

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

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Received 23 November 2011; accepted in revised form 24 December 2012; available online 5 January 2013

Abstract

The tungsten (W) species in marine ferromanganese oxides were investigated by wavelength dispersive XAFS method. We found that the W species are in distorted O_h symmetry in natural ferromanganese oxides. The host phase of W is suggested to be Mn oxides by μ -XRF mapping. We also found that the W species forms inner-sphere complexes in hexavalent state and distorted O_h symmetry on synthetic ferrihydrite, goethite, hematite, and δ -MnO₂. The molecular-scale information of W indicates that the negatively-charged WO_4^{2-} ion mainly adsorbs on the negatively-charged Mn oxides phase in natural ferromanganese oxides due to the strong chemical interaction. In addition, preferential adsorption of lighter W isotopes is expected based on the molecular symmetry of the adsorbed species, implying the potential significance of the W isotope systems similar to Mo.

Adsorption experiments of W on synthetic ferrihydrite and δ -MnO₂ were also conducted. At higher equilibrium concentration, W exhibits behaviors similar to Mo on δ -MnO₂ due to their formations of inner-sphere complexes. On the other hand, W shows a much larger adsorption on ferrihydrite than Mo. This is due to the formation of the inner- and outer-sphere complexes for W and Mo on ferrihydrite, respectively. Considering the lower equilibrium concentration such as in oxic seawater, however, the enrichment of W into natural ferromanganese oxides larger than Mo may be controlled by the different stabilities of their inner-sphere complexes on the Mn oxides. These two factors, (i) the stability of inner-sphere complexes on the Mn oxides and (ii) the mode of attachment on ferrihydrite (inner- or outer-sphere complex), are the causes of the different behaviors of W and Mo on the surface of the Fe/Mn (oxyhydr)oxides.

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1. INTRODUCTION

Tungsten (W) is below molybdenum (Mo) in the periodic table, and has a very similar chemical property to Mo. Both elements are redox sensitive trace metals with

many stable isotopes, which lead to their variable chemistry and isotopic ratios in geochemical and biological systems (e.g., Kletzin and Adams, 1996; Anbar 2004). In contrast to the extensive geochemical attention on Mo, geochemistry of W at Earth's surface environment is poorly understood

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because of the limited number of studies on it. Revealing the difference and/or similarity in their geochemical behaviors can lead to the development of new insights in biogeochemistry field.

In this study, we focus on the behavior of W in the modern oxic marine environment. Tungsten occurs in seawater as tungstate ion (WO_4^{2-}). From its chemical form similar to MoO_4^{2-} , W is sometimes expected to display a similar behavior to Mo. Tungsten has a long residence time of ca. 6000 years and exhibits a conservative vertical profile in the ocean like Mo (Sohrin et al., 1987). On the other hand, the concentrations of these elements are very different. The concentration of W in seawater is much smaller than that of Mo (molar ratio of Mo/W = ~ 1800) (e.g., Bruland, 1983; Sohrin et al., 1987, 1989, 1999), although the crustal abundance of W is almost the same as that of Mo (molar ratio of Mo/W in crust = ~ 3 ; Wedepohl, 1969; Bowen, 1979; Taylor and McLennan 1985, 1995). To understand the mechanisms controlling the geochemical behaviors of W and Mo in the modern oxic marine environment, the scavenging process of these elements from seawater should be clarified.

The adsorption to ferromanganese oxides is one of the most important scavenging processes for trace elements. The concentration of Mo in the marine environments is, indeed, controlled by this process: 45–70% of output is presumed to be incorporated into ferromanganese oxides in the budget of Mo in the marine system (Bertine and Turekian, 1973; Morford and Emerson, 1999; Siebert et al., 2003). In addition, the Mo isotopic composition in seawater is also affected by the reaction at the seawater/ferromanganese oxide interface. A large isotopic fractionation of Mo occurs during adsorption on ferromanganese oxides, leading to the heavier isotope of Mo remaining in seawater (Barling et al., 2001).

Similarly, this scavenging process at the solid/water interface can considerably influence the concentration and isotopic composition of W in seawater. While limited data are available on the abundance of W in marine environment, the ferromanganese oxides show the highest concentration of W ($\sim 100 \text{ mg kg}^{-1}$) among the various marine sediments (e.g., Baturin, 1988; Kunzendorf and Glasby, 1992; Kletzin and Adams, 1996; Koutsospyros et al., 2006). This represents an enrichment of W by ca. 6 orders of magnitude over the background seawater level. In addition, this enrichment factor is 2 orders of magnitude greater than that of Mo (Sohrin et al., 1987; Takematsu et al., 1990). Tungsten is relatively more enriched into ferromanganese oxides and/or Mo is more soluble into seawater, which may explain the large difference in their concentrations in seawater.

However, the cause of the different behaviors of W and Mo at the seawater/ferromanganese oxide interface is still unknown, due to the lack of fundamental information on the W species in ferromanganese oxides. Previously, we revealed the molecular structures of Mo on amorphous ferrihydrite, $\delta\text{-MnO}_2$, and natural ferromanganese oxides, and their close association with molecular-scale mechanisms of its enrichment and isotopic fractionation (Kashiwabara et al., 2009, 2011). On the other hand, no study on W at

the molecular scale has been conducted. Some previous studies discussed only the host phase association of W in natural ferromanganese oxides. Koschinsky and Hein (2003) suggested that W is preferentially associated with Fe (oxyhydr)oxides phase because of their coulombic interaction. However, sequential-leaching procedures employed in this study may have many problems such as incomplete selectivity for discrete phase, re-adsorption of dissolved component, and poor reproducibility (Tipping et al., 1985; Kersten and Fröstner, 1989). There are other studies suggesting that W may be associated with Mn as manganese tungstate compounds (MnWO_4) (Kunzendorf and Glasby, 1992; Takematsu et al., 1990; Li, 1981). This is based on the correlation analysis and/or assumption that negatively-charged oxyanions “should be adsorbed” on the positively-charged Fe (oxyhydr)oxides if they are removed by adsorption not by coprecipitation. However, very low concentration of W in seawater (less than 60 pmol L^{-1}) is questionable to be related to a coprecipitation process as tungstate compounds. As is the case with Mo, the X-ray absorption fine structure (XAFS) study, a direct and non-destructive spectroscopic approach, is needed to shed light on such a poor understanding of W in natural ferromanganese oxides.

The XAFS analysis of W in the natural ferromanganese oxides is challenging due to several analytical problems caused by the energy relationship of fluorescence X-rays between the trace amount of W and other major and enriched elements in natural ferromanganese oxides such as Ni, Cu, and Zn. For the 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 in the order of 10^5 (photons/s), which originates from the pulse shaping time of the amplifier at 100 ns order. Thus, intense scattering and fluorescence lines from the predominant elements, such as Fe and Mn, and/or interferences of K lines of Ni, Cu, and Zn ($1000 \text{ mg kg}^{-1} - 2\%$) inhibit us from obtaining high quality fluorescence XAFS spectra of W ($\sim 100 \text{ mg kg}^{-1}$).

To solve this problem, we applied the wavelength dispersive XAFS method, in which a bent crystal Laue analyzer (BCLA) was introduced in front of the Ge-SSD. This method enabled the selective extraction of the L line of W and achievement of the XAFS spectra with high S/B and S/N ratios. We previously applied this method for some trace elements in geochemical samples to improve the quality of their XAFS spectra (Takahashi et al., 2006; Yamamoto et al., 2008; Kashiwabara et al., 2010). In this study, geochemical discussion will be given, which is based on the structural information of W in natural ferromanganese oxides obtained by this method.

The aim of this study is to understand the geochemical behavior of W at the interface of seawater/ferromanganese oxides based on the molecular-scale information. We investigated the fundamental information on the W species in natural ferromanganese oxides such as (i) molecular symmetry, (ii) host phase association, and (iii) the mode of attachment (inner- or outer-sphere) of the surface complexes. We also conducted adsorption experiments of W using synthetic amorphous Fe (oxyhydr)oxide and Mn

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