in seawater ranging from 10 to 20 reported in literatures.[18–21] These results suggested that Sb and As may not fractionate in oxic marine environment, at least in the inorganic processes. Based on the present study, it can be said that solid–water distributions of Sb and As are similar each other when Sb^V and As^V are their predominant species in ferromanganese oxides, identical to their oxidation states in seawater.[1,9,18]

When Sb^V and As^V are predominant species both in ferromanganese oxides and seawater, the similarity of their solid–water distributions is estimated from thermodynamic data based on the linear free energy relationship.[22] In the theory, logarithm of surface complexation constant has a linear relationship to that of acid dissociation constant of anions (pK_a). The pK_a of Sb^V, $HSbO(OH)_4$, is reported to be 2.72, while that of As^V, H_3AsO_4, is 2.24.[22] The similar values between them show that the solid–water distributions for Sb^V and As^V sorbed at the surface of metal oxides are similar, as suggested from their abundances and oxidation states in ferromanganese oxides determined in this study. The similarity causes their similar vertical profiles of inorganic As and Sb in ocean[21] and residence times in seawater.[23] Various studies including the marine system reported in this work, the soil–water system under oxic conditions,[8] and the river–sediment system[17] showed that the solid–water distribution of Sb is similar to that of As under oxic conditions where Sb^V and As^V are dominant species.

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