

Estimation of the paleoenvironment based on the concentration and isotope ratio of molybdenum and tungsten in the Japan Sea sediment

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Molybdenum (Mo) and tungsten (W) are group 6 elements and exist as hexavalent oxoacid anion (MoO_4^{2-} , WO_4^{2-}) in the oxidative ocean. While Mo has concentration of about 107 mmol/kg in the modern ocean, it is easily precipitated as thiomolybdate in the euxinic environment. On the other hand, W has concentration of about 49 pmol/kg in the modern ocean. Although W is not precipitated in the euxinic environment^[1], it is 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 would be powerful proxies in paleoceanography. Recently, we have developed a new method of stable isotope ratio analysis for Mo and W in marine sediments on the basis of microwave digestion, chelating column extraction, anion exchange, and MC-ICP-MS. Using this method, we have analyzed a sediment core collected off Hokkaido in the Japan Sea (43°22'36.0"N, 140°04'10.0"E, 900 m depth) and estimated conditions at the middle depth in the Japan Sea in the past 46,530 years.

The high peaks of Mo concentration and Mo/W ratio suggested euxinic precipitation of Mo 10,000, 15,000, 30,000, and 46,000 years ago. However, $\delta^{98/95}\text{Mo}$ neither exceed 0.9‰ nor correlate with Mo/W ratio. Tungsten concentration was relatively uniform similarly with Al, and $\delta^{186/184}\text{W}$ was about 0‰ throughout the core, suggesting that the supply from land was fairly constant.

[1] Mohajerin, T. J.; Helz, G. R.; Johannesson, K. H., *Geochimica et Cosmochimica Acta* **2016**, *177*, 105-119.

[2] Kishida, K.; Sohrin, Y.; Okamura, K.; Ishibashi, J. I., *Earth and Planetary Science Letters* **2004**, *222* (3-4), 819-827.