

XAFS study on the solubilities into seawater and the enrichment mechanisms into ferromanganese nodules for molybdenum and tungsten

Teruhiko Kashiwabara[1]; Yoshio Takahashi[2]

[1] Earth and Planetary System Sci., Hiroshima Univ.; [2] Earth and Planetary Systems Sci., Hiroshima University

<http://www.geol.sci.hiroshima-u.ac.jp/~environ/>

Molybdenum (Mo) and tungsten (W) are important elements because of their possibilities as proxies of paleoceanographic environment. While crustal abundances of these elements are similar, their concentrations in the oxic-seawater are greatly different (molar ratio of Mo/W is around 1800) and the scavenging processes from the seawater are still debated. Particularly, enrichment mechanisms into the ferromanganese nodule, one of the most important inorganic scavenging processes, are unclear. In this study, hydrogenetic ferromanganese nodules, which contain both Mn oxide and Fe oxyhydroxide, were subjected to the XAFS analyses to determine directly the host phases and surface complex structures for Mo and W. Additionally, adsorption experiment of Mo and W to the Mn oxide and Fe oxyhydroxide were conducted to discuss the difference in their behaviors in the solid/water interface.

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). Concentrations and host phases of Mo and W were investigated by ICP-MS and XAFS analysis. Adsorption experiments were conducted using ferrihydrite and d-MnO₂ as adsorbents (adsorbent: 20 mg; Mo or W solution: 31.2 × 10⁻⁵ molL⁻¹ and 38.2 × 10⁻⁵ molL⁻¹ for ferrihydrite and d-MnO₂, respectively; the ratio of Mo (or W) to Fe (or Mn): 0.0167). Ionic strength was adjusted to 0.010 or 0.70 (as NaNO₃) at pH 4,5,6,7,8 and 9 for each solution. These solutions were shaken at 25 degree in a water bath. After 24h, concentrations of Mo and W in the solution were determined by ICP-MS and the coordination environments of Mo and W on the surface of solid phases were investigated by XAFS analysis. These XAFS measurements were performed at BL01B1, in SPring-8 and BL-12C in Photon Factory.

From the comparison among the XAFS spectra of Mo in the ferromanganese nodules, on ferrihydrite, and on d-MnO₂, it was revealed that d-MnO₂ was the dominant host phase for Mo. Mo formed outer-sphere complex on the surface of ferrihydrite, while the element formed inner-sphere complex on d-MnO₂. Additionally, adsorption envelopes using ferrihydrite showed that amount of adsorbed Mo decreased with the increase in ionic strength, while those using d-MnO₂ did not show the significant decrease of amount of adsorbed Mo with the increase of ionic strength, supporting the structure of the surface complexes of Mo by EXAFS. On the other hand, partition coefficient (=log([C_S]/[C_A]); C_S (ug g⁻¹) and C_A (ug mL⁻¹): concentrations of the sorbed and aqueous ion, respectively) of Mo to ferrihydrite (2.84-3.82) were larger than those to d-MnO₂ (2.24-2.54) under the condition similar to seawater (ionic strength: 0.70; pH: 7 or 8). Additionally, it was also revealed that W formed inner-sphere complex on both ferrihydrite and d-MnO₂. Adsorption envelopes of W to both adsorbents showed that the partition coefficient of W to ferrihydrite was larger by 1.3-1.7 times than that of Mo, while that of W to the d-MnO₂ was similar to that of Mo, which supports the difference of the surface complex structure between Mo and W on both adsorbents. However, EXAFS of W in the ferromanganese nodules cannot be obtained because of the low concentration. More detail analysis of the coordination environment of sorbed ion and adsorption experiment at other condition will be needed to understand the reasons why Mo mainly sorbed to d-MnO₂ and why W has a larger affinity to ferromanganese nodules than Mo.

Reference

1. K. Kishida et al., *Earth and Planetary Science Letters*, **222**, 819, 2004.
2. Y. Takahashi et al., *Geochimica et Cosmochimica Acta*, **64**, 2929, 2000.