Tungsten species in natural ferromanganese oxides related to its different behavior from molybdenum in oxic ocean

The elemental distribution at the solid/water interface is an important process in many fields of geochemistry. In marine environments, the distribution between seawater and ferromanganese oxides (FMOs), which are prevalent aggregates of Fe (oxyhydr)oxides and Mn oxides, greatly impacts the concentrations of trace elements in seawater. For example, molybdenum (Mo) is controlled by this process, since ca. 70% of its output is presumed to be incorporated into FMOs in a marine system. In addition, the isotopic composition of Mo in seawater is affected by the reaction at the seawater/FMO interface. Large isotopic fractionation of Mo occurs during adsorption on FMOs, leading to the heavier isotope of Mo remaining in seawater.

This study reveals the tungsten (W) species in natural FMOs and its difference from Mo. In contrast to the extensive geochemical attention on Mo, the geochemistry of W at the Earth's surface environment is poorly understood because of the limited number of studies on it. Revealing the difference and/or similarity in their geochemical behaviors may realize new insights in biogeochemistry fields. In modern oxic seawater, the concentration of W is much lower than that of Mo (molar ratio of Mo/W = ~1800) despite their similarity in crustal abundance and chemical characteristics (molar ratio of Mo/W in crust = ~3). This is due to the much larger enrichment of W in FMOs compared with Mo, but the origin has been a mystery for decades.

Although molecular-scale information is critical to understand the enrichment mechanism, a technical difficulty has prevented the XAFS analysis of W in natural FMOs. For trace elements, fluorescence XAFS is conventionally conducted with an energy-dispersive detector, such as a Ge solid-state detector (Ge-SSD). However, this detector has an upper counting limit on the order of 10^5 (photons/s) due to the pulse-shaping time of the amplifier, which is on the 100-ns order. Thus, intense scattering and fluorescence from predominant elements such as Fe and Mn and/or interferences of the K lines of Ni, Cu, and Zn (1000 $\mathrm{mg \cdot kg^{-1}}$ - 2%) prevent high quality fluorescence XAFS spectra of W (<100 $\mathrm{mg \cdot kg^{-1}}$) from being obtained. To deal with this problem, we applied wavelength-dispersive XAFS to W in FMOs. Introducing a bent crystal Laue analyzer (BCLA) in front of the Ge-SSD allows the L lines of W to be selectively extracted, providing spectra with higher S/B and S/N ratios.

First, we compared the spectral quality of the W L_3-edge XANES by the wavelength dispersive XAFS method to that by the conventional method to evaluate the effects of BCLA (Fig. 1). The XAFS measurements were conducted at **BL37XU**. In the conventional mode, the quality of the spectra (a) in Figs. 1(A-C) was poor mainly due to the intense interferences of Ni, Cu, and Zn. In contrast, the efficient removal of the background by the introduction of BCLA enabled us to obtain precise shape in the XAFS spectra (b) in Figs. 1(A-C). Significant improvements were due to the 13-fold increase in the S/B ratio and the 4.8-fold increase in the S/N ratio. These observations demonstrate that BCLA

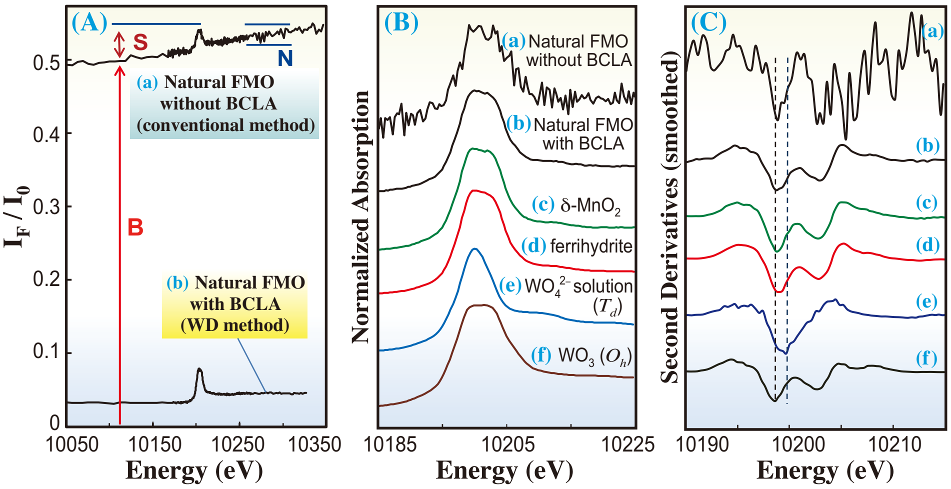

Fig. 1. Tungsten L_3-edge XANES spectra. **(A)** Raw spectra, **(B)-(C)** after background subtraction: **(B)** normalized spectra and **(C)** their second derivatives. Natural ferromanganese oxides **(a)** without BCLA and **(b)** with BCLA. W species adsorbed on **(c)** δ-MnO$_2$ and **(d)** ferrihydrite. Reference compounds of **(e)** WO$_4^{2-}$ solution and **(f)** WO$_3$.

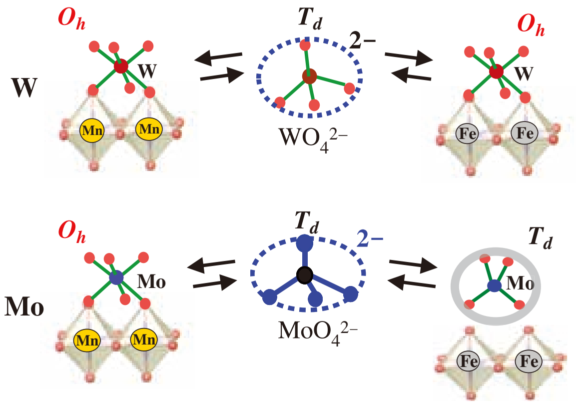

Fig. 2. Structural model of the W species adsorbed on synthetic Fe (oxyhydr)oxides and Mn oxides.

is suitable for the W L_3-edge XAFS measurements of natural FMOs containing approximately 50 mg·kg^{-1} of W with 1000-3500 mg·kg^{-1} of Ni, Cu, and Zn.

As a result, we found that the W species in natural FMOs has a distorted O_h symmetry. The host phase of W in natural FMOs seems to be Mn oxides. In addition, we also revealed the structure of the W species adsorbed on synthetic Fe/Mn (oxyhydr)oxides where all the W species are inner-sphere complexes in hexavalent and distorted O_h symmetry (Fig. 2). These findings indicate that similar to the case for Mo, the negatively-charged WO_4^{2-} ion mainly adsorbs on the negatively-charged Mn oxide phase in natural FMOs via a strong chemical interaction. On the other hand, a clear difference was found in their structure on Fe (oxyhydr)oxides: inner-sphere complex of W with symmetry change from T_d dissolved species to O_h adsorbed species and the outer-sphere complex of Mo without symmetry change.

These molecular-scale insights are consistent with their macroscopic adsorption behaviors on synthetic Mn oxides and Fe (oxhydr)oxides investigated in the laboratory (Fig. 3). For Mn oxides, the similar adsorptions between W and Mo are due to their formation of inner-sphere complexes. In contrast, the larger adsorption of W on Fe (oxhydr)oxides is due to its formation of inner-sphere complexes compared with the outer-sphere complexes for Mo. Especially, W shows a two order of magnitude larger enrichment on Fe (oxyhydr)oxides than Mo under conditions similar to seawater (pH 8, I = 0.70 M). This difference is comparable to the observation of a natural seawater/FMO system. Therefore, we consider that the formation of inner-sphere complexes of W on Fe (oxyhydr)oxide phases provide a molecular explanation for the larger enrichment of W than Mo into natural FMOs, which greatly affects their concentrations in modern oxic seawater.

In addition, isotopic fractionation of W during adsorption on Fe/Mn (oxyhydr)oxides, which has not yet been reported, is expected from the molecular symmetry. In the case of Mo, large isotopic fractionation occurs during adsorption on Mn oxides due to the structural difference between dissolved and adsorbed species. In contrast, Mo shows little or no fractionation during adsorption on Fe (oxyhydr)oxides due to the similarity of the local structure between adsorbed and dissolved species. These isotopic behaviors of Mo lead to extensive use of the Mo isotope system in paleo-environmental studies. In the case of W, the difference in the coordination number between dissolved and adsorbed species implies a striking isotopic fractionation of W during adsorption on both Fe (oxyhydr)oxides and Mn oxides. Although further studies are still necessary to elucidate the precise relationship between the structure and isotopic fractionation, the structural information indicates the potential importance of W isotope systems as a paleo-environmental proxy.

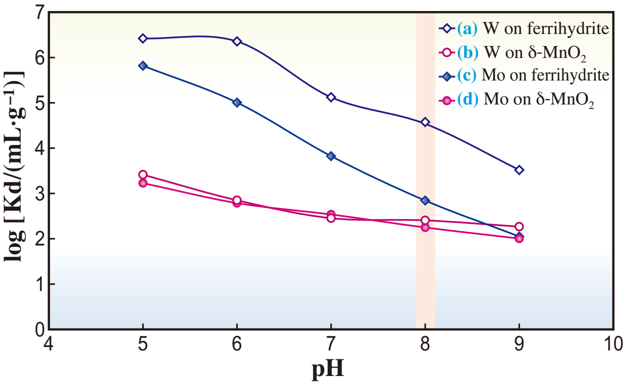

Fig. 3. Adsorption envelopes for W and Mo on ferrihydrite and δ-MnO_2 (I = 0.70 M, $NaNO_3$).

Teruhiko Kashiwabara[a,*] and Yoshio Takahashi[b]

[a] Research and Development (R&D) Center for Submarine Resources, JAMSTEC
[b] Dept. of Earth and Planetary Environmental Science, The University of Tokyo

*E-mail: teruhiko-kashiwa@jamstec.go.jp

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