

Division of Environmental Chemistry - Hydrospheric Environment Analytical Chemistry -

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Prof LI, Yuan-Hui University of Hawaii, USA, 1–3 April 2006

Scope of Research

Research activities are concerned with geochemistry, oceanography, limnology and analytical chemistry, which are important basic sciences in order to realize the sustainable society. Major research subjects are as follows: (i) Biogeochemistry of trace elements in the hydrosphere. The study also covers hydrothermal activity and deep biosphere. Major parts of these studies are based on field works. (ii) Iron uptake mechanism of phytoplankton. (iii) Ion recognition. (iv) Simulation of chemical reactions.

Research Activities (Year 2006)

Presentations

Geochemistry of Bioactive Trace Metals during the Mesoscale Iron Enrichment in the Subarctic Western North Pacific Gyre (SEEDS I and II), Nakatsuka S, Kinugasa M, Sohrin Y, Nishioka J, Takeda S, Tsuda A, 2006 Ocean Sciences Meeting, 20 February 2006.

Spatial and Temporal Distribution of Fe, Ni, Cu and Pb along 140E in the Southern Ocean in 2001/2002 Austral Summer, Sohrin Y, Lai X, Norisuye K, Mikata M, Minami T, Bowie A R, 2006 Ocean Sciences Meeting, 20 February 2006.

Novel Determination of Pd, Pt and Au in the Western North Pacific Seawater, Sohrin Y, Sato T, Norisuye K, Hatta M, Zhang J, 2006 Western Pacific Geophysics Meeting, 27 July 2006.

Inter-Basin Fractionation on the Distributions of Bioactive Trace Metals and Metal/Nutrient Ratios in the Sulu Sea, South China Sea and Western North Pacific, Norisuye K, Ezoe M, Nakatsuka S, Sohrin Y, 2006 West-

ern Pacific Geophysics Meeting, 27 July 2006.

Determination and Distribution of Zr, Hf, Ta and W in the North Pacific Ocean, Firdaus M L, Norisuye K, Sato T, Urushihara S, Nakagawa Y, Sohrin Y, 16th Annual V.M. Goldschmidt Conference 2006, 30 August 2006.

Determination of Trace Metals in Seawater Using ICP-MS after Concentration with NOBIAS Chelating Absorbent Column, Minami T, Urushihara S, Sohrin Y, The 55th Annual Meeting of the Japan Society for Analytical Chemistry, 22 September 2006.

Molecularly Imprinted Sol-Gel Absorbent for the Separation of Divalent Metal Ions, Umetani S, Taguchi Y, Kurahashi K, The 55th Annual Meeting of the Japan Society for Analytical Chemistry, 22 September 2006.

Grants

Sohrin Y, Interaction between Metallome and Proteome in the Marine Ecosystem, Grant-in-Aid for Scientific Research (A) (2), 1 April 2004–31 March 2007.

Distribution of Zr, Hf, Nb, Ta, Mo and W in the North Pacific Ocean

Comprehensive information of trace elements in seawater is important for understanding the marine system. Zr, Hf, Nb, Ta, Mo and W are adjacent elements in the periodic table. In seawater, Zr, Hf, Nb and Ta are dominated by hydroxide species such as $\text{Zr}(\text{OH})_5^-$, $\text{Hf}(\text{OH})_5^-$, $\text{Nb}(\text{OH})_6^-$ and $\text{Ta}(\text{OH})_6^-$, while Mo and W are present as MoO_4^{2-} and WO_4^{2-} . The hydroxide dominated elements are more reactive than the oxyacid dominated elements and thought to have potential as oceanographic tracers of external sources, physical mixing, and scavenging removal processes.

We have developed a solid-phase extraction method using TSK-8HQ as chelating resin to concentrate these elements in seawater [1]. The greatest advantage of this resin is its endurance to 5 M HF, since this is an effective eluent for the six metals. The analytes were quantitatively concentrated from 250 mL seawater with a 50 fold concentration factor through the column extraction and evaporation. Seawater samples were collected from the western North Pacific during the MR05-01 cruise of R/V Mirai (Figure 1) using a CTD carousel, on which Niskin-X samplers were mounted. The interior of the samplers was coated with Teflon and cleaned with detergent and HCl. A portion of seawater for dissolve species (D) was filtered through a 0.2 μm Nuclepore filter and acidified to pH 2.2 with HCl and HF. A portion of seawater for acid-dissolvable species (AD) was acidified without filtration. The acid-dissolvable element includes dissolved species and a labile particulate fraction dissolved during storage. It would contain species, such as iron hydroxides, adsorbed on clay minerals and incorporated in organism.



Figure 1. MIRAI; the research vessel used for the collection of sample.

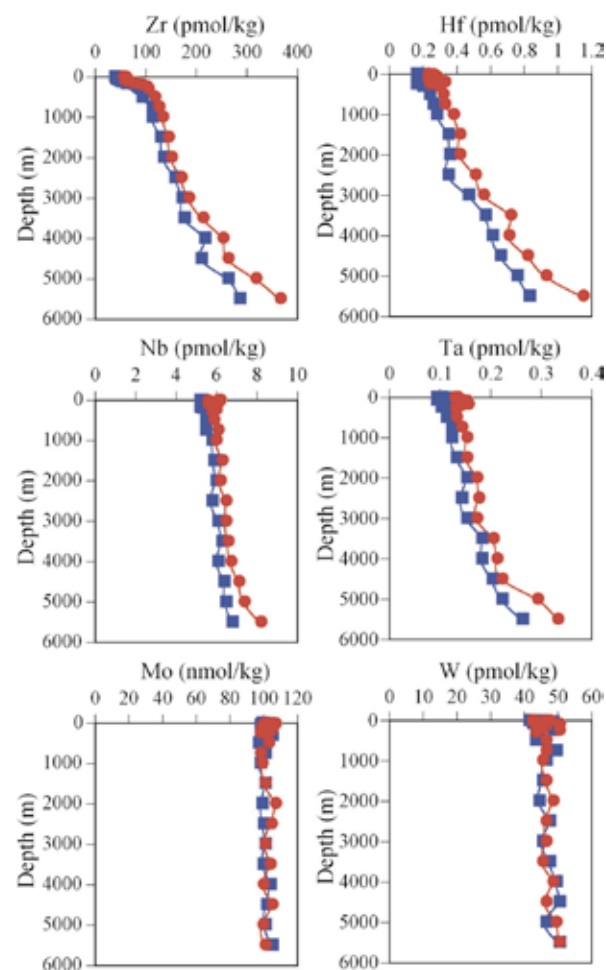


Figure 2. Vertical profiles of dissolved (■) and acid-dissolvable (●) elements at station K-4.

At station K-4 (35°N, 160°E), Zr and Hf show systematic enrichment with depth, Nb shows slight depletion in surface water, Ta shows enrichment in bottom water, whereas Mo and W show conservative vertical profiles (Figure 2). AD to D ratio for Zr, Hf, Nb and Ta are higher in the surface and bottom water compared to mid-depth, whereas concentrations for Mo and W show no significant difference between D and AD. We also determined the concentrations in coastal seawater, rain, river and hot spring water and observed that dissolved Zr/Hf, Nb/Ta and Mo/W ratios increase in the order of crust < river water < rain water < seawater. Thus, the mobility of Hf, Ta and W was lower than that of Zr, Nb and Mo.

[1] M. Lutfi Firdaus, K. Norisuye, T. Sato, S. Urushihara, Y. Nakagawa, S. Umetani and Y. Sohrin (2007) *Anal. Chim. Acta*, in press.

Norisuye K, Development of Analytical Method for Unstable Fe(II) in Seawater Based on *In situ* Preconcentration,

Grant-in-Aid for Young Scientists B, 1 April 2006–31 March 2007.