

Study on the distribution behavior of tungsten between seawater and ferromanganese using wavelength dispersive XAFS

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Tungsten (W) and molybdenum (Mo) are important elements due to their potential as proxies of paleoceanographic environment. Although they are congeners, they show contrasting distribution behaviors at solid/water interface under different redox conditions. In oxic modern marine environment, distribution between seawater and ferromanganese oxides, one of the most important scavenging processes, has impacts on their concentration in seawater, in which enrichment factor of W into ferromanganese oxides is greater than that of Mo. In this study, we performed wavelength dispersive X-ray absorption fine structure (XAFS) method to reveal coordination environment of W on solid phases which may be critical to its distribution at solid/water interface, and compared them to our previous findings on Mo (Kashiwabara et al., 2009). Our goal is to understand the difference in distribution of W and Mo between seawater and ferromanganese oxides based on structural information at molecular level.

Adsorption experiments were conducted using synthetic ferrihydrite and delta-MnO₂ as adsorbents, in which adsorption amount of W was determined by ICP-MS and structure of adsorbed species was investigated by XAFS. In addition, hydrogenetic ferromanganese oxides, collected from two sites in Pacific Ocean, were analyzed to reveal the coordination environment of W in natural samples. Conventionally, it is difficult to obtain high quality fluorescence XAFS spectra of trace amount of W because of interferences of intense scattering and/or fluorescence from other predominant elements, such as Fe, Mn, and Zn. Therefore, we applied wavelength dispersive XAFS method, in which Bent Crystal Laue Analyzer (BCLA) was used in front of Ge semiconductor detector to selectively extract fluorescence X-rays of W. These analyses were performed at BL01B1 and BL37XU in SPring-8.

From W L₁ and L₃-XANES spectra, it was revealed that W adsorbed on ferrihydrite and delta-MnO₂ was both in octahedral symmetry. It was also revealed that W formed inner-sphere complex on both adsorbents from W L₃-EXAFS spectra. Furthermore, structural information of W in natural ferromanganese oxides was obtained by the use of wavelength dispersive XAFS: W is in octahedral symmetry regardless of the dominance of tetrahedral WO₄²⁻ in seawater. We previously reported that (i) Mo forms an octahedral inner-sphere complex on delta-MnO₂ and a tetrahedral outer-sphere complex on ferrihydrite and that (ii) the host phase of Mo in natural ferromanganese oxides is delta-MnO₂. Based on the comparison between W and Mo, it was found that W and Mo form different surface complexes on ferrihydrite. On the other hand, distribution coefficient (= log ([C_s]/[C_l]); C_s (ug g⁻¹) and C_l (ug mL⁻¹) of W on ferrihydrite was larger than that of Mo while they were similar for adsorption on delta-MnO₂. Therefore, our results suggest that W exhibits large enrichment factor into ferromanganese oxides than Mo because it forms inner-sphere complex on ferrihydrite.

1. Kashiwabara et al., *Geochemical Journal*, 43, e31-e36, 2009.

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