

# 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

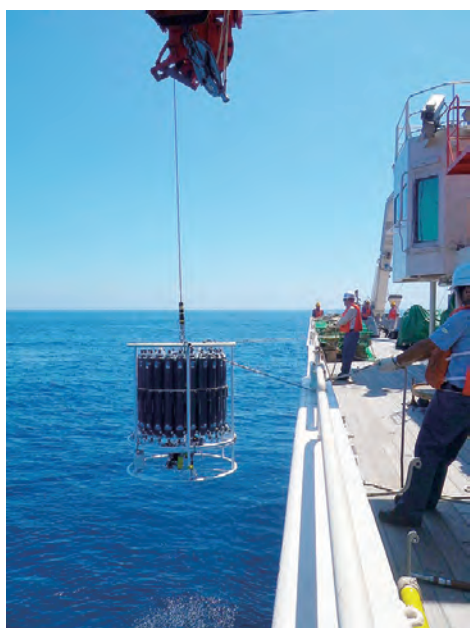
Marine Chemistry    Analytical Chemistry    Trace Elements  
Stable Isotopes    Metal Ion Recognition

### Selected Publications

- Zheng, L.; Minami, T.; Konagaya, W.; Chan, C.-Y.; Tsujisaka, M.; Takano, S.; Norisuye, K.; Sohrin, Y., Distinct Basin-scale-distributions of Aluminum, Manganese, Cobalt, and Lead in the North Pacific Ocean, *Geochim. Cosmochim. Acta*, **254**, 102-121 (2019).
- Zheng, L.; Sohrin, Y., Major Lithogenic Contributions to the Distribution and Budget of Iron in the North Pacific Ocean, *Sci. Rep.*, **9**, [11652-1]-[11652-9] (2019).
- Sieber, M.; Conway, T. M.; de Souza, G. F.; Obata, H.; Takano, S.; Sohrin, Y.; Vance, D., Physical and Biogeochemical Controls on the Distribution of Dissolved Cadmium and Its Isotopes in the Southwest Pacific Ocean, *Chem. Geol.*, **511**, 494-509 (2019).
- Tanaka, Y.; Tsujisaka, M.; Zheng, L.; Takano, S.; Sohrin, Y., Application of NOBIAS Chelate-PA 1 Resin to the Determination of Zirconium, Niobium, Hafnium, and Tantalum in Seawater, *Anal. Sci.*, **35**, 1015-1020 (2019).
- Yang, S.-C.; Welter, L.; Kolatkar, A.; Nieva, J.; Waitman, K. R.; Huang, K.-F.; Liao, W.-H.; Takano, S.; Berelson, W. M.; West, A. J.; Kuhn, P.; John, S. G., A New Anion Exchange Purification Method for Cu Stable Isotopes in Blood Samples, *Anal. Bioanal. Chem.*, **411**, 765-776 (2019).

## Major Lithogenic Contributions to the Distribution and Budget of Iron in the North Pacific Ocean

Recent studies have elucidated that iron (Fe) is a critical trace metal that influences the productivity of marine ecosystems and the biogeochemical cycles of other elements in the modern ocean. However, our understanding of the biogeochemistry of Fe remains incomplete. Herein, we report basin-scale and full-depth sectional distributions of total dissolvable iron (tdFe), dissolved iron (dFe), and labile particulate iron (lpFe = tdFe – dFe) in the North Pacific Ocean, as observed during three cruises of the GEOTRACES Japan program. We found that lpFe dominates tdFe and is significantly correlated with labile particulate aluminum (lpAl):  $lpFe \text{ [nmol kg}^{-1}] = (0.544 \pm 0.005) lpAl \text{ [nmol kg}^{-1}] + 0.11 \pm 0.04$ ,  $r^2 = 0.968$ ,  $n = 432$ . The results indicate a major lithogenic contribution to the distribution of particulate Fe. For dFe, the unique distribution is attributed to the combined effects of biogeochemical cycling, manganese reduction, and lithogenic contribution. Based on concurrent observations of Fe, Al, and manganese (Mn), we infer that the width of the boundary scavenging zone is approximately 500 km off the Aleutian shelf. We estimate the inventory of tdFe in the North Pacific as  $1.1 \times 10^{12}$  mol, which is approximately four times that of dFe. Our results emphasize the potential importance of lpFe in the ocean's iron cycle.



**Figure 1.** Clean water sampling during the KH-12-4 cruise.

## Precise Analysis of the Concentrations and Isotopic Compositions of Molybdenum and Tungsten in Geochemical Reference Materials

Molybdenum (Mo) is a redox-sensitive element and its concentrations and stable isotope compositions are widely used as a redox proxy in paleoceanography. Tungsten (W) is an emerging new isotope proxy, which has potential as a tracer for hydrothermal and early diagenetic processes. We present a new method for the precise and accurate analysis of Mo and W concentrations and isotope compositions from one single sample aliquot, thus saving mass of a sample and making the results directly comparable without concerns related to analytical or natural sample heterogeneity. After acid digestion, Mo and W are separated from the sample matrix using chelating resin NOBIAS Chelate-PA1 and anion exchange resin AG1 X8. Matrix removal is highly efficient: the remaining percentage is  $10^{-2}$  to  $10^{-5}\%$  with respect to the initial weight. Subsequently, samples are measured for Mo and W concentrations and isotope compositions using multi-collector inductivity coupled plasma mass spectrometry (MC-ICP-MS). For mass bias correction and determination of concentrations, we use standard-sample bracketing and in addition an external correction method employing ruthenium (Ru) for Mo and rhenium (Re) for W. This double correction approach results in an external reproducibility of or below 0.10‰ (2SD) for  $\delta^{98}\text{Mo}$  and 0.05‰ for  $\delta^{186}\text{W}$ . We present data for Mo and W in 12 geological reference materials including igneous rocks, sedimentary rocks, marine sediments, and manganese nodules. For Mo our method reproduces published values for the geological standard materials within analytical error of published values. For W, although published data do not always agree for a given geological standard material, our data agree within error with more recent data. We interpret a cause of the deviations is due to unknown effects of a desolvating nebulizer for MC-ICP-MS.