



## Different partitioning behaviors of molybdenum and tungsten in a sediment–water system under various redox conditions



Yusuke Watanabe<sup>a</sup>, Teruhiko Kashiwabara<sup>b</sup>, Jun-ichiro Ishibashi<sup>c</sup>, Oki Sekizawa<sup>d,e</sup>, Kiyofumi Nitta<sup>e</sup>, Tomoya Uruga<sup>e</sup>, Yoshio Takahashi<sup>a,\*</sup>

<sup>a</sup> Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

<sup>b</sup> Japan Agency for Marine–Earth Science and Technology, 2-15 Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan

<sup>c</sup> Faculty of Sciences, Kyushu University, 6-10-1, Hakozaki, Higashi, Fukuoka 812-8581, Japan

<sup>d</sup> Innovation Research Center for Fuel Cells, The University of Electro-Communications, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

<sup>e</sup> Japan Synchrotron Radiation Research Institute, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

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### ABSTRACT

Molybdenum (Mo) and tungsten (W) are redox-sensitive elements that exhibit contrasting geochemical behaviors under different redox and/or sulfidic conditions despite belonging to the same group in the periodic table. In this study, the geochemistry of Mo and W in a sediment–porewater system was investigated using a core sample collected from sediment containing hydrothermal minerals (Izena Hole, Okinawa, Japan). The Mo contents in the sediment and the porewater were quantified to calculate the partition coefficient  $K_d$  (concentration ratio of the solid phase to the aqueous phase) for Mo. However, the W concentration in the porewater was exceedingly low to be detected. Thus, we also conducted laboratory experiments simulating the sediment–porewater system to clarify the partitioning behaviors of Mo and W under redox conditions. X-ray absorption near-edge structure (XANES) spectra were obtained to determine the chemical species of Mo and W in sediment at different depths to understand the chemical processes of Mo and W. In particular, high-sensitivity XANES spectroscopy using wavelength-dispersive fluorescence mode was applied to W  $L_3$  edge XANES spectra to reduce the interference signals from coexistent elements (Zn and Ni). This step thereby facilitating the identification of oxygen- and sulfur-coordinated species for W in the sediments.

The collected core sample covered a broad range of redox conditions under various hydrogen sulfide ( $H_2S$ ) concentrations depending on the depth. The presence of iron oxides in the upper layer suggested an oxic condition above within 4 cm depth below the seafloor (cmbsf). Iron and Zn sulfide minerals were found in deeper layers (16–24 cmbsf) and indicated the reductive conditions formed in such layer. Hydrogen sulfide was also observed in the porewater of the deeper layer. Analyses for Mo in the natural sediments, as well as XANES analyses, revealed that the  $K_d$  was higher in the deeper layer, with high pyrite and  $H_2S$  contents, than in the upper layer. These results implied that Mo was removed from the porewater under reductive and/or sulfidic conditions. The chemical species of Mo was also an oxygen-coordinated species in the upper layer (0–8 cmbsf). Meanwhile, the detection of sulfide in the deeper layer suggests that Mo sulfidation is an important reaction in Mo enrichment in sediments.

On the other hand, at all the depths, W formed oxygen-coordinated species in the sediment. The subtle change of  $K_d$  for W with depth suggested that  $H_2S$  did not affect the W adsorption in our samples. Hence, the Mo/W ratio in the sediments increased with the development of reducing conditions and vice versa in the coexistent porewater. Speciation analysis revealed that the high stability of oxygen-coordinated species of W was responsible for the variations of the Mo/W ratio under various redox conditions.

### 1. Introduction

Atmospheric and oceanic environments have been changing throughout earth's evolution, and these alterations are typically

reflected in the increased atmospheric oxygen. Through the oxygenation of the earth's environment, oxidation–reduction (redox) conditions have been evolving in the aqueous environment such as in the paleocean. Elemental concentrations in the ocean are affected strongly by the

\* Corresponding author.

E-mail address: [ytakaha@eps.s.u-tokyo.ac.jp](mailto:ytakaha@eps.s.u-tokyo.ac.jp) (Y. Takahashi).

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redox conditions. These elements exhibit variations in oxidation states and their dissolved species, which ultimately control their geochemical behaviors (Saito et al., 2003). The concentrations of bioessential elements in the ocean throughout the earth's history have been investigated in biogeochemistry (Anbar, 2008). The changes in these concentrations are highly complex. For trace elements, such as molybdenum (Mo) and tungsten (W), the sediment–seawater partitioning behavior is a key factor in understanding their geochemical behaviors. Molybdenum and W belong to the same group in the periodic table and possess similar chemical properties. Their geochemical behaviors are strongly dependent on the redox and sulfide concentrations in the oceanic environment. In modern oxic seawater, the elements prefer to dissolve as tetrahedral oxyanions ( $\text{MoO}_4^{2-}$  and  $\text{WO}_4^{2-}$ ) (Turner et al., 1981). These two oxyanions have long residence times, and their concentrations display conservative depth profiles in the water column (Sohrin et al., 1987, 1998). Although Mo and W show similar chemical properties, the concentrations of Mo and W in seawater are 106 nM and 60 pM, respectively (Sohrin et al., 1987). The molar ratio of dissolved Mo/W ratio in seawater is 1800, whereas that in crustal rock is only 3 (Sohrin et al., 1987). The difference in the water solubilities of Mo and W can be explained by the interaction between seawater and ferromanganese oxide as previously studied (Siebert et al., 2003; Kashiwabara et al., 2011, 2013). However, under anoxic or euxinic conditions (reducing conditions in the presence of hydrogen sulfide ( $\text{H}_2\text{S}$ )), organic carbon and sulfide minerals, such as pyrite ( $\text{FeS}_2$ ), should be considered in understanding the geochemical behaviors of Mo and W. Molybdenum is regarded as an effective paleo-redox tracer because of its distinct geochemical behavior in oxic and euxinic environments (Helz et al., 1996; Adelson et al., 2001; Dahl et al., 2013; Takahashi et al., 2014). Under sulfidic conditions, Mo forms thiomolybdate species ( $\text{MoO}_n\text{S}_{4-n}^{2-}$ ) and strongly interacts with organic matters and sulfide particles (Erickson and Helz, 2000; Brucker et al., 2009). Several burial processes of Mo to euxinic sediments have been proposed. These processes include coprecipitation with Fe to form  $\text{Fe}_3\text{Mo}_3\text{S}_{14}$ , reduction to Mo(V), and interactions with dissolved organic matters and polysulfide. However, the chemical processes controlling the behaviors in natural euxinic environments remain unclear (Chappaz et al., 2014).

Similar to Mo, thiotungstate ( $\text{WO}_n\text{S}_{4-n}^{2-}$ ) can form in the presence of sulfide from W. However, their formation constants reveal that the complete transformation from  $\text{WO}_4^{2-}$  to  $\text{WS}_4^{2-}$  occurs only at high sulfide concentrations, unlike in Mo (Erickson and Helz, 2000; Mohajerin et al., 2014). The positive correlation between dissolved W and S(–II) concentrations indicates that the formed  $\text{WS}_4^{2-}$ , which may be less particle reactive than  $\text{MoS}_4^{2-}$ , may augment the solubility of W (Cui and Johannesson, 2017). This phenomenon is directly opposite to that of Mo, which decreases in solubility when  $\text{MoS}_4^{2-}$  forms (Mohajerin et al., 2014, 2016). These results suggest that the water solubilities of Mo and W in a euxinic ocean differ from that in an oxic ocean. However, what factor controls the difference in solubilities of Mo and W under sulfidic conditions is unclear. The solid–water partitioning behaviors of Mo and W under sulfidic conditions must first be understood to clarify the difference.

To comprehend the solubilities of Mo and W under sulfidic conditions and compare the results with those under oxic conditions, we studied the sediment–porewater partitioning behaviors of Mo and W in the sediments, which contain hydrothermally derived materials, such as sulfide and sulfate minerals. The sediment–porewater system exhibited various redox conditions depending on the depth through the early diagenesis in the sedimentary environment. Using a sediment core sample, we performed various chemical analyses, including both quantitative and speciation analyses, to determine the natural partitioning behavior of Mo between sediment and porewater. In laboratory experiments, W must be added into the sediment–porewater system to obtain the partitioning data of W. Nonetheless, the results seemed reasonable because Mo was also added to the system, and the results

coincided with the Mo data obtained from a natural system.

Speciation analyses were conducted on trace-level Mo and W in natural sediments by X-ray absorption near-edge structure (XANES) spectroscopy to clarify the partitioning behaviors of Mo and W. XANES analysis is a powerful tool for elucidating the chemical species of trace elements in natural samples. However, the fluorescence XANES analysis of W through the W  $L\alpha$  line in natural sediments presents analytical problems derived from the interferences of fluorescence X-rays from other major elements in sediments, such as the Ni  $K\alpha$  and Zn  $K\beta$  lines. Previous studies attempted to reduce these interferences by applying the wavelength-dispersive XANES (WD-XANES) method, which introduces a bent crystal Laue analyzer (BCLA) in front of the Ge solid-state detector (SSD) (Takahashi et al., 2006; Kashiwabara et al., 2013). In the present study, we first measured chemical form of trace-level W (< 1 mg/kg) in natural sediments near the hydrothermal vent using WD-XANES method.

On the basis of the partitioning and speciation of Mo and W under various redox conditions, we identified the chemical processes that control the partitioning behaviors of Mo and W in the sediment–porewater (seawater) system. These chemical processes drove the differences in the responses of Mo and W behaviors to the redox conditions in the sediment–porewater system.

## 2. Samples and analytical methods

### 2.1. Sample collection and chemical analyses

Sediment and porewater samples were collected from the 1187 MB core, which was located 30 m south of the Dragon Chimney in the Hakurei field (27°14.928'N, 127°4.148'E). The samples were obtained from a water depth of 1603 m in the Izena Hole during the NT10-17 cruise of the *R/V Natsushima* in September 2010 (Kawagucci et al., 2011; Ishibashi et al., 2014; Miyoshi et al., 2015). Hydrothermal activities were found near the sampling point. The sediment core was acquired by an acrylic push corer (MBARI-type corer; Nakaseama et al., 2008) for short coring. This corer was attached to a remotely operated vehicle Hyper-Dolphin. The sediment core was 24 cm long and changes in color with depth. These color alterations suggest the differences in redox conditions, an important parameter in the sediment behaviors of Mo and W (Fig. 1). The core sample was cut horizontally at 4 cm intervals. Each layer was then sealed in an airtight polyethylene bag purged with  $\text{N}_2$  gas and stored at 4 °C to avoid chemical oxidation of the sediments. Prior to sealing, each sediment was pressed with a clamp to extract the porewater. The extracted porewater samples were filtered through a 0.45  $\mu\text{m}$  membrane filter (Advantech, polycarbonate) and then separated for on-board and on-shore analyses, respectively. Immediately following the porewater extraction, pH,  $\text{H}_2\text{S}$  concentrations, and alkalinity were measured by a pH meter (glass electrode, Horiba, Kyoto, Japan), methylene blue colorimetric analysis (Cline, 1969), and pH titration by 0.1 M HCl (Gran method, Drever, 1997), respectively, under the on-board analysis. Meanwhile, the redox potential was measured by a Ag/AgCl electrode (Fujiwara Sci., PRN-41) converted to Eh value in the hydrogen electrode scale. In the laboratory, the concentrations of sulfate ( $\text{SO}_4^{2-}$ ) and magnesium (Mg) in the porewater were measured by ion chromatography (ICS1100, Thermo scientific, USA). The porewater samples used for inductively coupled plasma mass spectrometry (ICP-MS: Agilent Technology 7700 ×, Tokyo, Japan) to measure the trace elements were then acidified by adding 2 wt%  $\text{HNO}_3$  solution to prevent the incidental precipitation of various minerals.

In the laboratory, packed sediments were opened in an anaerobic chamber (Ar: 95%;  $\text{H}_2$ : 5%) (Coy Laboratory Products, USA), where the oxygen concentration was maintained below 1 ppm. The sediments were then dried and homogenized with agate mortar in the anaerobic chamber. After homogenization, the major element composition of the sediments was measured by X-ray fluorescence analysis (XRF; ZSX-101, Rigaku, Japan) using the glass bead method (Kawano, 2010). Total

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