# **Division of Environmental Chemistry** – Hydrospheric Environment Analytical Chemistry –

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## **Scope of Research**

(i) Biogeochemistry of trace elements in the hydrosphere: Novel analytical methods are developed for trace metals and their isotopes. Distribution of trace elements in the hydrosphere and their effects on the ecosystem are investigated. The study also covers hydrothermal activity, deep biosphere, and paleocean. (ii) Ion recognition: Novel ligands and ion recognition system are designed, synthesized, and characterized.



### KEYWORDS

Marine Chemistry Stable Isotopes Analytical Chemistry Trace Elements Metal Ion Recognition

#### **Recent Selected Publications**

Ueki, R.; Zheng, L.; Takano, S.; Sohrin, Y., Distributions of Zirconium, Niobium, Hafnium, and Tantalum in the Subarctic North Pacific Ocean Revisited with a Refined Analytical Method, *Geochem J.*, **57**, 143-154 (2023).

Matsuoka, K.; Tatsuyama, T.; Takano, S.; Sohrin, Y., Distribution of Stable Isotopes of Mo and W from a River to the Ocean: Signatures of Anthropogenic Pollution, *Front. Mar. Sci.*, **10** (2023).

Sieber, M.; Lanning, N. T.; Bian, X.; Yang, S.-C.; Takano, S.; Sohrin, Y.; Weber, T. S.; Fitzsimmons, J. N.; John, S. G.; Conway, T. M., The Importance of Reversible Scavenging for the Marine Zn Cycle Evidenced by the Distribution of Zinc and Its Isotopes in the Pacific Ocean, *J. Geophys. Res.: Oceans*, **128** (2023).

Alam, M.; Muguli, T.; Gurumurthy, G. P.; Arif, M.; Sohrin, Y.; Singh, A. D.; Radhakrishna, T.; Pandey, D. K.; Verma, K., Hydroclimatic Conditions and Sediment Provenance in the Northeastern Arabian Sea since the Late Miocene: Insights from Geochemical and Environmental Magnetic Records at IODP Site U1457 of the Laxmi Basin, *Geol Mag.*, **160**, 813-829 (2023).

Iwase, M.; Isobe, K.; Zheng, L.; Takano, S.; Sohrin, Y., Solid-Phase Extraction of Palladium, Platinum, and Gold from Water Samples: Comparison between a Chelating Resin and a Chelating Fiber with Ethylenediamine Groups, *Anal. Sci*, **39**, 695-704 (2023).

### Distribution of Stable Isotopes of Mo and W from a River to the Ocean: Signatures of Anthropogenic Pollution

Molybdenum (Mo) and tungsten (W) are redox-sensitive elements, and their stable isotope ratios have attracted attention as paleoceanographic proxies. However, our knowledge of the distribution of stable Mo and W isotopes in the modern hydrosphere remains limited. In this study, we provided the concentrations and isotope ratios of dissolved Mo and W in the oceans (the North Pacific and Indian Oceans), marginal seas (East China and the Sea of Japan), and a river-estuary system in Japan (from the Uji-Yodo rivers to Osaka Bay). In the North Pacific and Indian Oceans, the W concentration was  $48.2 \pm 6.2$  pmol/ kg (ave  $\pm 2$ sd, n = 109),  $\delta^{186/184}$ W was  $0.52 \pm 0.06$  ‰, the Mo concentration was  $105.1 \pm 8.0$  nmol/kg, and  $\delta^{98/95}$ Mo was  $2.40 \pm 0.06$  %. The results indicate that W has the constant concentration and isotopic composition in the modern ocean as well as Mo. In the East China Sea and the Sea of Japan, the W concentration and  $\delta^{186/184}$ W in the upper water (< 1000 m depth) were different from those in the ocean (W = 56  $\pm$  18 pmol/kg,  $\delta^{186/184}W$  = 0.45  $\pm$  0.06  $\infty$ , n = 24). However, the concentrations in deeper water were congruent with those in the oceans (W =  $49.9 \pm 7.6$ pmol/kg,  $\delta^{186/184}$ W = 0.50 ± 0.02 ‰, *n* = 7). The Mo concentration was 105.4  $\pm$  3.1 nmol/kg and  $\delta^{98/95}Mo$  was 2.36  $\pm 0.03 \% (n = 31)$  throughout the water column, congruent with those in the ocean. In the Uji River-Yodo River-Osaka Bay system, the W concentration reached 1074 pmol/kg and  $\delta^{186/184}$ W reached 0.20 ‰. We propose that the enrichment of W with a low  $\delta^{186/184}$ W in the river-estuary system and marginal seas is caused by anthropogenic pollution. Anthropogenic Mo pollution was not detected in marginal seas. However, the Mo concentration and  $\delta^{98/95}$ Mo showed high anomalies above the mixing line of river water and seawater in the lower Yodo River and Osaka Bay, implying possible anthropogenic pollution of Mo in the metropolitan area.



Figure 1. Sampling stations of this study: A, global map; B, map of the Uji River-Yodo River-Osaka Bay system.

### Distributions of Zirconium, Niobium, Hafnium, and Tantalum in the Subarctic North Pacific Ocean Revisited with a Refined Analytical Method

Although zirconium (Zr), niobium (Nb), hafnium (Hf), and tantalum (Ta) in seawater are potential tracers for water masses, their determination is still a challenge in analytical chemistry. We have refined our preconcentration method using 8-hydroxyquinoline chelating resin (TSK-8HQ) and reinvestigated concentration profiles of the four elements in dissolved (d) and total dissolvable (td) fractions at five different stations from 47 °N, 160 °E to 51 °N, 160 °W in the subarctic North Pacific Ocean. The new method has saved analytical time and reduced systematic errors compared with previous methods. The concentration ranges were 30 - 276 pmol/kg for dZr, 1.0 - 2.6 pmol/kg for dNb, 0.09 - 0.78 pmol/kg for dHf, and 0.006 - 0.026 pmol/kg for dTa in the subarctic North Pacific Ocean. The concentrations of Zr and Hf increased from surface water to deep water, whereas those of Nb and Ta were nearly constant over the water depth. The profiles of dZr, dNb, and dHf were consistent with those in previous studies. However, we found that dTa is uniformly distributed at  $0.015 \pm 0.005$ pmol/kg (mean  $\pm$  sd, n = 75), which is approximately onefifth of that in a previous study. It is likely that the previous dTa data were affected by a systematic error. Negligible differences between td and d fractions suggest that the particulate concentrations of these elements are lower than those reported in a previous study.

Comparison of dissolved Ta at crossover stations



Figure 2. Graphical abstract of this study.