

## Solid-water distributions of Mo and W in water-sediment system under various redox condition

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The concentration of W dissolved in the modern ocean is considerably lower than that of Mo, although Mo and W have similar chemical characteristics, since both elements belong to Group 6. It is considered that W is adsorbed significantly onto iron-manganese oxides, while in contrast Mo is difficult to adsorb on the iron-manganese oxide due to the difference in the surface complexes formed at the oxide surface (Kashiwabara et al., 2011). On the other hand, under the reductive ocean such as in the early earth, the concentration of these trace elements might be controlled by adsorption onto sulfides. In this system, it is assumed that Mo is adsorbed significantly onto the sulfide and is removed from seawater, while in contrast W is difficult to adsorb on the sulfide and dissolved in seawater. In other words, by the changes of redox condition due to the evolution of the atmosphere from low oxygen to high oxygen concentrations, the water solubilities of Mo and W in the primordial ocean are expected to be contrastive to the modern ocean. However, water solubilities of Mo and W under reductive ocean are not well known in particular from chemical process within the phenomena. Thus, purpose of this study is to clarify the solid-water distributions of Mo and W under reductive condition by adsorption experiments and analysis of marine sediments with their interstitial waters.

Based on the adsorption experiments, adsorption of Mo and W onto pyrite was larger at lower pH, possibly due to the larger positive charges induced at lower pH. However, it was found that adsorption distribution coefficient of Mo was about 8 times larger than that of W. XANES spectra showed that adsorption forms, or chemical species, of the both elements were also sulfide. However, the formation of Mo sulfide was not affected by pH, whereas formation of W sulfide did not proceed under high pH condition where W sulfide was not observed. Thus, the water solubility of W is most likely greater than that of Mo in the sediment under reductive condition.

The preference of formation of sulfur-bound species for Mo than W and larger affinity of Mo to the sulfide than W were the opposite result to what we found for their solid-water distributions under oxic condition. In the latter system, W forms more stable surface complex to iron-manganese oxides, which results in the larger solubility of Mo in water compared with W.

To confirm the suggestions from laboratory studies, abundances and speciation analyses were conducted for the hydrothermal water-sediment system in the mid-Okinawa Trough, especially for Mo. For the sediment samples, variation of chemical species of Fe and S estimated by their K-edge XANES indicates that redox condition became reductive at greater depth in the sediment. As a result of the distribution between sediment and interstitial water, a larger  $K_d$  values were obtained at deeper layer for Mo. In addition, XANES spectra indicated that dominant species of Mo was oxygen-bound species in oxidative shallow layer, while tetravalent sulfide was dominant in reductive deep layer.

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