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# Solid-water distribution of molybdenum and tungsten under reducing ocean

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The concentrations of trace elements in the ocean are controlled by their adsorption onto ferromanganese oxide. Molybdenum (Mo) and Tungsten (W) have similar chemical characteristics since they are congener of belonging to Group 6 family, so they have similar chemical feature. However, the concentration of the dissolved W in the ocean is considerably smaller lower than that of Mo, since the concentration of trace elements in the ocean is dominated by adsorption to ferromanganese oxides. Tungsten is easier adsorbed significantly onto the ferromanganese oxides is and is removed from seawater, while Mo is difficult to be adsorbed on the ferromanganese oxides and is readily dissolved in seawater. On the other hand, under the reductive ocean like early earth, the concentration of these trace elements in the ocean might be dominated by adsorption on sulfides. In other words, by changes in redox status condition due to the Earth's evolution, the water solubility of Mo and W are expected to be reverse to the present ocean. However, the solubility of Mo and W under reductive ocean is largely unknown. Therefore, in this study, adsorption experiments were conducted under various systems conditions to simulate reductive ocean in order to investigate the solid phase-liquid phase distribution behaviors of Mo and W under these systems. Adsorption structure and distribution coefficients of Mo and W were determined by using X-ray adsorption fine structure (XAFS) and inductively coupled plasma mass spectrometry (ICP-MS), respectively. The measurement results showed that adsorption distribution coefficient of Mo is about 8 times larger than that of W, and the two elements can be readily adsorbed onto pyrite under low-pH condition. Although their adsorbed chemical species are also sulfide, while the formation of Mo sulfide is did not affected by the pH, while formation of W sulfide did not proceed under high pH condition, where W sulfide was not generated. Thus, the water solubility of W is more likely greater than that of Mo under reductive condition where the solubility is dominated sulfide.