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

#### http://inter3.kuicr.kyoto-u.ac.jp/scope\_E.html



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### **Scope of Research**

- (i) Biogeochemistry of trace elements in the hydrosphere: Novel analytical methods are developed for trace metals and isotopes. Distribution of trace elements in the hydrosphere and its effects on 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**

Analytical Chemistry Marine Chemistry Trace Elements Stable Isotopes Metal Ion Recognition



#### **Selected Publications**

Firdaus, M. L.; Minami, T.; Norisuye, K.; Sohrin, Y., Strong Elemental Fractionation of Zr-Hf and Nb-Ta across the Pacific Ocean, *Nature Geoscience*, **4**, 227-230 (2011).

Li, Y. -H.; Sohrin, Y.; Takamatsu, T., Lake Biwa and the Ocean: Geochemical Similarity and Difference, *Limnology*, **12**, 89-101 (2011). Sohrin, Y.; Bruland, K. W., Global Status of Trace Elements in the Ocean, *TrAC Trends in Analytical Chemistry*, **30**, 1291-1307 (2011). Cid, A. P.; Urushihara, S.; Minami, T.; Norisuye, K.; Sohrin, Y., Stoichiometry among Bioactive Trace Metals in Seawater on the Bering Sea Shelf, *Journal of Oceanography*, **67**, 747-764 (2011).

# Strong Elemental Fractionation of Zr–Hf and Nb–Ta across the Pacific Ocean

Understanding the circulation of water masses in the world's oceans is critical to our knowledge of the Earth's climate system. Trace elements and their isotopes have been explored as tracers for the movement of water masses. One type of candidate elements is the high-field-strength elements zirconium (Zr), hafnium (Hf), niobium (Nb) and tantalum (Ta). Here we measure the distributions of dissolved Zr, Hf, Nb and Ta along two meridional sections in the Pacific Ocean that extend from 65°S to 10°N and from 10°S to 50°N. We find that all four elements tend to be depleted in surface water. In the deep oceans, their concentrations rise along our transects from the Southern Ocean to the North Pacific Ocean, and show strong correlations with the concentration of silicate. These results indicate that terrigenous sources are important to the budget of Zr, Hf, Nb and Ta in seawater, compared with hydrothermal input. Unexpectedly, the weight ratios for Zr/Hf fall between 45 and 350 and those for Nb/Ta between 14 and 85 in Pacific seawater, higher than the ratios observed in fresh water, in the silicate Earth or in chondritic meteorites. We conclude that the fractionation of Zr/Hf and Nb/Ta ratios will be useful for tracing water masses in the ocean.



Figure 1. Meridional sectional distribution of DZr/DHf and water masses in the Pacific Ocean.

#### Stoichiometry among Bioactive Trace Metals in Seawater on the Bering Sea Shelf

The distribution of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater was investigated on the Bering Sea shelf (56-64°N, 165-169°W) in September 2000. The unfiltered and filtered seawater samples were used for determination of total dissolvable (TD) and dissolved (D) metals (M), respectively. The TDM concentrations were generally higher than in the Pacific Ocean. TDCd was highest in deep water of the outer shelf domain and dominated by dissolved species. The other TDM were highest at stations close to the Yukon River delta and had higher fractions of labile particulate (LP) species that were obtained as the difference between TDM and DM. DAl, DNi, and DCu were characterized by input from the Yukon River. DMn and DCo showed maximums on the bottom of the coastal domain, suggesting influence of sedimentary Mn reduction. The correlations of DZn, DCd, and macronutrients indicated their distributions were largely controlled through uptake by microorganisms and remineralization from settling particles. All these three processes (river input, sedimentary reduction, and biogeochemical cycle) had influence on the distribution of DFe. DPb was fairly uniformly distributed in the study area. The stoichiometry of DMs in the Bering Sea shelf showed enrichment of Co and Pb and depletion of Ni, Cu, Zn, and Cd compared to that in the North Pacific. The LPM/LPAl ratio revealed significant enrichment of the other eight metals against the crustal abundance, suggesting importance of formation of Fe-Mn oxides and adsorption of trace metals on the oxides.



Figure 2. Observation in the Bering Sea during the R/V Mirai MR00-K06 cruise in September 2000.