Isotopic composition and concentration of molybdenum and tungsten in geological materials and the Japan Sea sediments: new proxies for paleoceanography

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Molybdenum (Mo) and tungsten (W) are hexavalent forming oxoacid anions (MoO_4^{2-}, WO_4^{2-}) in the oxic ocean. Although Mo has a high concentration of ~100 nmol/kg in the modern ocean, it is easily precipitated as thiomolybdate in the euxinic environment. On the other hand, W has a concentration of ~50 pmol/kg in the modern ocean and is hardly precipitated in the euxinic environment[1], being highly enriched in hydrothermal fluids[2]. Therefore, we expect that the Mo/W concentration ratio and the stable isotope ratio of Mo and W in marine sediments will be potential proxies for paleoceanography.

We have developed a new method for stable isotope ratio analysis of Mo and W in geological materials, analyzing reference materials (igneous rocks, manganese nodules, and marine sediments) and a sediment core collected off Hokkaido in the Japan Sea (43°22'36.0"N, 140°04'10.0"E, 900 m depth). Three reference samples of igneous rocks had approximately constant isotope ratios of Mo and W (0.2-0.5‰ for $\delta^{98/95}$Mo and 0-0.2‰ for $\delta^{184/182}$W), while there was a significant variation in the concentration of W (1-8 ppm). Five reference samples of marine sediments had larger variations in the concentration and isotopic composition (0.1-22 ppm for Mo, 0.06-6 ppm for W, –0.6-1.0‰ for $\delta^{98/95}$Mo, and 0-0.3‰ for $\delta^{184/182}$W). In the sediment core, Mo concentration and Mo/W ratio showed four high peaks, but $\delta^{98/95}$Mo did not exceed 0.8‰ and correlate with the Mo/W ratio. $\delta^{184/182}$W was ~0‰ throughout the core. We will discuss the mechanisms controlling Mo and W in the sediments and the possibility of Mo and W as paleoenvironment proxies.

[1] Mohajerin *et al*. (2016) *Geochimica et Cosmochimica Acta*, ***177*,** 105-119.

[2] Kishida *et al*. (2004) *Earth and Planetary Science Letters*, ***222*** (3-4), 819-827.

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