Determination of the stable isotope ratio of molybdenum and tungsten in marine sediments

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Molybdenum and tungsten are group 6 elements and exist as hexavalent oxoacid anion (MoO_4^{2-}, WO_4^{2-}) in the oxidative ocean. Mo is transformed to thiomolybdate and reduced to tetravalent, precipitating from the reductive ocean to sediments[1]. The concentration and the stable isotope ratio of Mo in marine sediments are studied as proxies for oxidation-reduction environments. In the modern ocean, the concentration of W is about 50 pM. Although W is conservatively distributed in the modern ocean similarly with Mo, W is not reduced and soluble under the reductive condition. In addition, W is highly enriched in the hydrothermal fluids[2]. Therefore, it is expected that the Mo/W concentration ratio in marine sediments would be a proxy for redox condition and that the stable isotope ratio of W would be a new proxy for hydrothermal activities. The objective of this study is to extract Mo and W from sediment samples and to precisely measure the isotope ratio of Mo and W in marine sediments using MC-ICP-MS.

A sediment sample was decomposed with a microwave digestion system (Speedwave MWS-3$^+$, Berghof). The decomposed sample was evaporated, dissolved in 0.2% HNO_3, and passed through a NOBIAS Chelate-PA1 column (Hitachi High Technologies) to extract Mo and W from co-existing elements in sediments. The eluate from the NOBIAS Chelate-PA1 column was evaporated, dissolved in 0.5 M HF- 0.4 M HCl, and passed through the column filled with anion exchange resin (AG1-X8, Bio-Rad) to separate Mo and W. Then, the isotope ratio of Mo and W was measured by MC-ICP-MS. The mass discrimination effect was corrected with an external correction technique by doping Ru for Mo and Re for W.

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