

# 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.; Takano, S.; Minami, H.; Sohrin, Y., Distribution and Stoichiometry of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in Seawater Around the Juan de Fuca Ridge, *J. Oceanogr.*, **75**, 669-685 (2017).

Takano, S.; Tanimizu, M.; Hirata, T.; Shin, K. T.; Fukami, Y.; Suzuki, K.; Sohrin, Y., A Simple and Rapid Method for Isotopic Analysis of Nickel, Copper, and Zinc in Seawater Using Chelating Extraction and Anion Exchange, *Anal. Chim. Acta*, **967**, 1-11 (2017).

Nakashima, Y.; Shimizu, A.; Maruo, M.; Sohrin, Y., Trace Elements Influenced by Environmental Changes in Lake Biwa: (I) Seasonal Variations under Suboxic Hypolimnion Conditions during 2007 and 2009, *Limnol.*, **17**, 151-162 (2016).

Sohrin, Y.; Nakashima, Y.; Maruo, M., Trace Elements Influenced by Environmental Changes in Lake Biwa: (II) Chemical Variations in the Hypolimnion over the Last Half-century, *Limnol.*, **17**, 163-173 (2016).

Minami, T.; Konagaya, W.; Zheng, L.; Takano, S.; Sasaki, M.; Murata, R.; Nakaguchi, Y.; Sohrin, Y., An Off-line Automated Preconcentration System with Ethylenediaminetriacetate Chelating Resin for the Determination of Trace Metals in Seawater by High-resolution Inductively Coupled Plasma Mass Spectrometry, *Anal. Chim. Acta*, **854**, 183-190 (2015).

Takano, S.; Tanimizu, M.; Hirata, T.; Sohrin, Y., Isotopic Constraints on Biogeochemical Cycling of Copper in the Ocean, *Nat. Commun.*, **5**, [5663-1]-[5663-7] (2014).

## Estimation of the Paleoenvironment Based on the Concentration and Isotope Ratio of Molybdenum and Tungsten in the Japan Sea Sediment

Molybdenum (Mo) and tungsten (W) are group 6 elements and exist as hexavalent oxoacid anion ( $\text{MoO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ) in the oxidative ocean. While Mo has concentration of about 107 mmol/kg in the modern ocean (Nakagawa *et al.* 2012), it is easily precipitated as thiomolybdate in the euxinic environment. On the other hand, W has concentration of about 49 pmol/kg in the modern ocean. Although W is not precipitated in the euxinic environment (Mohajerin *et al.* 2016), it is highly enriched in hydrothermal fluids (Kishida *et al.* 2004). Therefore, we expect that the Mo/W concentration ratio and the stable isotope ratio of Mo and W in marine sediments would be powerful proxies in paleoceanography. Recently, we have developed a new method of stable isotope ratio analysis for Mo and W in marine sediments on the basis of microwave digestion, chelating column extraction, anion exchange separation, and determination by multicollector inductively coupled mass spectrometry (MC-ICP-MS). Using this method, we have analyzed a sediment core collected off Iwanai, Hokkaido in the Japan Sea (43°22'36.0"N, 140°04'10.0"E, 900 m depth) and estimated environmental changes at the bottom of the Japan Sea middle depth in the past 46,530 years. The high peaks of Mo concentration and Mo/W ratio suggested euxinic precipitation of Mo 10,000, 15,000, 30,000, and 46,000 years ago. However,  $\delta^{98/95}\text{Mo}$  neither exceed 0.9‰ nor correlate with the Mo/W ratio. Tungsten concentration was relatively uniform similarly to Al, and  $\delta^{186/184}\text{W}$  was about 0‰ throughout the core, suggesting that chemical supply from land was fairly constant.

Kishida K, Sohrin Y, Okamura K, Ishibashi J (2004) Tungsten enriched in submarine hydrothermal fluids. *Earth Planet Sci Lett* 222 (3-4):819-827. doi:10.1016/j.epsl.2004.03.034

Mohajerin TJ, Helz GR, Johannesson KH (2016) Tungsten–molybdenum fractionation in estuarine environments. *Geochim Cosmochim Acta* 177:105-119. doi:10.1016/j.gca.2015.12.030

Nakagawa Y, Takano S, Firdaus ML, Norisuye K, Hirata T, Vance D, Sohrin Y (2012) The molybdenum isotopic composition of the modern ocean. *Geochim J* 46 (2):131-141. doi:10.2343/geochemj.1.0158

## Distributions of Dissolved and Labile Particulate Trace Metals (Al, Mn, Fe, Co, Ni, Cu, Cd, and Pb) in Seawater on 160°W in the North Pacific

The North Pacific Ocean is at the end of general ocean circulation, characterized by influx of North Pacific Inter-

mediate Water and by aeolian supply of dust and aerosol through westerly wind. GEOTRACES ocean section studies of trace metals in seawater have covered the Atlantic Ocean but still limited in the Pacific Ocean. Recently, we have reported the distributions of trace metals around the Juan de Fuca Ridge (Zheng *et al.* 2017). In this study, we report the distributions of Al, Mn, Fe, Co, Ni, Cu, Cd, and Pb in dissolved (d) and labile particulate (lp) fractions on 160°W in the North Pacific, where seawater samples were collected during the R/V Hakuho-Maruh KH-05-2 cruise in August-September 2005. The dAl concentrations were low at high latitude stations and the bottom maximum extended from south to north. DFe and lpFe concentrations took maxima at station ST14 that is ~190 km off the Aleutian Islands and decreased sharply when leaving from the continent. Both d and lp Mn and Co showed a maximum in surface water (~20 m) at ST14 and nearly constant concentrations in deep water. DNi and dCd showed nutrient-type distributions. lpNi and lpCd were not detected. DCu increased almost linearly from surface to a depth of 4,000 m. There was a strong correlation between dCu and Si down to a depth of 2000 m ( $r^2 = 0.747$ ), but dCu substantially increased in deep water due to supply from the sediment. For Pb, the lp fraction was hardly detectable and d fraction showed a subsurface maximum centered at a depth of ~200 m, ~35°N. It is likely that anthropogenic Pb in aerosol particles caused by coal burning in the Asian continent falls to the Pacific Ocean, is subducted with surface seawater, and then spreads throughout the North Pacific Ocean by ocean currents.

Zheng L, Minami T, Takano S, Minami H, Sohrin Y (2017) Distribution and stoichiometry of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater around the Juan de Fuca Ridge. *J Oceanogr* 73 (5):669-685. doi:10.1007/s10872-017-0424-2



**Figure 1.** A snapshot at seawater sampling during the R/V Hakuho Maru KH-17-3 cruise.