

## Comparison of Adsorption Behavior of Molybdenum and Tungsten to Pyrite Under Reductive Condition

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Molybdenum (Mo) and tungsten (W) belong to the same group in the periodic table. They exist as molybdate ( $\text{MoO}_4^{2-}$ ) and tungstate ( $\text{WO}_4^{2-}$ ) in modern sea water respectively, and have very similar chemical properties each other. It is considered that the environmental behavior of both elements depend on redox condition. For example, the crustal abundance of W is almost same as that of Mo, while the concentration of W in modern seawater is 1800 times smaller than that of Mo (molar ratio) (Sohrin et al., 1987). It is considered that adsorption to ferromanganese oxides is one of the most important removal processes in sea water (Kashiwabara et al., 2011; 2013). On the other hand, it is possible that sulfide minerals such as pyrite controlled the concentration of trace elements including Mo and W in the palaeocean under reductive condition. Moreover, in some thermophilic bacteria (*hyperthermophilic archaea*) which inhabit in hydrothermal environment, W enzymes are substituting the role of nitrogen fixation performed by Mo enzymes in the present living things. Thus it is possible that solubilities of elements and essentiality for living bodies are related to each other. However, the solubilities of Mo and W in palaeocean are unclear because few studies have been conducted about adsorption behavior of Mo and W to sulfide minerals under reductive condition. In this study, adsorption experiment of Mo and W to pyrite was conducted using anaerobic chamber which can control the concentration of oxygen to clarify the adsorption behavior of these elements under reductive condition. To estimate the distribution coefficient (Kd), adsorbed amount of Mo and W were measured by ICP-MS, and X ray absorption fine structure (XAFS) measurements were conducted to study adsorption mechanisms of these elements to pyrite.

Concentration of sulfide ion ( $\text{S}^{2-}$ ), pH values, and ionic strength were controlled in the adsorption experiment. Under the acidic condition (pH= 4.0), Mo was adsorbed to pyrite better than W, and the adsorbed amount of both elements were decreased with increase in pH. It is suggested that both Mo and W existed as sulfide species both liquid and solid phases from the results of W L3 edge XANES and Mo K edge XANES. On the other hand, in the absence of  $\text{S}^{2-}$ , both Mo and W existed as oxygen-coordinated species in liquid phase, while only Mo adsorbed on pyrite as sulfur-coordinated species. These results suggest that Mo is adsorbed on pyrite strongly by forming inner sphere complex as sulfide, while W is adsorbed weakly via outer-sphere complexation.

Our experimental study clarified that Mo is adsorbed to pyrite to a larger degree than W, which is the opposite case to distribution behavior to ferromanganese oxide. In palaeocean environment, we suggest the solubility of W was higher than that of Mo, indicating that the solubilities of these elements were varied with changes of the redox condition of earth's environment, and it is possible that the difference of solubilities affected the essentiality of elements for living bodies.

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