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– Hydrospheric Environment Analytical Chemistry –

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Dr BHUSHAN, Ravi   Physical Research Laboratory, India, 9 November

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 systems are designed, synthesized and characterized.

KEYWORDS

Analytical Chemistry
Marine Chemistry
Trace Elements
Stable Isotopes
Metal Ion Recognition

[left] The last work day of Assist Prof Firdaus on 29 September 2010.
[right] Prof Yuan-Hui Li (University of Hawaii) and Lake Biwa on 26 April 2008.

Selected Publications

Li YH, Sohrin Y, Takamatsu T: Lake Biwa and the Ocean: Geochemical Similarity and Difference, *Limnology*, DOI: 10.1007/s10201-010-0326-0 (2010).

Minami T, Higo E, Nakatsuka S, Cid AP, Vu TDH, Norisuye K, Sohrin Y: Development of the Multielemental Determination Method for Bioactive Trace Metals in Open Ocean Seawater and Its Application to International Intercalibration, *Bunseki Kagaku*, **59,** 1087-1096 (2010) (in Japanese).

Nakatsuka S, Okamura K, Takeda S, Nishioka J, Firdaus ML, Norisuye K, Sohrin Y: Behaviors of Dissolved and Particulate Co, Ni, Cu, Zn, Cd and Pb during a Mesoscale Fe-enrichment Experiment (SEEDS II) in the Western North Pacific, *Deep-Sea Research II*, **56,** 2822-2838 (2009).

Nakagawa Y, Firdaus ML, Norisuye K, Sohrin Y, Irisawa K, Hirata T: Precise Isotopic Analysis of Mo in Seawater Using Multiple Collector-Inductively Coupled Mass Spectrometry Coupled with a Chelating Resin Column Preconcentration Method, *Analytical Chemistry*, **80,** 9213-9219 (2008).

Sohrin Y, Urushihara S, Nakatsuka S, Kono T, Higo E, Minami T, Norisuye K, Umetani S: Multielemental Determination of GEOTRACES Key Trace Metals in Seawater by ICPMS after Preconcentration Using an Ethylenediaminetriacetic Acid Chelating Resin, *Analytical Chemistry*, **80,** 6267-6273 (2008).

Lake Biwa and the Ocean:
Geochemical Similarity and Difference

The average compositions of water, bottom sediments, Mn crusts and Mn concretions from Lake Biwa are re-examined, in conjunction with those of seawater, oceanic pelagic clay, and deep-sea Mn nodules. The purpose is to gain additional insights into the geochemical behaviors of elements in Lake Biwa and the ocean, which are quite different in ionic strength, pH, water residence times, sediment accumulation rates, carbon fluxes to sediments, and the redox potential in sediments. Excluding a few milli-meters of oxic surface sediment, there is no appreciable accumulation of Mn in the Lake Biwa bottom sediments, due to reducing condition there. Consequently, other B-type cations (such as Fe, Ga, Cu, Pb, Co, Sn, and Bi; with sub-shell valence electron configuration of d1-10) are also less concentrated in the lake sediments than in the oceanic pelagic clay. In turn, B-type cations have much higher dissolved concentrations in the lake water than in the ocean. Rare earth elements (REE) mainly form organic complexes in the lake water, and carbonate complexes in the ocean (Figure 1). REE are mostly associated with de-tritus aluminosilicate phases in the Lake Biwa sediments, but with phosphate phases in the deep sea sediments. Fe and Mn oxide phases are clearly separated in marine Mn nodules and crusts, but not in Mn crusts and concretions from Lake Biwa. Useful parameters such as the enrich-ment factor and the distribution coefficient of elements between solid and liquid phases were estimated in both systems for further discussions.
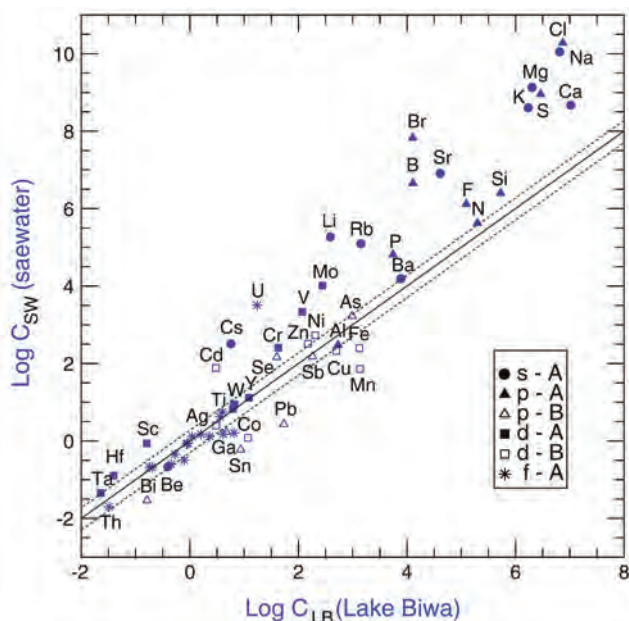
Figure 1. The average concentrations of elements (10^{-9} g/L) in Lake Biwa water (C_{LB}) versus that in seawater (C_{SW}). All in logarithm scale.

Ion Imprinted Sol-gel Materials for the Separation of Metal Ions

Much attention has been paid to a molecular (ion) im-printing technique as a method to prepare highly selective adsorbents. Recently, a novel organic-inorganic hybrid sorbent was proposed by Dai et al. employing Cu(II) and surfactant micelles as templates. We prepared some new sorbents based on this hierarchical double-imprinting concept using Cu(II), Zn(II), Ni(II), Co(II), Cd(II) and Pd(II) as templates (Figure 2).

The sorbents were prepared through self-hydrolysis, self-condensation, and co-condensation of the cross-linking agent (tetraethylorthosilicate) and the functional precursor in an alkaline media in the presence of cetyltrimethyl-ammonium bromide. The bifunctional ligands such as 3-(2-aminoethylamino)propyltrimethoxysilane (AAPTS) and 3-(2-aminoethylamino)methyltrimethoxysilane (AAMTS) were employed.

Adsorption of Cu(II) and Zn(II) to Cu imprinted sorbent with AAMTS (Cu/AAMTS) and to control blank sorbent (non/AAMTS) has been examined. 23% of Cu(II) and 20% of Zn(II) were adsorbed to non/AAMTS sorbent, and 99% and 22% to Cu/AAMTS. The effect of Cu(II) imprinting is quite meaningful for AAMTS rather than AAPTS. The adsorptions of metal ions to Zn(II), Ni(II), Co(II), Cd(II) and Pd(II) imprinted sorbents were also examined.
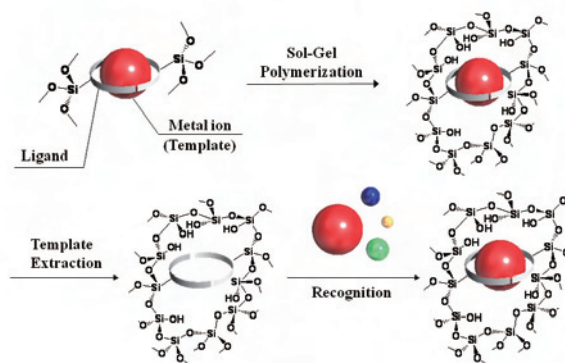

Figure 2. Ion imprinted functional silica gel sorbent.