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モリブデンおよびタングステンの水溶解性に及ぼす酸化還元環境の影響 Influence of redox condition on the solubilities of Mo and W

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It is well known that concentrations of trace elements in sea water are primarily correlated with their concentrations in serum levels in animals. This fact suggests that the availability of each trace element from the environment is an important factor whether the element is essential or not for biota. Thus, the chemistry deciding the concentrations of trace elements in sea water can be basic information on the understanding of the history of essential elements in biota. From this point of view, a twin element, Mo and W, is of great interest, since (i) Mo is an essential element but W is toxic to almost all biota at present, but (ii) some hyperthermophilic archaea appear to be W dependent. These facts suggest that W could be more abundant in primordial ocean or in hydrothermal water. To approach this matter, we think that it is primarily important to compare the chemistries controlling the solubilities of Mo and W in the present seawater and primordial marine environment where primitive life evolved.

Solubilities of trace elements in sea water are often controlled by adsorption reactions on solid phases in contact to the aqueous phase. Based on our laboratory experiments and analyses of natural samples in terms of their concentrations and speciation by X-ray absorption spectroscopy (XAS), we found that the solubilities of W and Mo in oxic seawater at present are controlled by their surface complexes on Fe hydroxides, outer sphere complex or inner sphere complex. The former is more soluble than the latter, since the latter has direct chemical bonding to the oxide surface. The formation of inner-sphere complex, in turn, is related to the acidity of the oxyanions such as molybdate and tungstate ions. Thus, it was revealed that the concentrations of oxyanions including Mo, W, As, and Se in sea water are primarily controlled by the acidity of the oxyanions.

On the other hand, solubilities of Mo and W in possible primordial marine environment that can be rich in sulfide were discussed based on the adsorption reactions of Mo and W on sulfide minerals (pyrite and pyrrhotite) and analyses of sediment core samples collected near the hydrothermal vent systems in the Izena Cauldron, Okinawa Trough. The core sample was particularly selected since the sulfide minerals were formed at 20 cm depth, but not at the surface within the core. The analyses of the samples at various depths from the core enable us to compare the Mo and W solubilities and reactions controlling the concentrations. As a result, formation of sulfidic species of Mo was confirmed at the 20 cm depth, but not at the surface for Mo. Although W species cannot be determined by XAS, formation of sulfidic species of W was not found in the sediment samples which were incubated under reducing condition in laboratory, where a small amount of Mo was in the sulfide form. This result suggests that the solubilities of Mo and W in "sulfide world", or the environment where primitive life evolved, can be controlled by their affinities to sulfur.

キーワード: モリブデン, タングステン, 海水, 溶解性, スペシエーション