Comparison of distribution behavior of molybdenum and tungsten to pyrite under reductive condition

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Introduction

Molybdenum (Mo) and tungsten (W) are present as oxyanions (MoO_4^{2-} and WO_4^{2-}) in modern sea water. Although they have similar chemical properties, dissolved concentration of Mo is about 1800 times higher than W because of its lower affinity to iron and manganese oxide minerals [1,2]. On the other hand, the solubilities of Mo and W in palaeocean are unclear because few studies have been conducted about adsorption behavior of these elements to sulfide minerals under reductive condition. On the other hand, 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 [3]. Thus it is possible that solubilities of elements and essentiality for living bodies are related to each other. In this study, adsorption experiment of Mo and W to pyrite under reductive condition was conducted to clarify the mechanism of the difference between the adsorption behavior of Mo and W.

Results and discussion

Concentration of sulfide ion (S^{2-}), pH, and ionic strength were controlled in the adsorption experiment. Molybdenum was adsorbed to pyrite to a larger degree than W under all the experimental conditions examined. It is suggested that both Mo and W are present as sulfide species both in liquid and solid phases based on the results of XANES analysis. On the other hand, in the absence of S^{2-}, these ions existed as oxygen-coordinated species in liquid phase, while only Mo adsorbed on pyrite as sulfur-coordinated species. This 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, we suggest that 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 have affected the essentiality of elements for living bodies.

[1] Sohrin *et al*. (1987) *Mar. Chem*. **22**, 95-103. [2] Kashiwabara *et al*. (2013) *Geochim. Cosmochim. Acta* **75**, 5762–5784. [3] Kletzin & Adams (1996) *FEMS Microbiol. Rev*. **18**, 5–63.