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研究課題番号	R7-R3
研究課題名	Palaeoceanographic redox reconstruction of the Black Sea (BS)
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1. Research purpose and objective: The robustness of Mo as a palaeoredox indicator depends on the sequestration mechanism of Mo but the uncertainty regarding Mo isotopes fractionation is still complex in the euxinic sediments than previously studied. The observed $\delta^{98/95}$Mo (1.64±0.04%) value from reduced continental margin is different $\delta^{98/95}$Mo (2.3%) from restricted basin (Nagler et al., 2011). However, research on the mechanism of W isotopes fractionation in euxinic condition is insubstantial. Therefore, simultaneous study of Mo and W in the euxinic sediment from the Black Sea can infer early digenesis effect on Mo and W isotopes fractionation mechanism led to help the reconstruction of the earth geological oxygenation history. This study analyzed sediment samples from northwestern and southeastern Black Sea to decipher the role of early digenesis effect on $\delta^{98/95}$Mo and $\delta^{186/184}$ W isotopes fractionation in the euxinic condition.

2. Samples and Method: The sediment samples collected from northwestern Black Sea (44.588°N, 31.922°E) and southeastern Black Sea (42.365°N, 35.492°E) were subjected to the decomposition (Tsujisaka et al., 2019), TSK-8HQ solid phase extraction and AG1-X8 anion exchange extraction (Matsuoka et al., 2023 with modification) procedure.

2.1. Organic and inorganic material were decomposed through HNO_3 (7 mL) and H_2O_2 (0.7 mL) while HF (3 mL) was used to decompose the silicate mineral. The residue was redissolved in 0.06 M HCl for the chromatographic separation of Mo and W.

2.2. TSK-8HQ column was cleaned using 2 M NH_3 and 3 M HNO_3 followed by Ultrapure water (UW) after then conditioned using 0.06 M HCl (pH, 1.2-1.4). The matrix elements were removed using 0.06 M HNO_3. The adsorbed Mo and W onto the resin were eluted using 5 M HF in the opposite direction than other steps. The eluate

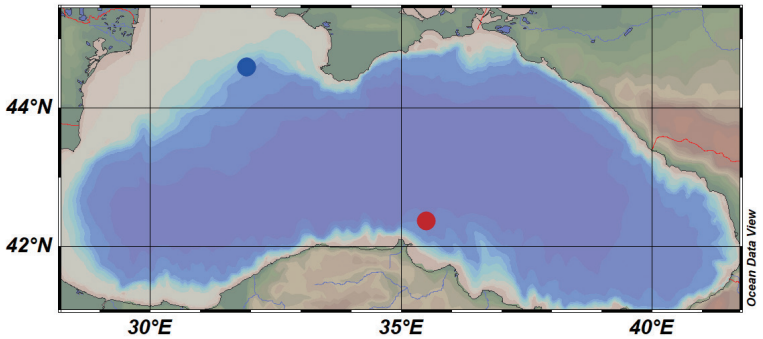

Figure 1. Blue and red colors on the map represent northwestern and southeastern Black Sea.

having Mo and W were evaporated at 130°C and residue was redissolved in 0.5 M HF–0.4 M HCl solution.

2.3. AG1-X8 column was cleaned using 6 M HNO_3 (2 mL) and succeed by UW (3 mL) while condition through 0.5 M HF–0.4 M HCl (2 mL). The sample was loaded onto column and Fe was removed using same as conditioning solution while Ti, Zr and Hf were removed through 0.05 M HF–9 M HCl (0.3 mL). The W and Mo were eluted using 5 M HCl and 1 M HNO_3 respectively. The purified solutions having Mo and W in an individual PFA vials were evaporated at 130°C. The residue of Mo and W were redissolved in 1% HNO_3 and 0.05% TMAH respectively.

2.4. Stable Mo and W isotope ratios were measured using Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, USA) at the Research Institute for Humans and Nature (RIHN), Japan. The fractionation of the stable isotopes during analysis were monitored using Ru and Re for Mo and W respectively. The delta (‰) value was calculated relative to NIST SRM 3134 and 3163 for Mo and W respectively (Tsujisaka et al., 2019).

3. Achievements:

3.1. Stable Mo and W isotopes data have been generated.

3.2. Sediments sample (n=12) from northwestern and southeastern Black Sea have been sent to Laboratory of Radiocarbon Dating, Tokyo University for Radiocarbon (^{14}C) dating analysis.

3.3. Abstract submitted to Goldschmidt 2026 international conference.

3.4. Generated data from this study will be published in peer reviewed journal.

3.5. Conference:

Mahboob Alam, Matsuoka Kohei, Yoshiki Sohrin, 2026. A revised analytical method for stable Mo and W isotopes in sediments: implications for paleoenvironmental reconstruction. Goldschmidt 2026, July 12–17, Montréal, Quebec, Canada.

3.6. Publication:

Mahboob Alam, Matsuoka Kohei, Yoshiki Sohrin, Shotaro Takano, 2026. Optimization of analytical method for stable Mo and W isotopes in sediments: insights from the Black Sea. Chemical Geology (under preparation).

4. Acknowledgement:

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5. References:

1. Matsuoka, K., Tatsuyama, T., Takano, S., & Sohrin, Y. (2023). Distribution of stable isotopes of Mo and W from a river to the ocean: signatures of anthropogenic pollution. Frontiers in Marine Science, 10, 1182668.
2. Nägler, T. F., Neubert, N., Böttcher, M. E., Dellwig, O., & Schnetger, B. J. C. G. (2011). Molybdenum isotope fractionation in pelagic euxinia: Evidence from the modern Black and Baltic Seas. Chemical Geology, 289(1–2), 1–11.
3. Tsujisaka, M., Takano, S., Murayama, M., & Sohrin, Y. (2019). Precise analysis of the concentrations and isotopic compositions of molybdenum and tungsten in geochemical reference materials. Analytica Chimica Acta, 1091, 146–159.