EXPRESS LETTER

A XAFS study on the mechanism of isotopic fractionation of molybdenum during its adsorption on ferromanganese oxides

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Due to its potential as a paleoredox proxy, there have been many studies on Mo isotopic fractionation during adsorption onto ferromanganese oxides in seawater. However, the mechanisms of both adsorption and isotopic fractionation are still under debate due to the lack of structural information on the adsorbed species. In this study, XAFS analyses were performed to reveal the mechanism, based on structural information at the molecular level, of Mo isotopic fractionation during adsorption onto ferromanganese oxides. Molybdenum L_3-edge XANES and K-edge EXAFS revealed that Mo species adsorbed on the surface of ferrihydrite was a tetrahedrally coordinated outer-sphere complex, while that on δ-MnO_2 was an octahedrally coordinated inner-sphere complex. Additionally, it was also revealed that δ-MnO_2 was the dominant host phase of Mo in the hydrogenetic ferromanganese nodules from the comparison of their XAFS spectra. Previous studies reported that lighter isotopes of Mo were preferentially incorporated into ferromanganese oxides from seawater. This fractionation can be explained based on the structural difference between tetrahedral MoO_4^{2-} (=a major species in seawater) and the octahedral species adsorbed on the Mn oxide phase in ferromanganese nodules. In contrast, little change in Mo local structures during its adsorption onto ferrihydrite also suggested the little or no fractionation of Mo isotopes in the presence of Fe hydroxides without Mn oxides. These facts imply that the Mo isotopic composition in ancient marine sediments can distinguish redox boundaries of $Fe^{2+}/Fe(OH)_3$ and of the more oxic Mn^{2+}/MnO_2.

Keywords: molybdenum, XAFS, isotopic fractionation, ferromanganese oxides, paleoredox

INTRODUCTION

The adsorption-desorption reaction is an important process that controls the geochemical behaviors of trace elements in the environment. Especially, ferromanganese crusts and nodules, which are prevalent aggregates of iron hydroxide and manganese oxide on the seafloor, are important adsorbents for various elements in oxic marine environment, which controls their concentrations in seawater through the high adsorptive abilities of iron hydroxide and manganese oxide (Chester, 1990; Takahashi *et al.*, 2007). Molybdenum is one of these elements, that is, around 70% of output is presumed to be incorporated into ferromanganese oxides in the budget of Mo in the marine system (Bertine and Turekian, 1973; Siebert *et al.*, 2003). This element is a redox-sensitive trace metal with seven stable isotopes and is essential in many bio-

logical processes; therefore, the biogeochemistry of Mo in marine environments is widely discussed (Bertine and Turekian, 1973; Siebert *et al.*, 2003; Anbar and Knoll, 2002).

Recently, it has been reported that lighter isotopes of Mo were preferentially incorporated into ferromanganese oxides from seawater (Barling *et al.*, 2001; Siebert *et al.*, 2003). This fractionation between seawater and ferromanganese oxides is the largest (~2‰; $^{97}Mo/^{95}Mo$), compared with other elements with smaller fractionations (<±1‰/amu) during their sorption onto oxide surfaces (Johnson, 2004; Johnson *et al.*, 2005; Rehkamper *et al.*, 2002; Ellis *et al.*, 2004; Icopini *et al.*, 2004; Crosby *et al.*, 2005; Pokrovsky *et al.*, 2005; Teutsch *et al.*, 2005; Gelabert *et al.*, 2006). This fact also means that the heavier isotopes are left in seawater and the Mo isotopic composition in seawater can change depending on the abundance of ferromanganese oxides in the marine system. Therefore, the molybdenum isotope ratios, for example $^{97}Mo/^{95}Mo$, in ancient marine sediments are expected to be used as a signature of global-paleocean redox conditions and

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many studies have focused on this promising tool (Anbar, 2004; Barling and Anbar, 2004; Weeks *et al.*, 2007; Wasylenki *et al.*, 2008; Arnold *et al.*, 2004; Pearce *et al.*, 2008; Poulson *et al.*, 2006; Voegelin *et al.*, 2009).

On the other hand, the mechanism of this marked fractionation of the Mo isotope is still under debate due to poor understanding of the adsorption process onto ferromanganese oxides. Many previous studies performed quantum mechanical calculations of fractionation factors between the dominant species in seawater (MoO_4^{2-}) and various candidates of adsorbed species to explain the Mo isotopic offset observed between seawater and ferromanganese oxides theoretically (Tossell, 2005; Weeks *et al.*, 2007; Wasylenki *et al.*, 2008). The calculated fractionation factors, however, were significantly smaller than the experimental values in most cases, which may be due to poor knowledge of the adsorbed Mo species. Experimentally, the host phase of Mo in natural ferromanganese oxides was investigated mainly by sequential extraction experiments or correlation analysis (Kuhn *et al.*, 2003; Koschinsky and Hein, 2003; Shimmield and Price, 1986). However, these are indirect methods which can be subject to poor reproducibility due to re-adsorption and incomplete selectivity of each phase, leading to the different conclusions among previous reports.

To reveal the mechanisms of adsorption and isotopic fractionation, it is necessary to make clear the coordination environment of the adsorbed Mo species. In this study, we performed XAFS analyses to understand the adsorption process based on the structural information at the molecular level, which is also critical to understand the mechanism of the isotopic fractionation during adsorption.

<center>EXPERIMENTAL</center>

Natural samples of hydrogenetic ferromanganese nodules were selected from two sites in the Pacific Ocean; D535 in the South Pacific Ocean (13.0°S, 159.2°W, 5222 m depth), and AD14 around the Marshall Islands (14.1°N, 167.2°W, 1617 m depth) (Takahashi *et al.*, 2000, 2007; Kashiwabara *et al.*, 2008). Average major element compositions were (Mn, Fe) = (27.9 wt %, 16.4 wt %) and (29.5 wt %, 16.7 wt %) for D535 and AD14, respectively. As reference materials for measurements, MoO_4^{2-} solution, MoO_3, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, MoO_2 and Mo-sorbed ferrihydrite and δ-MnO_2 were chosen. The MoO_4^{2-} solution was prepared by dissolving $Na_2MoO_4\cdot2H_2O$ (Wako, Japan) into MQ water and adjusted to 0.10 M. The pellets of MoO_3, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ and MoO_2 (Wako, Japan) were made by dilution with BN to 10 wt %. Mo-sorbed samples were prepared by adding 10 mL of 0.30 mM MoO_4^{2-} solution to 20 mg ferrihydrite or δ-MnO_2,
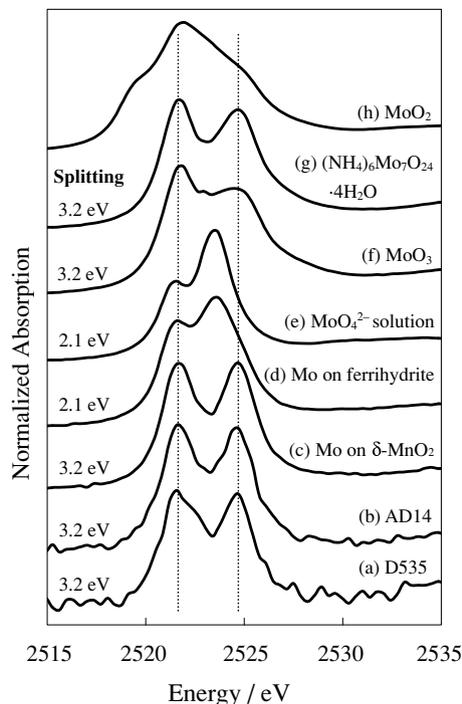
Fig. 1. *Mo L_3-edge XANES spectra and their splitting values.*

which were respectively synthesized according to Schwertmann and Cornell (2000) and Foster *et al.* (2003). Ionic strength was adjusted to 0.70 M ($NaNO_3$) and pH was maintained at 8.0 by adding a small amount of NaOH solution. After 24 h, suspensions were filtered and the solid phases were packed into polyethylene bags as adsorbed samples. These samples and the natural ferromanganese nodules were subjected to XAFS analyses.

Molybdenum K-edge (20.004 keV) EXAFS and L_3-edge (2.523 keV) XANES were measured at BL01B1 in SPring-8 (Hyogo, Japan) and BL-9A in Photon Factory (Tsukuba, Japan), respectively. Molybdenum K-edge EXAFS provides quantitative information about the distances to neighboring atoms and the coordination numbers, while L_3-edge XANES is sensitive to the local symmetry because at this edge, the d-orbital is involved in bonding related to formation of surface complexes. In both measurements, the white beam from a bending magnet was monochromatized by a Si(111) doublecrystal monochromator. K-edge EXAFS spectra for the natural and adsorbed samples were measured in fluorescence mode with a 19-element Ge solid-state detector, while those for reference materials, except for the adsorbed samples, were measured in transmission mode. The measurements were conducted under ambient condition. The energy of the X-ray was calibrated with the first peak of Mo foil at 20.004 keV. On the other hand, the L_3-edge
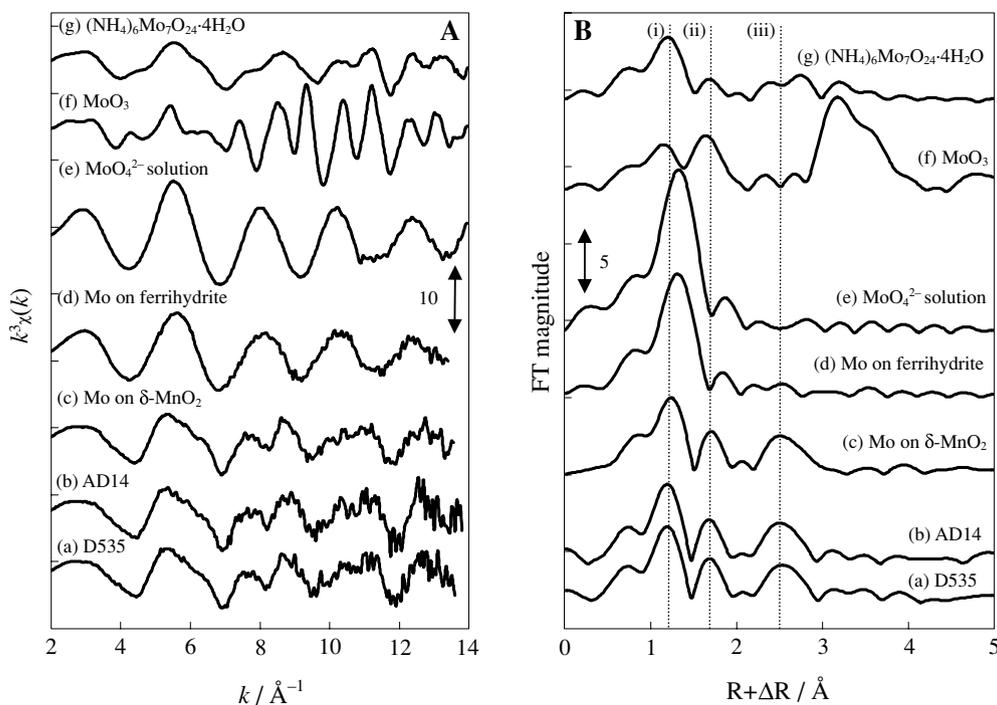
Fig. 2. Mo K-edge EXAFS spectra. A: k^3-weighted $\chi(k)$ spectra, B: RSF of A (phase shift not corrected). (i), (ii): Mo–O of distorted octahedra, (iii) Mo–Mn of inner-sphere complex.

spectra of natural and adsorbed samples were measured in fluorescence mode with a Lytle detector, while reference materials were measured in conversion electron yield mode. The energy was calibrated with the first peak of $Na_2MoO_4 \cdot 2H_2O$ at 2.523 keV. The measurements for the L_3-edge spectra were conducted at room temperature in a helium atmosphere.

RESULTS AND DISCUSSION

Molybdenum L_3-edge XANES spectroscopy is a useful probe for Mo local symmetry because it has widely been reported for Mo(VI) compounds that the variable splitting in the L_3-edges reflects the ligand field splitting of d-orbitals, where smaller splitting (1.8–2.6 eV) was observed for Mo(VI) in tetrahedral symmetry compared to that of octahedral symmetry (3.1–4.5 eV) (Aritani *et al.*, 1996; Bare *et al.*, 1993). The splitting and edge energy of the spectra summarized in Fig. 1, demonstrate that Mo is present as Mo(VI) in all the samples except for MoO_2 (Fig. 1(h)). Additionally, the degree of splitting in Mo adsorbed on ferrihydrite and in MoO_4^{2-} solution (Figs. 1(d) and (e)) corresponds to that of tetrahedrally coordinated Mo(VI) (2.1 eV), suggesting that the Mo species adsorbed on ferrihydrite and dissolved in water are tetrahedral. On the other hand, larger splittings corresponding to octahedral Mo(VI) (3.2 eV)

were found in the spectra of Mo adsorbed on δ-MnO_2, Mo in ferromanganese oxides (Figs. 1(a)–(c)) and also for MoO_3 and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Figs. 1(f) and (g)), indicating that these species were in octahedral symmetry regardless of the predominance of tetrahedral MoO_4^{2-} in solution or in seawater (Bryne, 2002; Oyerinde *et al.*, 2008).

Figures 2A and B show the k^3-weighted $\chi(k)$ spectra of Mo K-edge EXAFS and their radial structural functions (RSF; phase shift not corrected). The $k^3\chi(k)$ of Mo adsorbed on δ-MnO_2 (Fig. 2A(c)) contains many features that indicate the complexity of coordination around Mo, while the spectrum of Mo adsorbed on ferrihydrite (Fig. 2A(d)) is dominated by one major oscillation function, similar to that of MoO_4^{2-} solution (Fig. 2A(e)). MoO_3 and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Figs. 2A(f) and A(g)) also show complex oscillations, but their frequencies and amplitudes are clearly different. The RSF confirms the differences among the $k^3\chi(k)$ spectra; Mo adsorbed on δ-MnO_2 (Fig. 2B(c)) exhibits a split in Mo–O peaks (=(i) and (ii) in Fig. 2B) and a prominent peak due to the Mo–Mn shell (=(iii) in Fig. 2B; third shell), indicating inner-sphere complexation with distorted symmetry of Mo on δ-MnO_2. On the other hand, only one prominent peak due to Mo–O was observed in the MoO_4^{2-} solution and Mo adsorbed on ferrihydrite (Figs. 2B(e) and B(d)), suggesting outer-sphere complexation of MoO_4^{2-} on ferrihydrite. The RSF

of MoO_3 and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Figs. 2B(f) and B(g)) also show the splitting of the Mo–O shell as distorted symmetry with further Mo–Mo shell at $R + \Delta R = 2.5–3.5$ Å.

From the excellent agreement between the spectra of natural ferromanganese nodules (Figs. 2A(a), A(b), B(a) and B(b)) and that of Mo adsorbed on δ-MnO_2 (Figs. 2A(c) and B(c)), we can conclude that the host phase of Mo in hydrogenetic ferromanganese nodules is δ-MnO_2. Previously, some reports suggested that MoO_4^{2-}, a major species in seawater, was preferentially adsorbed onto slightly positively charged iron hydroxide due to the negative charge of the ion (Kuhn *et al.*, 2003; Koschinsky and Hein, 2003). As revealed directly by our XAFS analyses, however, this is not even the case for the hydrogenetic ferromanganese nodules that contain iron hydroxide at concentrations similar to those of manganese oxide.

A similar XAFS analysis was applied to hydrothermal ferromanganese crusts (Kuhn *et al.*, 2003), in which the content of manganese oxide was dominant (42–49%) over iron hydroxide (~1%). They concluded that the third shell in RSF was due to Mo, showing that Mo was present as the heptamolybdate species, the source of which was hydrothermal fluid. In the case of hydrogenetic ferromanganese oxides, however, it is reasonable to consider that the third shell of Figs. 2B(a)–(c) is the Mo–Mn shell due to the formation of an inner-sphere complex bound to δ-MnO_2, and not due to the polymerization of Mo for the reasons stated below. Firstly, polymolybdate species cannot exist in normal seawater (Mo concentration: ~0.11 μM) around pH 8, although they could be dominant at lower pH (<pH 5) and higher Mo concentration above 10^{-3} M (Oyerinde *et al.*, 2008). Secondly, third shells (=(iii) in Fig. 2B) in the spectra of Mo sorbed on δ-MnO_2 (Fig. 2B(c)) and Mo in hydrogenetic ferromanganese nodules (Figs. 2B(a) and B(b)) were successfully fitted with Mn; the best matched results are 2.0 O atoms at 1.68 Å, 4.0 O atoms at 2.27 Å and 1.0 Mn atom at 3.04 Å. The results suggest the formation of a bidentate mononuclear complex on the δ-MnO_2 surface with a Mn–O bond length of 1.90 Å (Foster *et al.*, 2003). Considering the uncertainty in coordination number of the third shell, other geometric models are also possible, the details of which will be reported elsewhere. In any case, however, an inner-sphere surface complex is formed during the adsorption of Mo onto δ-MnO_2.

For iron hydroxides, on the other hand, adsorption experiments of Mo onto ferrihydrite were previously performed by some researchers (Gustafsson, 2003; Balistrieri and Chao, 1990). They suggested that Mo formed inner-sphere complexes on ferrihydrite by the indirect methods such as titration or surface complex modeling. In this study, the formation of outer-sphere complex of Mo on ferrihydrite was also revealed by Mo K-edge EXAFS for the first time.

Based on the above discussion, the structural information obtained in this study about Mo adsorption onto ferromanganese oxides is as follows: Mo forms a tetrahedrally coordinated outer-sphere complex on ferrihydrite, while it forms an octahedrally coordinated inner-sphere complex on δ-MnO_2. The host phase of Mo in natural hydrogenetic ferromanganese oxides is δ-MnO_2. In any case, Mo is present as Mo(VI) on oxide surfaces.

In previous investigations of Mo isotopic fractionation in adsorption experiments, Mo showed little or no fractionation during adsorption to ferrihydrite (Malinovsky *et al.*, 2007), whereas preferential adsorption of the lighter isotope to δ-MnO_2 with heavier isotope remaining in solution was found, which is similar to the offset between natural ferromanganese oxides and seawater (Barling and Anbar, 2004; Wasylenki *et al.*, 2008). On the other hand, quantum mechanical insights demonstrate that the heavier isotope preferentially partitions into stronger bonding environments (e.g., higher oxidation state, highly covalent bonds, low-spin configuration for transition elements, or lower-coordination number) in the equilibrium isotopic fractionation (Bigeleisen and Mayor, 1947; Schauble, 2004). In the case of Mo adsorption, these experimental and theoretical findings can be clearly linked by the structural information obtained in this study: an outer-sphere complex adsorbed on ferrihydrite has the same symmetry with MoO_4^{2-} and similar Mo–O bonding strength, leading to little or no isotopic fractionation in the Mo/iron hydroxide system; Mo species adsorbed on the surface of δ-MnO_2 has different distorted symmetry with a larger oxygen coordination number of 6 and weaker bonding environment than the 4 coordinated MoO_4^{2-}, leading to preferential adsorption of lighter Mo isotopes in the Mo/manganese oxide system. Additionally, the fact that the dominant host phase of Mo in natural ferromanganese oxides is δ-MnO_2 clearly indicates that the isotopic offset between ferromanganese oxides and seawater is mainly caused by the adsorption on δ-MnO_2. The structural difference between the adsorbed species on δ-MnO_2 and the aqueous one can be explained by two possible processes (Wasylenki *et al.*, 2008): (i) structural change from aqueous species of MoO_4^{2-} to the adsorbed species during the adsorption reaction or (ii) selective adsorption of minor species in equilibrium with MoO_4^{2-} in solution. Although it is difficult to distinguish these two possibilities, it should also be noted that the different coordination environment of adsorbed species from dissolved MoO_4^{2-} must be of critical importance to induce this large isotopic fractionation, where the association with δ-MnO_2 surface plays a key role.

These fractionation mechanisms are important in considering the Mo isotopic ratios in ancient sediments as

paleoredox signatures of marine environments because manganese oxide occurs under more oxic condition than iron hydroxide (Roy, 2006). It can be presumed that the Mo isotopic composition in seawater does not change in the presence of iron hydroxides but without manganese oxides. However, it can drastically change when marine environments have become oxic enough for the occurrence of manganese oxide in the earth's history. Consequently, Mo isotope ratios in the ancient sediments can be sensitive indicators of the redox boundary of Mn^{2+}/MnO_2, which is more oxic than the redox boundary related to the oxidation of Fe(II). In the future, more detailed discussions of the paleoredox conditions specified by the Mo isotope can be expected based on this research.

Our results demonstrate the critical importance of the structural information of the adsorbed species in understanding the mechanisms of both adsorption and isotopic fractionation of Mo. This study will lead to further understandings of these mechanisms, which will contribute to the robust application of the Mo isotope system in geochemistry.

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