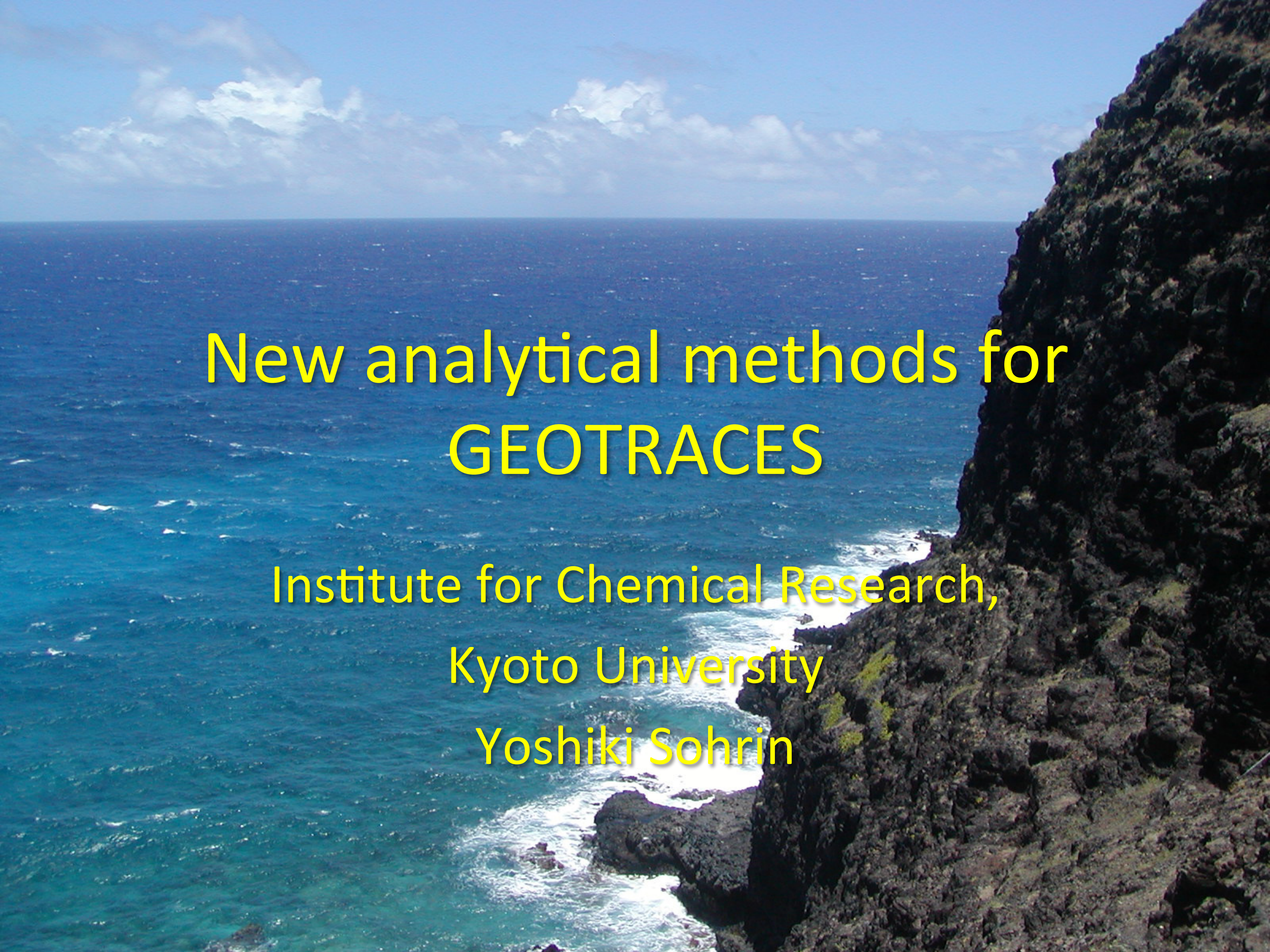


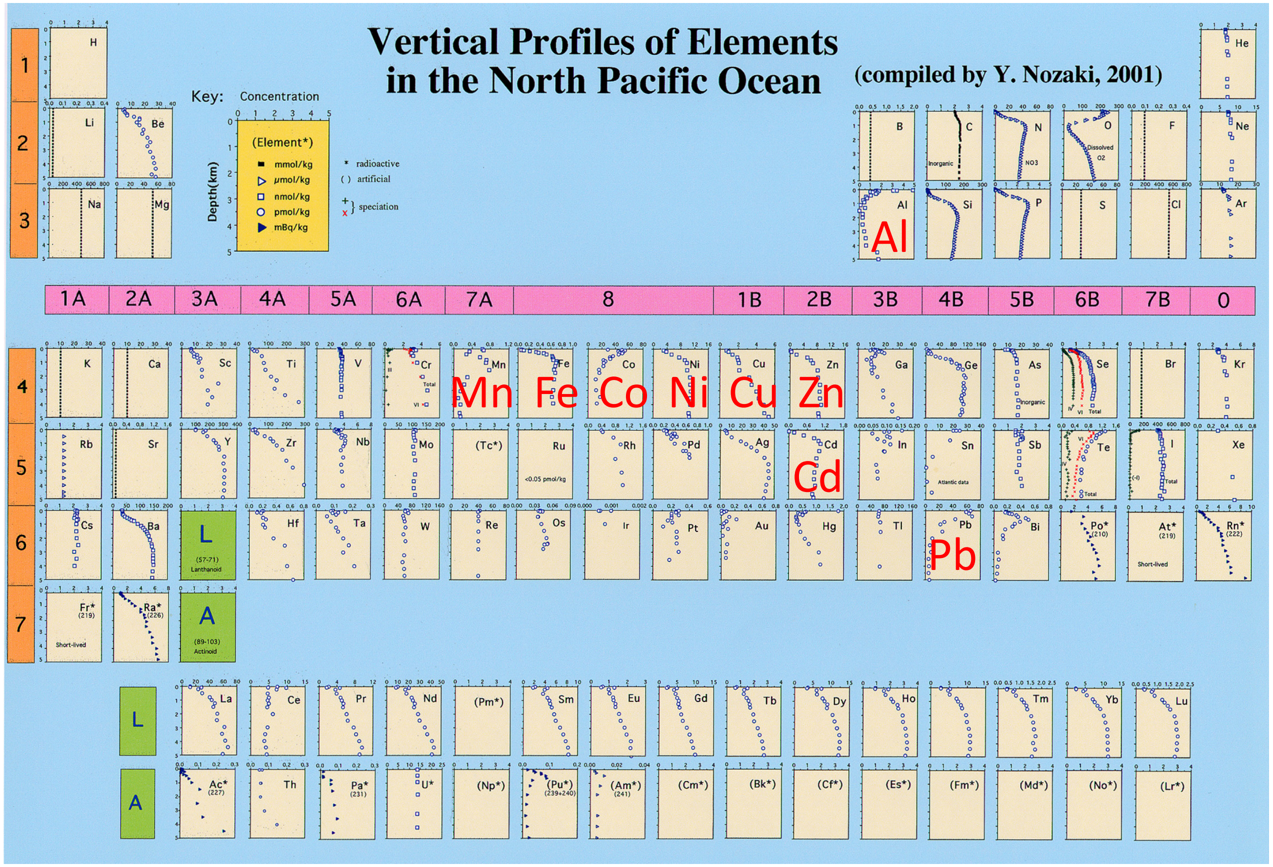
New analytical methods for GEOTRACES

Institute for Chemical Research,
Kyoto University
Yoshiki Sohrin

New analytical methods for trace elements in seawater

- Multielemental determination
  - High field strength elements: Zr, Hf, Nb, Ta, and W (Firdaus et al. 2007)
  - Particulate Co, Ni, Cu, Zn, Cd, and Pb (Nakatsuka et al. 2007)
  - Bioactive trace metals: Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb (Sohrin et al. 2008)
    - Automation of the preconcentration (Minami et al. 2015)
- Stable isotope ratio analysis
  - Mo (Nakagawa et al. 2008)
  - Cu (Takano et al. 2013)

Bioactive Trace Metals


Vertical Profiles of Elements in the North Pacific Ocean

(compiled by Y. Nozaki, 2001)

- Essential and/or toxic to organisms
- Key parameters for GEOTRACES
  - Al Tracer of lithogenic material
  - Mn Tracer of redox cycling
  - Fe Essential micronutrient
  - Cu Micronutrient; potentially toxic at high concentration
  - Zn Micronutrient; potentially toxic at high concentration
  - Cd Essential micronutrient; paleoproxy for nutrient
  - Pb isotopes Tracer of natural and contaminant sources

Basic procedure for analysis of dissolved trace metals

Sampling Niskin-X sampler

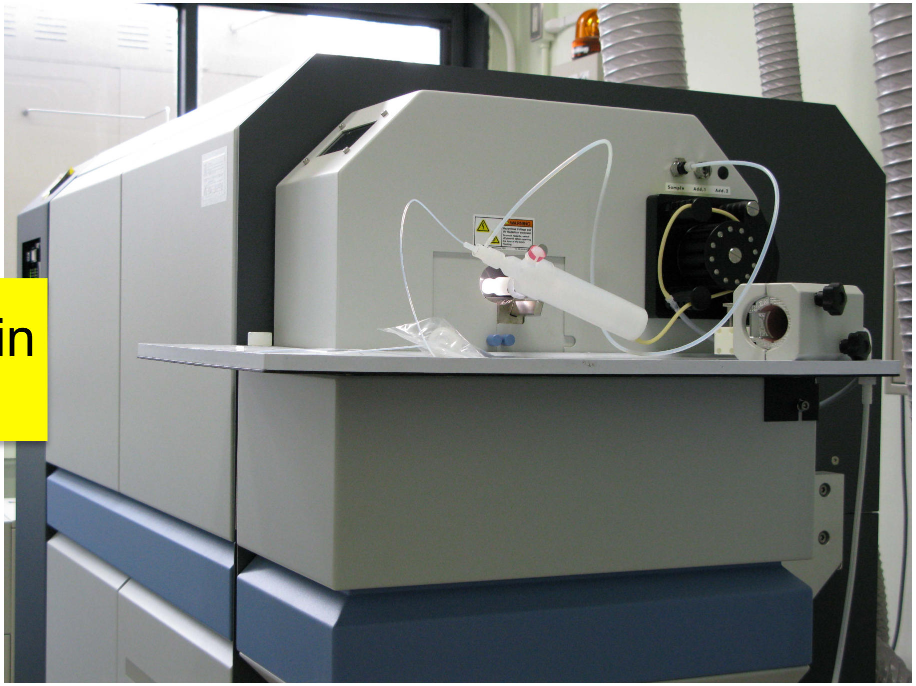
Pretreatment

Filtration Pore size of ~0.2 μm

Acidification $\sim 10^{-2}$ M HCl

Preconcentration Chelating resin extraction

Determination ICP-MS



ELEMENT2, Thermo Fisher

Multielemental determination

Anal. Chem. **2008,** *80,* 6267–6273

Multielemental Determination of GEOTRACES Key Trace Metals in Seawater by ICPMS after Preconcentration Using an Ethylenediaminetriacetic Acid Chelating Resin

Yoshiki Sohrin,* Shouhei Urushihara, Seiji Nakatsuka, Tomohiro Kono, Eri Higo, Tomoharu Minami, Kazuhiro Norisuye, and Shigeo Umetani

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

GEOTRACES is an international research project on marine biogeochemical cycles of trace elements and their isotopes. GEOTRACES key trace metals in seawater are Al (8−1000 ng/kg), Mn (4−300 ng/kg), Fe (1−100 ng/kg), Cu (30−300 ng/kg), Zn (3−600 ng/kg), and Cd (0.1−100 ng/kg), of which global oceanic distribution will be determined on a number of research cruises. This work introduces a novel method of solid-phase extraction to determine Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater by adjusting the pH of the sample to 6 and carrying out a single preconcentration step. The trace metals were collected from ~120 mL of seawater using a column of a chelating resin containing the ethylenediaminetriacetic acid functional group and eluted with ~15 mL of 1 M HNO_3. Mn and Fe in the eluate were measured by inductively coupled plasma mass spectrometry (ICPMS) using the dynamic reaction cell mode, and the other metals were measured using the standard mode. Using this procedure, the trace metals were collected quantitatively, while >99.9% of alkali and alkaline earth metals in seawater were removed. The procedural blank was <7% of the mean concentration in deep ocean waters, except 16% for Pb. The overall detection limit was <14% of the mean concentration in deep ocean waters. The RSD was <9%. Our values for the trace metals in the certified reference materials of seawater NASS-5 and nearshore seawater CASS-4 agreed with the certified values (except that there is no certified value for Al). This method was also successfully applied to the reference materials of open-ocean seawater produced by the SAFe program. Our Fe concentrations were 5.9 ± 0.7 ng/kg for surface water (S1) and 50.4 ± 2.9 ng/kg for deep water (D2), which are in agreement with the interlaboratory averages of 5.4 ± 2.4 and 50.8 ± 9.5 ng/L, respectively. The data for other metals were oceanographically consistent.

A coordinated global research project, GEOTRACES, is investigating processes and quantify fluxes that control the distributions of key trace elements and isotopes (TEIs) in the ocean and establishing the sensitivity of these distributions to changing environmental conditions.[1] The core activity of the GEOTRACES program is the measurement of a range of TEIs along full-depth ocean sections through each of the major ocean basins within the next few decades. Some TEIs are assigned as key parameters and are expected to be measured on all GEOTRACES ocean section cruises. The key trace elements are Al (8−1000 ng/kg), Mn (4−300 ng/kg), Fe (1−100 ng/kg), Cu (30−300 ng/kg), Zn (3−600 ng/kg), and Cd (0.1−100 ng/kg). These trace metals other than Al serve as micronutrients for organisms.[2] Models suggest that Fe is a growth-limiting factor for a number of taxa in wide regions of the ocean.[3] Al is a tracer of mineral dust, and Mn is a tracer of redox cycling.[4] Cd is a proxy for the nutrient content of waters in paleoceanography.

A simple, rapid, accurate, and precise method is invaluable for the GEOTRACES section study. However, it has been difficult to determine the key trace metals at the same time due to contamination and interference from major constituents. Inductively coupled plasma mass spectrometry (ICPMS) is the most promising technique for multielemental determination of trace metals. Some trace metals have been determined by ICPMS just after dilution of seawater.[5–7] Although this technique is simple, the sensitivity is not adequate to determine the concentrations in the open ocean and the signals usually suffer from drift and suppression due to the seawater matrix. Thus, preconcentration from major constituents is crucial to accurate and precise determination of trace metals.

The preconcentration methods that have been applied to seawater include solvent extraction and coprecipitation. Recently an $Mg(OH)_2$ coprecipitation method has been applied to determine Fe and Mn in seawater. Although it is simple and uses only NH_3,

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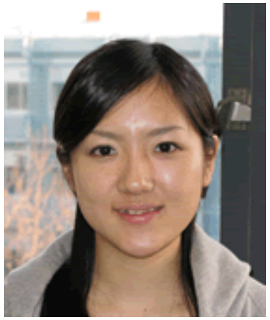
* To whom correspondence should be addressed. E-mail: sohrin@scl.kyoto-u.ac.jp. Tel: +81 774 38 3100. Fax: +81 774 38 3099.

(1) GEOTRACES Planning Group, *GEOTRACES Science Plan*; Scientific Committee on Oceanic Research: Baltimore, MD, 2006.
(2) Morel, F. M. M.; Milligan, A. J.; Saito, M. A. In *The Oceans and Marine Geochemistry*; Elderfield, H. , Ed.; Elsevier-Pergamon: Oxford, 2003; Treatise on Geochemistry, *Vol. 6*, pp 113−143.
(3) Moore, J. K.; Doney, S. C.; Lindsay, K. *Global Biogeochem. Cycles* **2004**, *18*, GB4028.
(4) Chester, R. *Marine Geochemistry*, 2nd ed.; Blackwell: Malden, MA, 2000.
(5) Alves, L. C.; Allen, L. A.; Houk, R. S. *Anal. Chem.* **1993**, *65*, 2468–2471.
(6) Field, M. P.; LaVigne, M.; Murphy, K. R.; Ruiz, G. M.; Sherrell, R. M. *J. Anal. At. Spectrom.* **2007**, *22*, 1145–1151.
(7) Turetta, C.; Cozzi, G.; Barbante, C.; Capodaglio, G.; Cescon, P. *Anal. Bioanal. Chem.* **2004**, *380*, 258–268.

10.1021/ac800500f CCC: $40.75 © 2008 American Chemical Society
Published on Web 07/23/2008

- Single step preconcentration using NOBIAS Chelate-PA1 for Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb in seawater
- 75 quotations (Scopus)

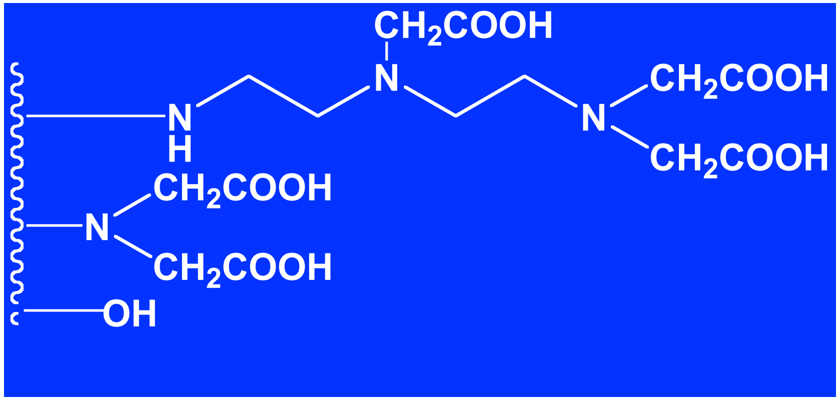
Urushihara

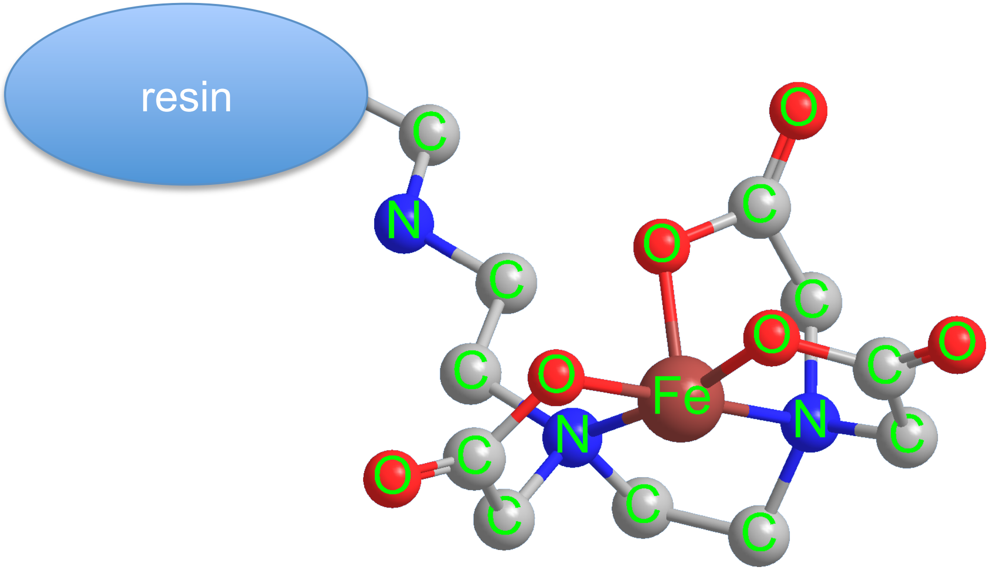


Higo

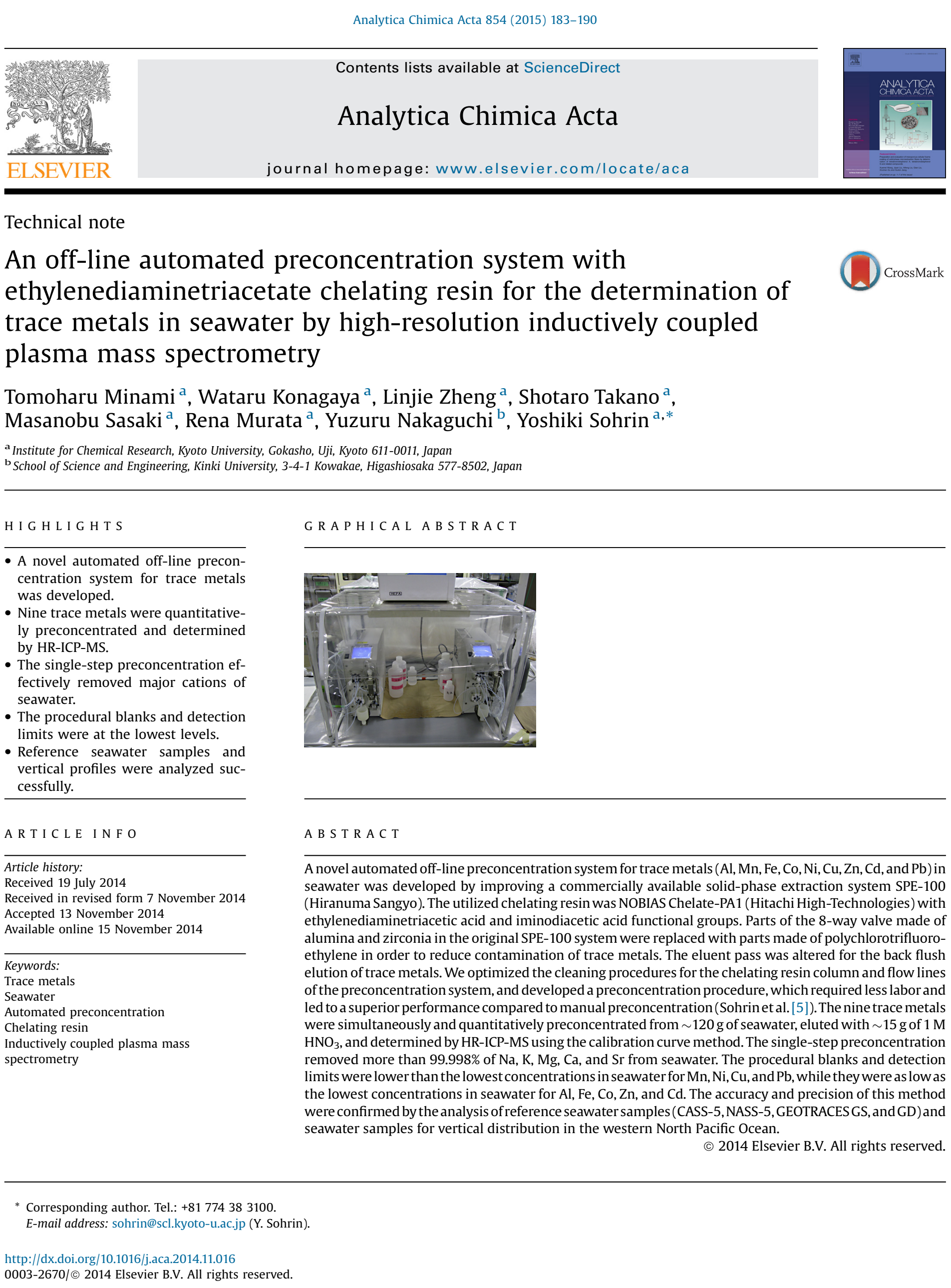
Minami

NOBIAS Chelate-PA1 (Hitachi High-Tech)





- Noble chelating resin with ethylenediamine triacetate group
  - Form stable complexes with trace metals through making five coordination bonds
  - Effectively eliminate alkali and alkaline earth metals
- Made of hydrophilic polyhydroxymethacrylate resin
  - Chemical and physical stability
  - Low blanks of trace metals



Analytica Chimica Acta 854 (2015) 183–190

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journal homepage: www.elsevier.com/locate/aca

Technical note

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

Tomoharu Minami[a], Wataru Konagaya[a], Linjie Zheng[a], Shotaro Takano[a], Masanobu Sasaki[a], Rena Murata[a], Yuzuru Nakaguchi[b], Yoshiki Sohrin[a,*]

[a] *Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*
[b] *School of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashiosaka 577-8502, Japan*

HIGHLIGHTS

- A novel automated off-line preconcentration system for trace metals was developed.
- Nine trace metals were quantitatively preconcentrated and determined by HR-ICP-MS.
- The single-step preconcentration effectively removed major cations of seawater.
- The procedural blanks and detection limits were at the lowest levels.
- Reference seawater samples and vertical profiles were analyzed successfully.

GRAPHICAL ABSTRACT

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Chelating resin
Inductively coupled plasma mass spectrometry

ABSTRACT

A novel automated off-line preconcentration system for trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) in seawater was developed by improving a commercially available solid-phase extraction system SPE-100 (Hiranuma Sangyo). The utilized chelating resin was NOBIAS Chelate-PA1 (Hitachi High-Technologies) with ethylenediaminetriacetic acid and iminodiacetic acid functional groups. Parts of the 8-way valve made of alumina and zirconia in the original SPE-100 system were replaced with parts made of polychlorotrifluoroethylene in order to reduce contamination of trace metals. The eluent pass was altered for the back flush elution of trace metals. We optimized the cleaning procedures for the chelating resin column and flow lines of the preconcentration system, and developed a preconcentration procedure, which required less labor and led to a superior performance compared to manual preconcentration (Sohrin et al. [5]). The nine trace metals were simultaneously and quantitatively preconcentrated from $\sim$120 g of seawater, eluted with $\sim$15 g of 1 M HNO_3, and determined by HR-ICP-MS using the calibration curve method. The single-step preconcentration removed more than 99.998% of Na, K, Mg, Ca, and Sr from seawater. The procedural blanks and detection limits were lower than the lowest concentrations in seawater for Mn, Ni, Cu, and Pb, while they were as low as the lowest concentrations in seawater for Al, Fe, Co, Zn, and Cd. The accuracy and precision of this method were confirmed by the analysis of reference seawater samples (CASS-5, NASS-5, GEOTRACES GS, and GD) and seawater samples for vertical distribution in the western North Pacific Ocean.

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E-mail address: sohrin@scl.kyoto-u.ac.jp (Y. Sohrin).

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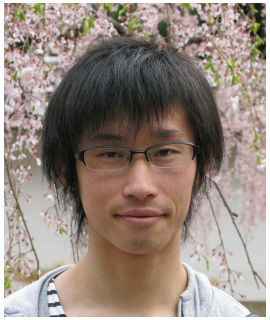
Automated preconcentration

- Off-line single step preconcentration of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb from seawater
- Low blank and high precision
- Reducing an operation burden
- 11 quotations (Scopus)

Minami

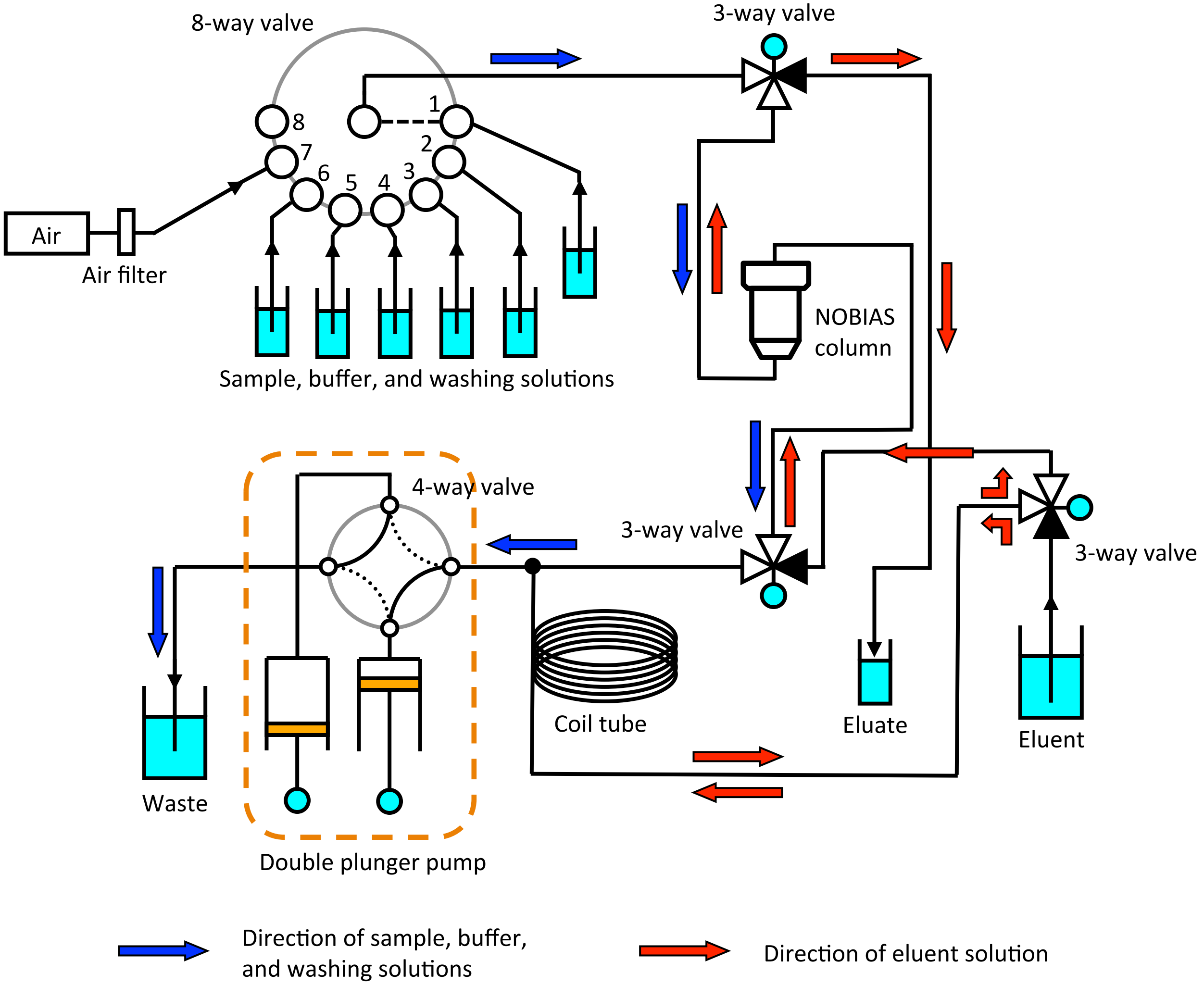


Konagaya

Zheng

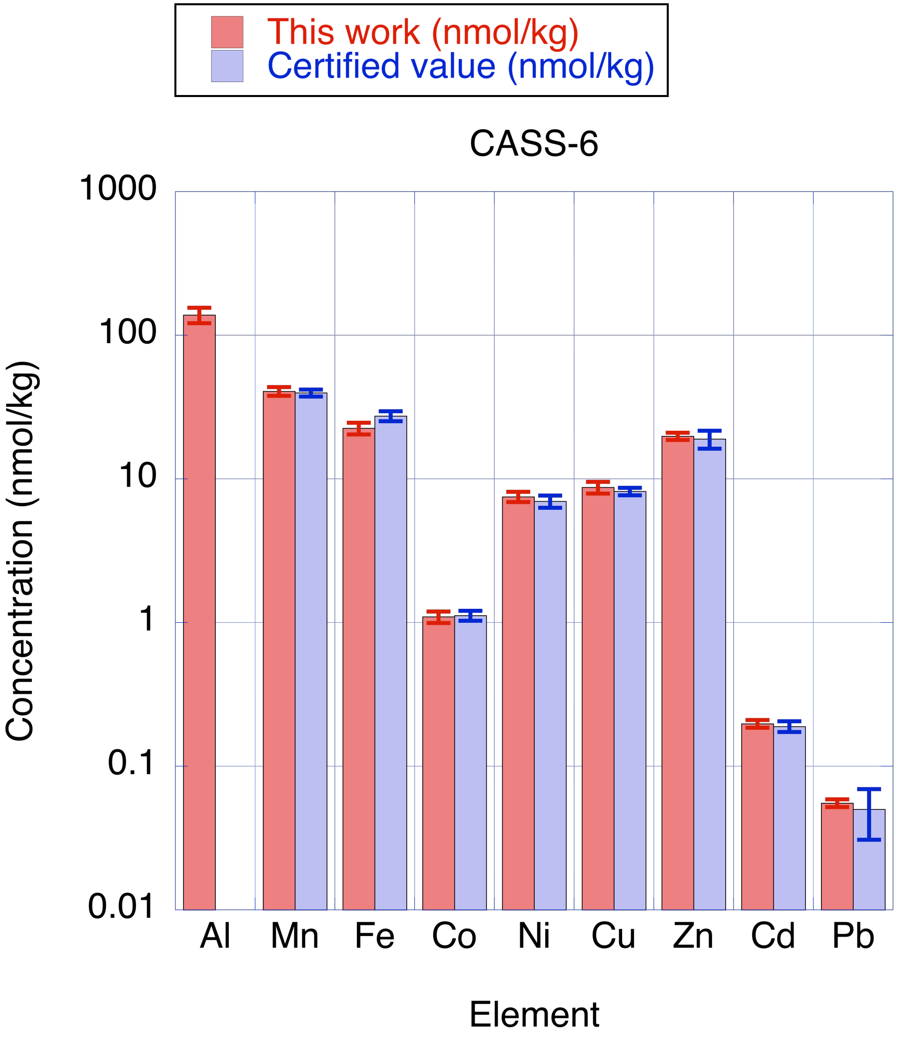
Automated preconcentration system

SPE-100, Hiranuma Sangyo
~¥900,000

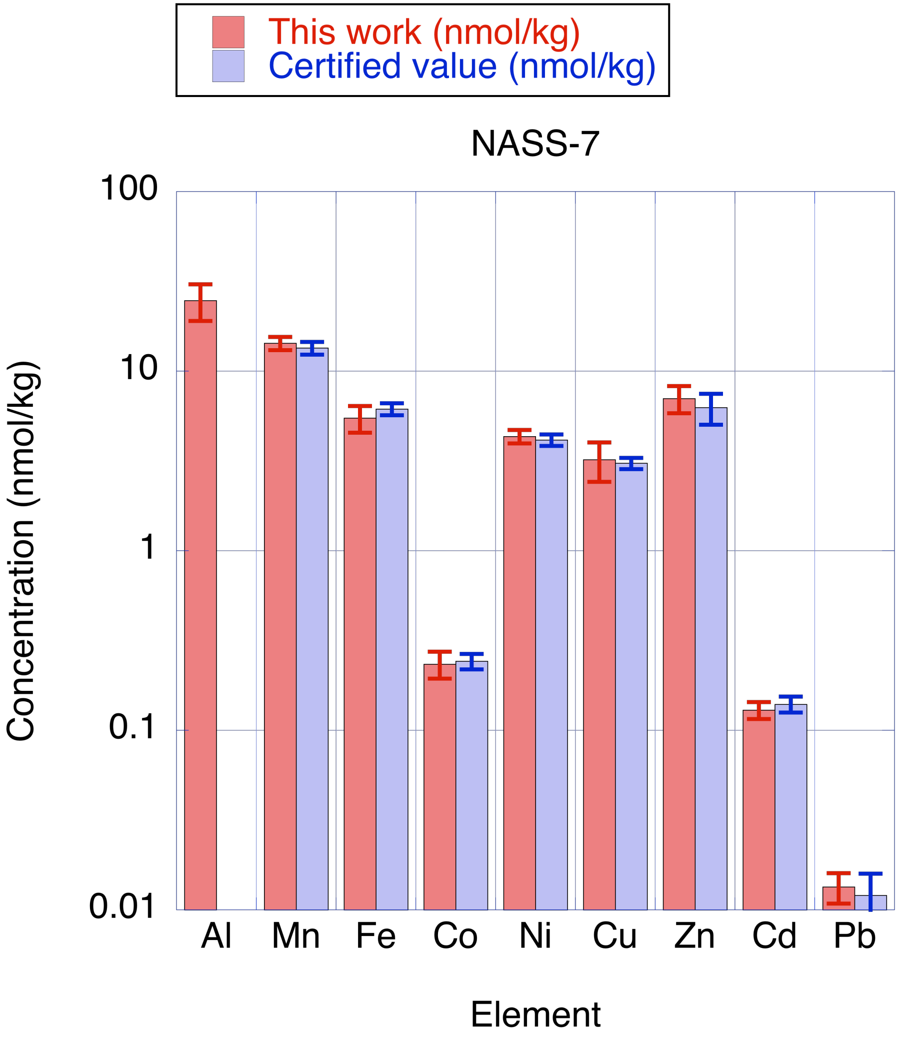


Optimized materials, flow line, cleaning method, and preconcentration program
Minami, T. et al. Anal. Chim. Acta 854, 183-190 (2015).

CASS-6 & NASS-7



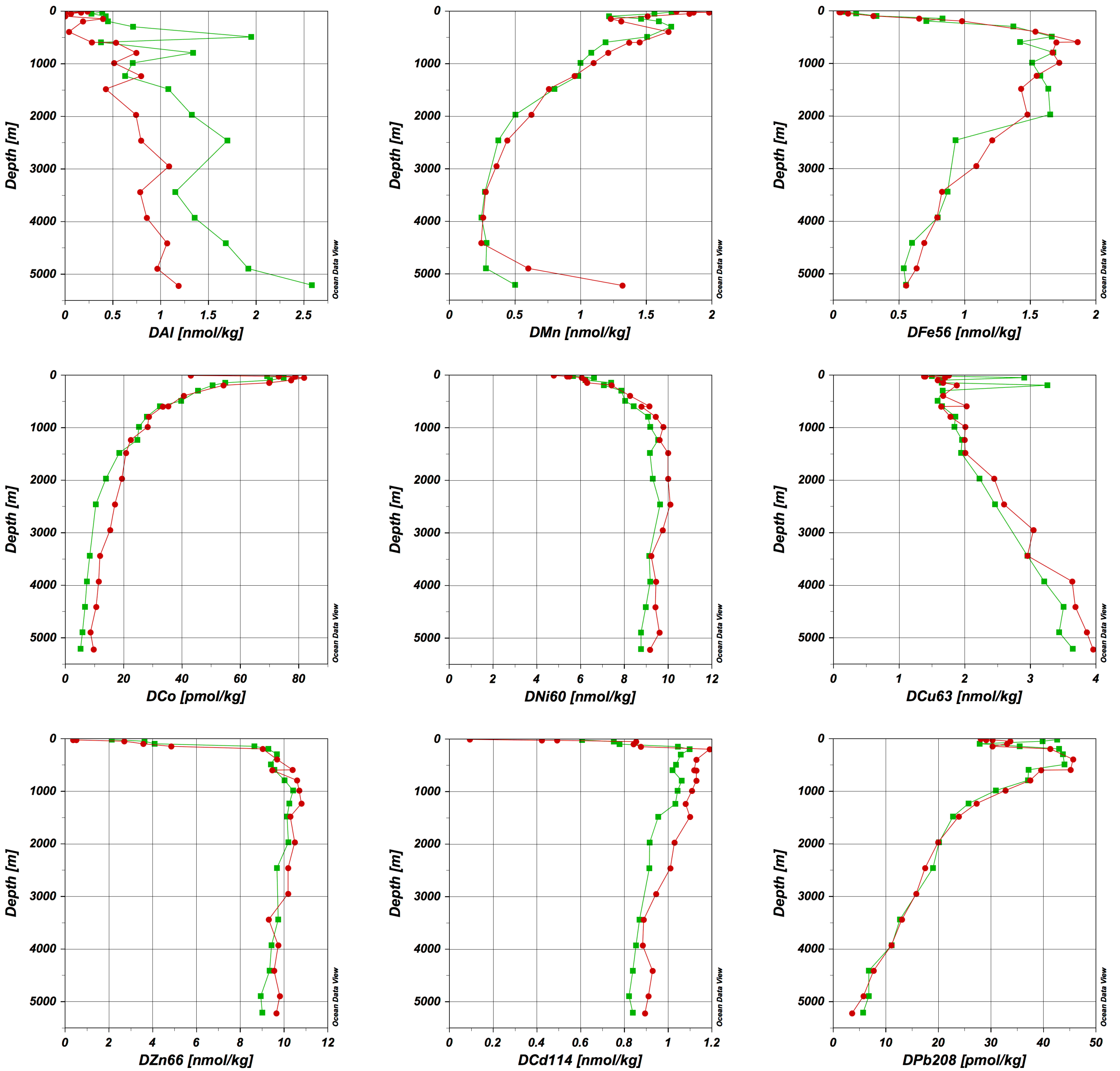
🟥 This work (nmol/kg)
🟦 Certified value (nmol/kg)
CASS-6
Concentration (nmol/kg)
1000
100
10
1
0.1
0.01
Al
Mn
Fe
Co
Ni
Cu
Zn
Cd
Pb
Element



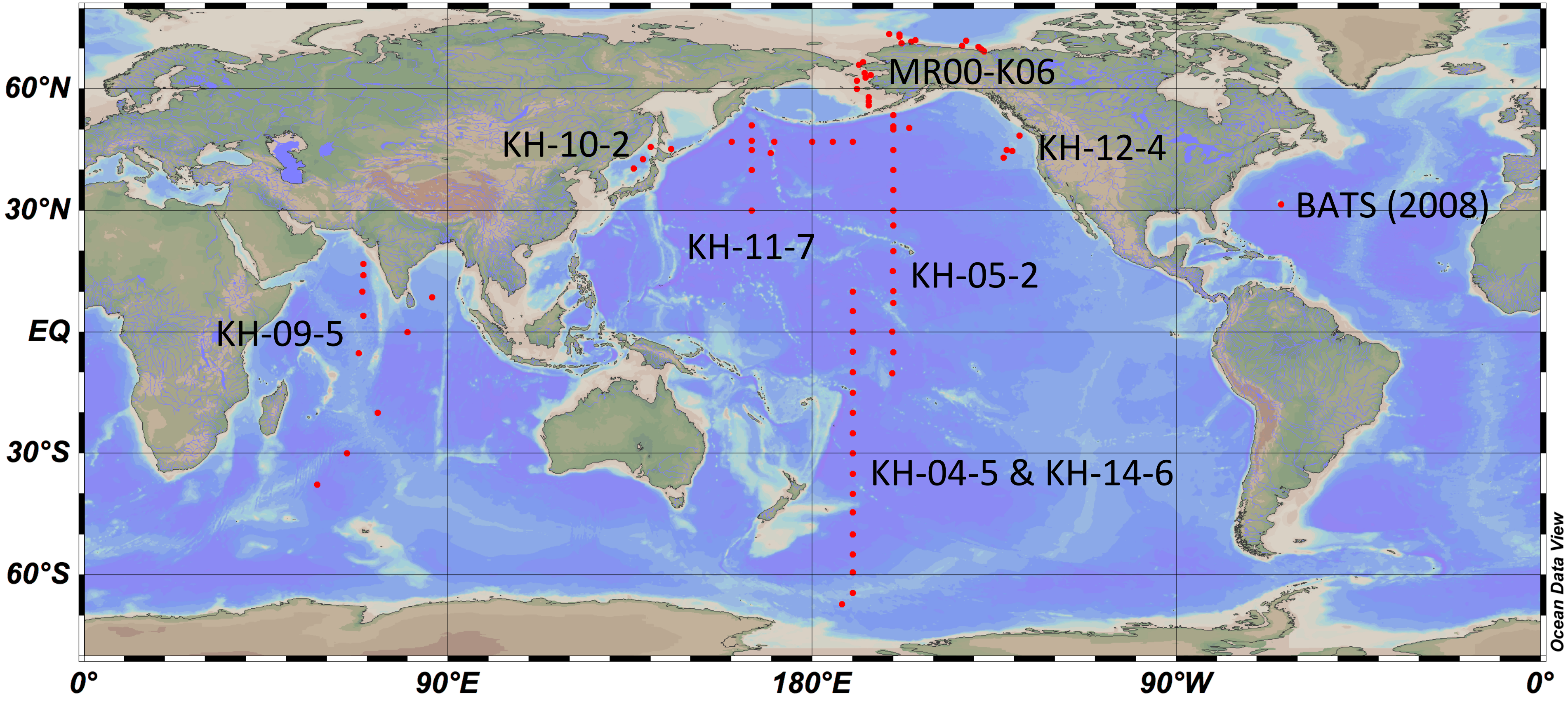
🟥 This work (nmol/kg)
🟦 Certified value (nmol/kg)
NASS-7
Concentration (nmol/kg)
100
10
1
0.1
0.01
Al
Mn
Fe
Co
Ni
Cu
Zn
Cd
Pb
Element

TR16 (■) & BD07 (●)

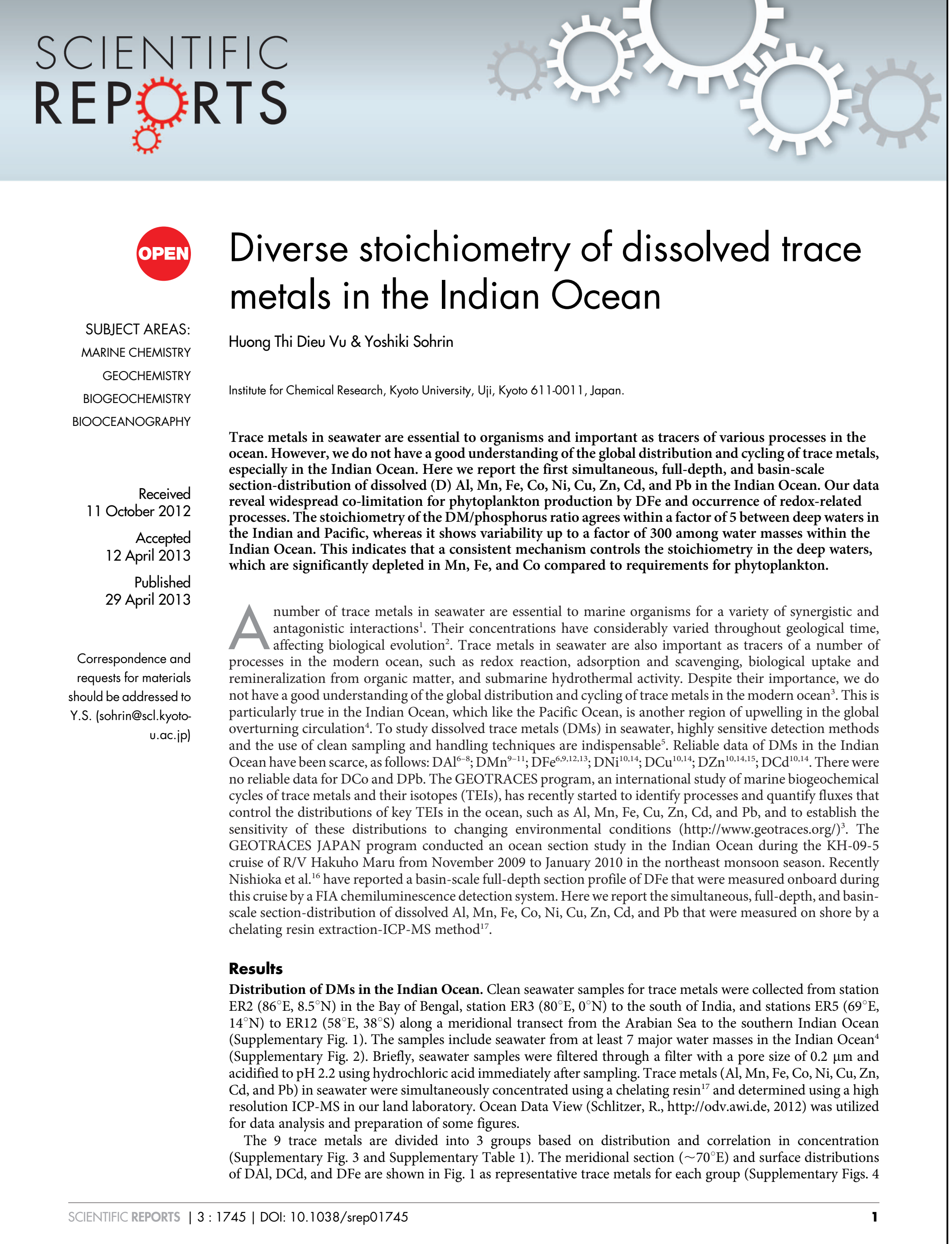
- TR16 (160.047°E, 47.007°N; 28 Jul 2011, KH-11-7), 0.2-μm pore Nuclepore filter
- BD07 (160.09°E, 47.00°N; 28 Aug 2012, KH-12-4), 0.2-μm AcroPak Capsule
- Capsule removed colloidal Al?



Sampling stations



~1,400 samples（Jun 2016 ）



SCIENTIFIC REPORTS

OPEN

Diverse stoichiometry of dissolved trace metals in the Indian Ocean

SUBJECT AREAS:
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GEOCHEMISTRY
BIOGEOCHEMISTRY
BIOOCEANOGRAPHY

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Trace metals in seawater are essential to organisms and important as tracers of various processes in the ocean. However, we do not have a good understanding of the global distribution and cycling of trace metals, especially in the Indian Ocean. Here we report the first simultaneous, full-depth, and basin-scale section-distribution of dissolved (D) Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in the Indian Ocean. Our data reveal widespread co-limitation for phytoplankton production by DFe and occurrence of redox-related processes. The stoichiometry of the DM/phosphorus ratio agrees within a factor of 5 between deep waters in the Indian and Pacific, whereas it shows variability up to a factor of 300 among water masses within the Indian Ocean. This indicates that a consistent mechanism controls the stoichiometry in the deep waters, which are significantly depleted in Mn, Fe, and Co compared to requirements for phytoplankton.

A number of trace metals in seawater are essential to marine organisms for a variety of synergistic and antagonistic interactions[1]. Their concentrations have considerably varied throughout geological time, affecting biological evolution[2]. Trace metals in seawater are also important as tracers of a number of processes in the modern ocean, such as redox reaction, adsorption and scavenging, biological uptake and remineralization from organic matter, and submarine hydrothermal activity. Despite their importance, we do not have a good understanding of the global distribution and cycling of trace metals in the modern ocean[3]. This is particularly true in the Indian Ocean, which like the Pacific Ocean, is another region of upwelling in the global overturning circulation[4]. To study dissolved trace metals (DMs) in seawater, highly sensitive detection methods and the use of clean sampling and handling techniques are indispensable[5]. Reliable data of DMs in the Indian Ocean have been scarce, as follows: DAl[6–8]; DMn[9–11]; DFe[6,9,12,13]; DNi[10,14]; DCu[10,14]; DZn[10,14,15]; DCd[10,14]. There were no reliable data for DCo and DPb. The GEOTRACES program, an international study of marine biogeochemical cycles of trace metals and their isotopes (TEIs), has recently started to identify processes and quantify fluxes that control the distributions of key TEIs in the ocean, such as Al, Mn, Fe, Cu, Zn, Cd, and Pb, and to establish the sensitivity of these distributions to changing environmental conditions (http://www.geotraces.org/)[3]. The GEOTRACES JAPAN program conducted an ocean section study in the Indian Ocean during the KH-09-5 cruise of R/V Hakuho Maru from November 2009 to January 2010 in the northeast monsoon season. Recently Nishioka et al.[16] have reported a basin-scale full-depth section profile of DFe that were measured onboard during this cruise by a FIA chemiluminescence detection system. Here we report the simultaneous, full-depth, and basin-scale section-distribution of dissolved Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb that were measured on shore by a chelating resin extraction-ICP-MS method[17].

Results

Distribution of DMs in the Indian Ocean. Clean seawater samples for trace metals were collected from station ER2 (86°E, 8.5°N) in the Bay of Bengal, station ER3 (80°E, 0°N) to the south of India, and stations ER5 (69°E, 14°N) to ER12 (58°E, 38°S) along a meridional transect from the Arabian Sea to the southern Indian Ocean (Supplementary Fig. 1). The samples include seawater from at least 7 major water masses in the Indian Ocean[4] (Supplementary Fig. 2). Briefly, seawater samples were filtered through a filter with a pore size of 0.2 μm and acidified to pH 2.2 using hydrochloric acid immediately after sampling. Trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) in seawater were simultaneously concentrated using a chelating resin[17] and determined using a high resolution ICP-MS in our land laboratory. Ocean Data View (Schlitzer, R., http://odv.awi.de, 2012) was utilized for data analysis and preparation of some figures.

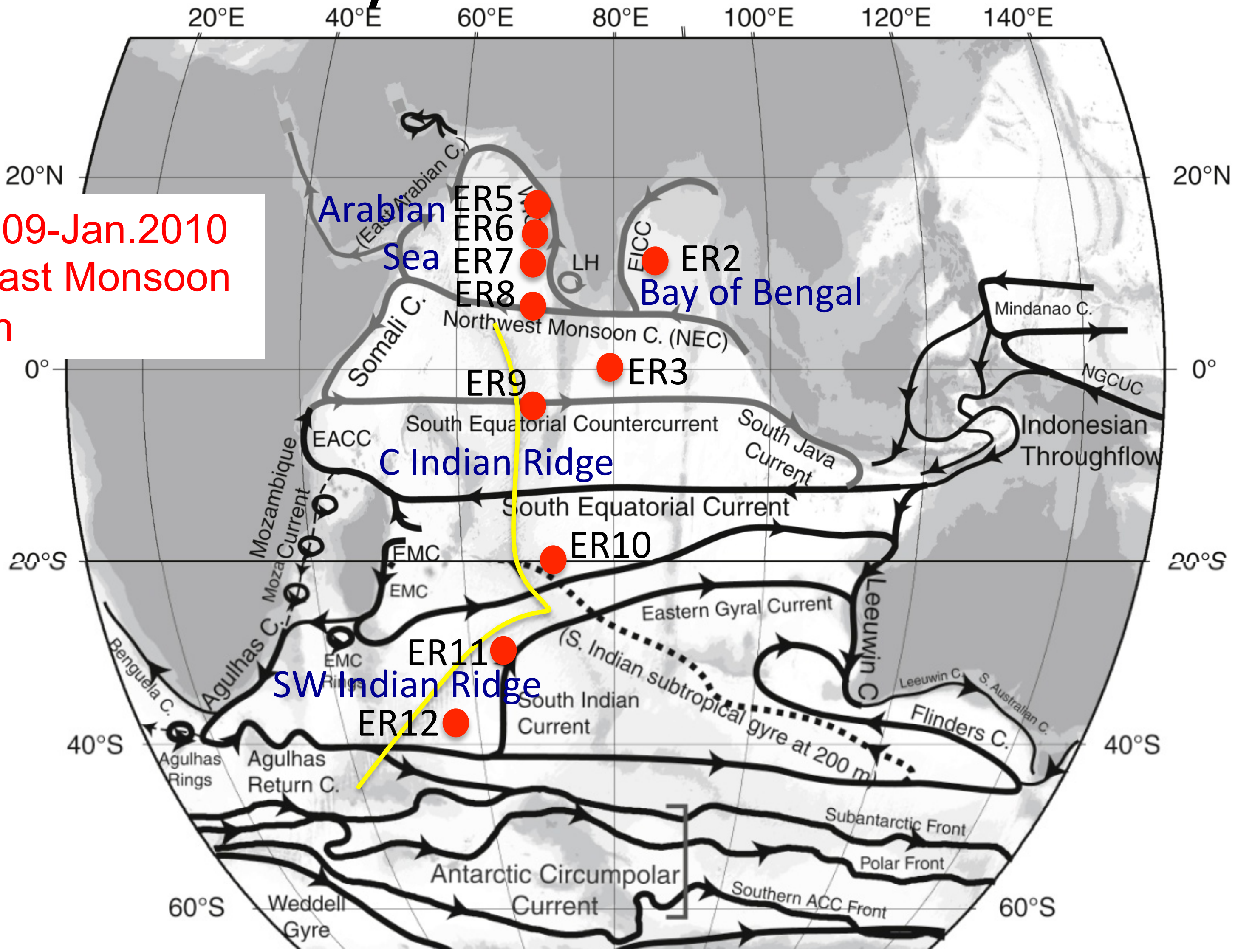
The 9 trace metals are divided into 3 groups based on distribution and correlation in concentration (Supplementary Fig. 3 and Supplementary Table 1). The meridional section (~70°E) and surface distributions of DAl, DCd, and DFe are shown in Fig. 1 as representative trace metals for each group (Supplementary Figs. 4

Indian Ocean

- Dissolved Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb
- M/P ratio varies substantially among water masses in the Indian Ocean
- Extensive Redfield ratio is not valid. Deep water lacks Mn, Fe, and Co
- 13 quotations (Scopus)

Huong T.D. Vu

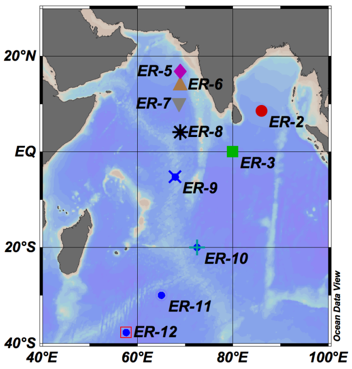
Sampling stations during KH-09-5 cruise of R/V Hakuho Maru

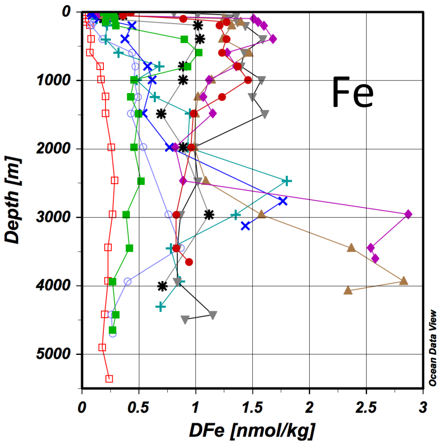


Nov.2009-Jan.2010
Northeast Monsoon
Season

Based on Talley, Pickard (2011)

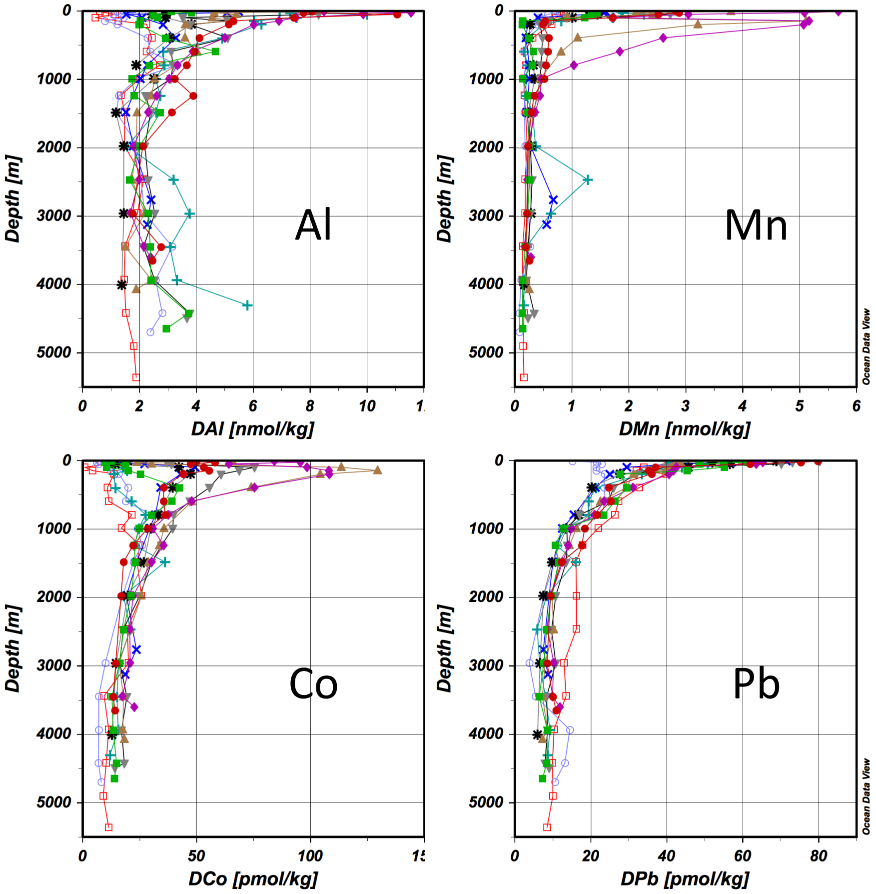
Vertical profiles of dMs



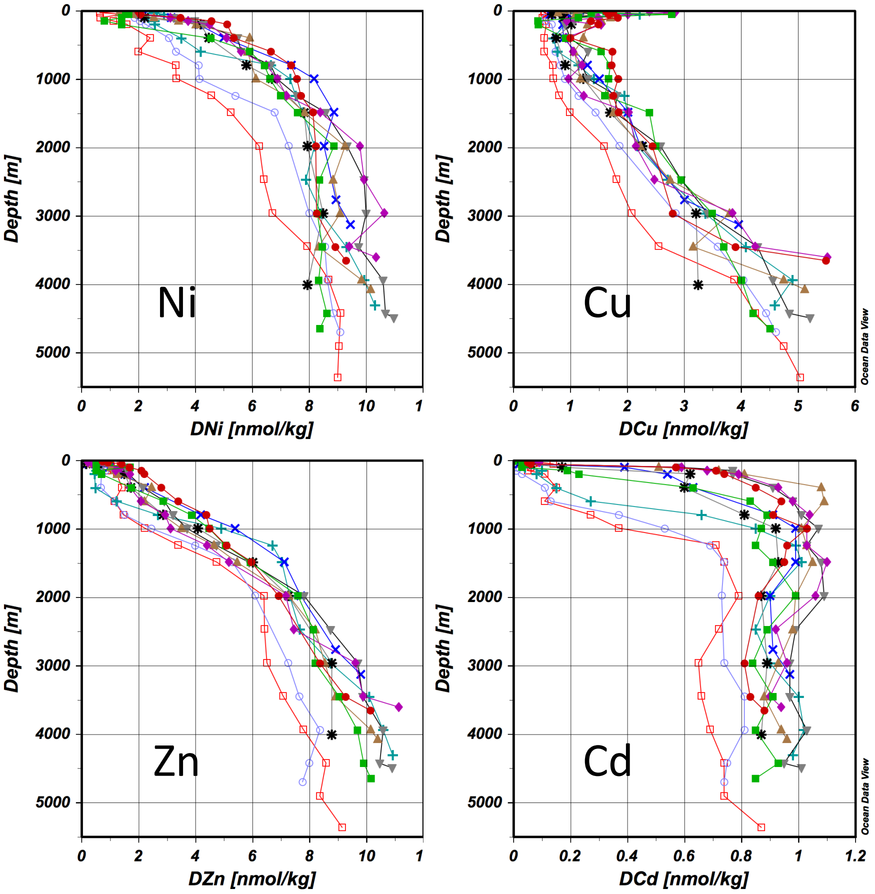


(3) Recycled and scavenged-type

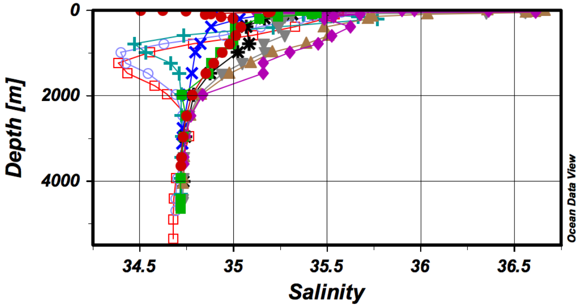
(1) Scavenged-type

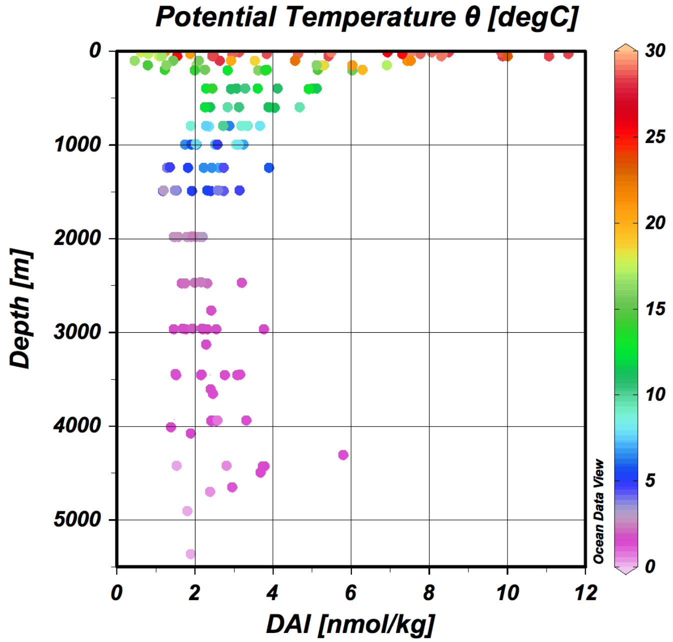


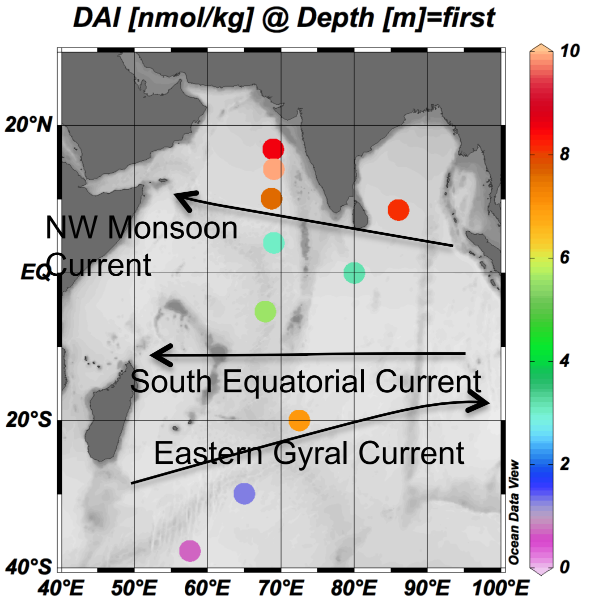
(2) Nutrient-type

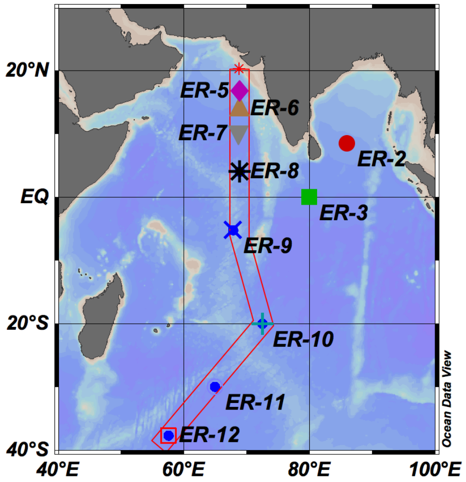


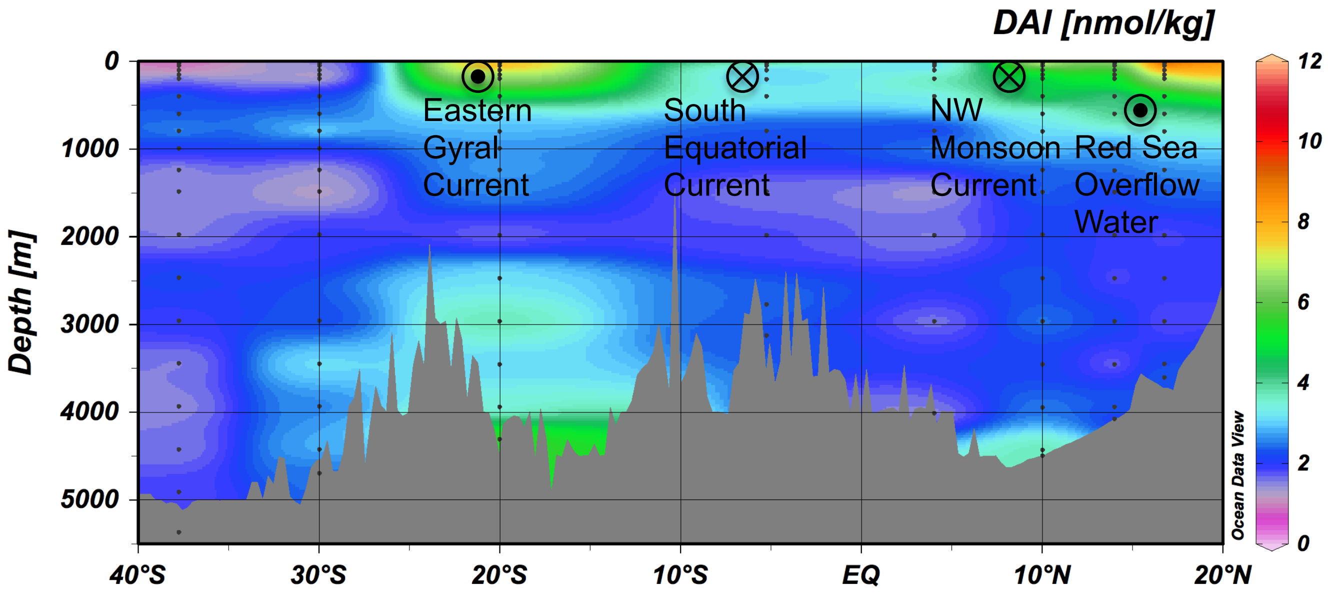
Aeolian dust and surface current: dAl





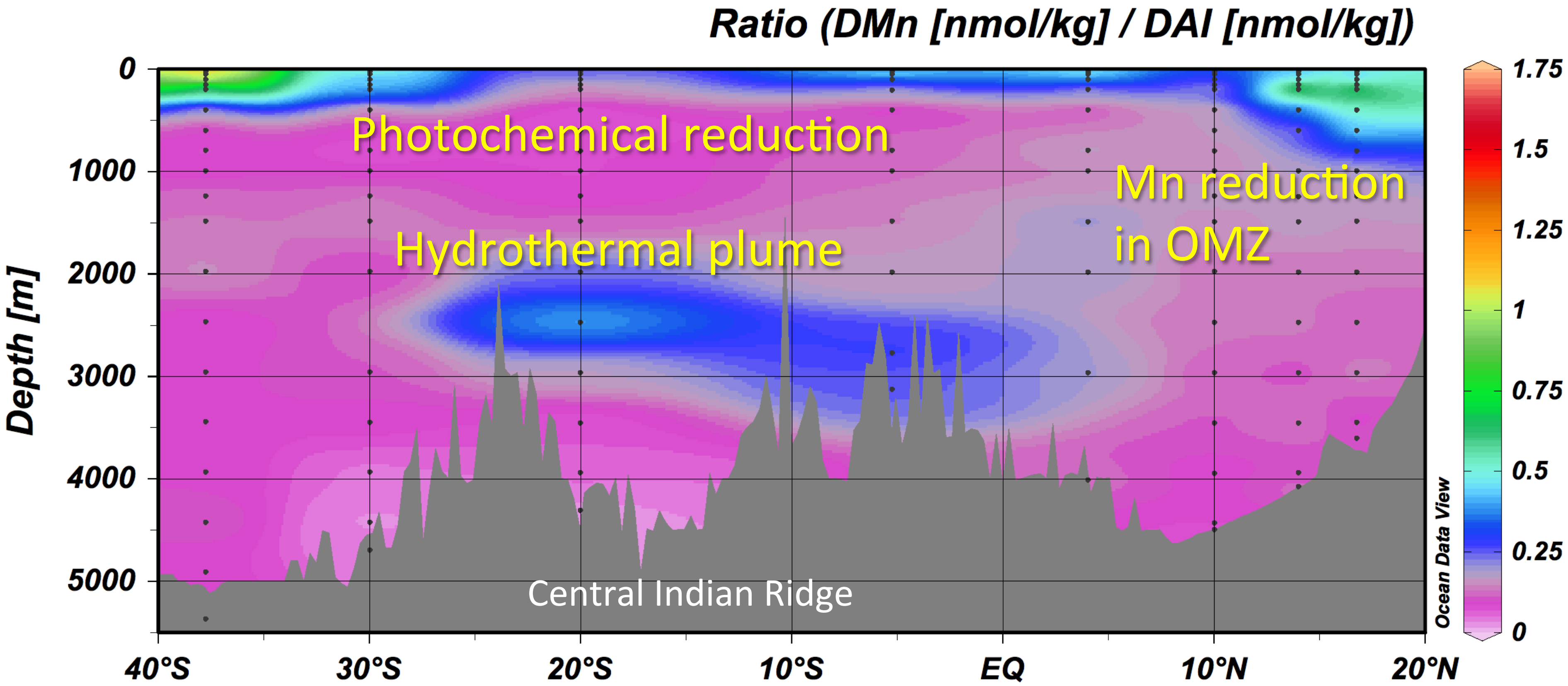






- Surface maximums of dAl extended to ~600 m depth, suggesting supply both from aeolian dust and from currents

dMn/dAl ratio as a redox tracer



Photochemical reduction

Hydrothermal plume

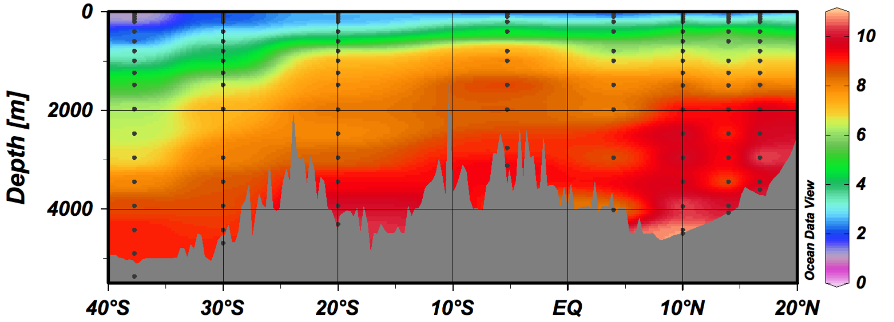
Mn reduction in OMZ

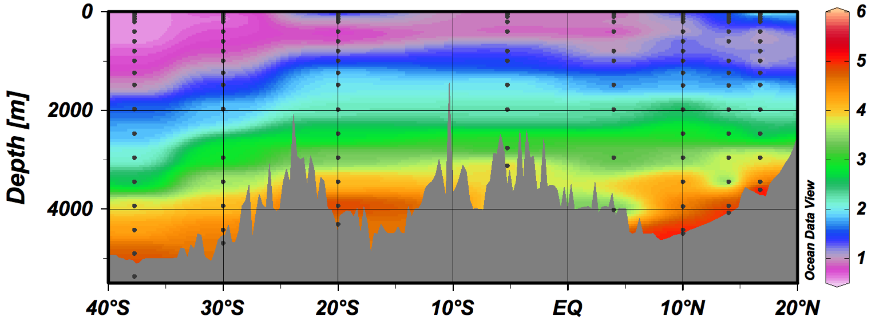
Central Indian Ridge

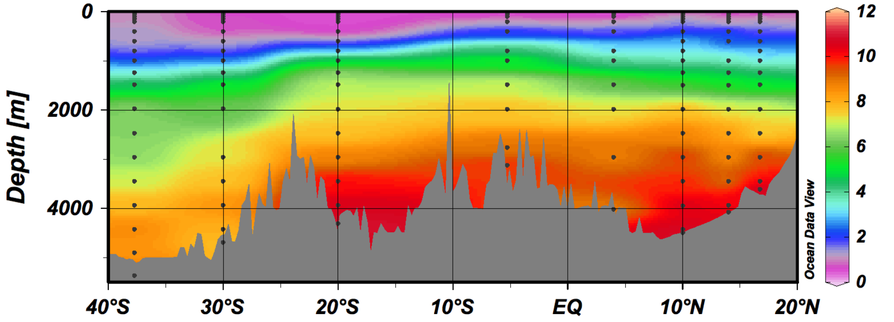
Mn/Al = 0.007 in the Arabian Sea aerosol (Chester et al. 1991)

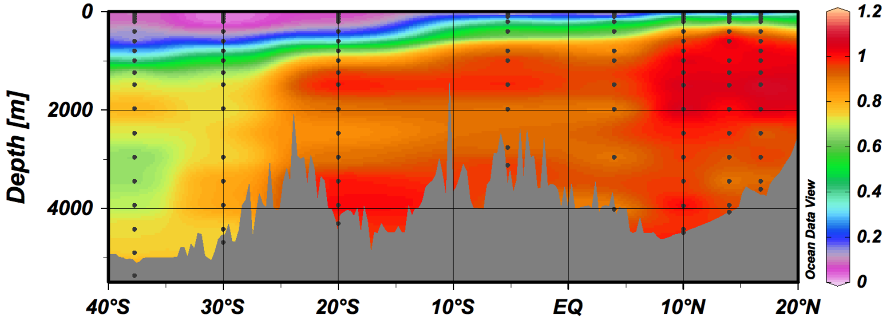
Vu, H. T. D. & Sohrin, Y. Scientific Reports 3, doi:10.1038/srep01745 (2013).

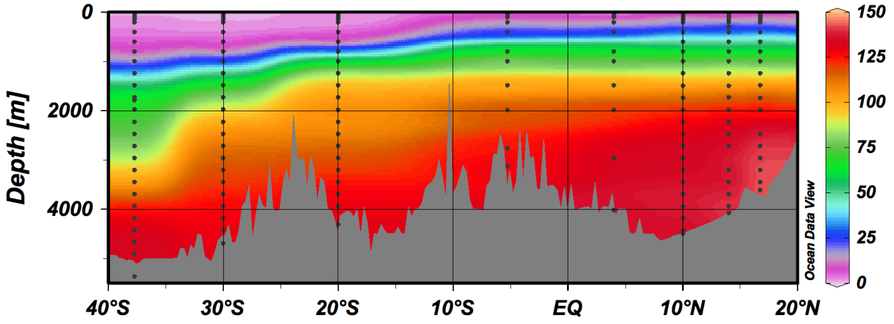
Recycle type elements

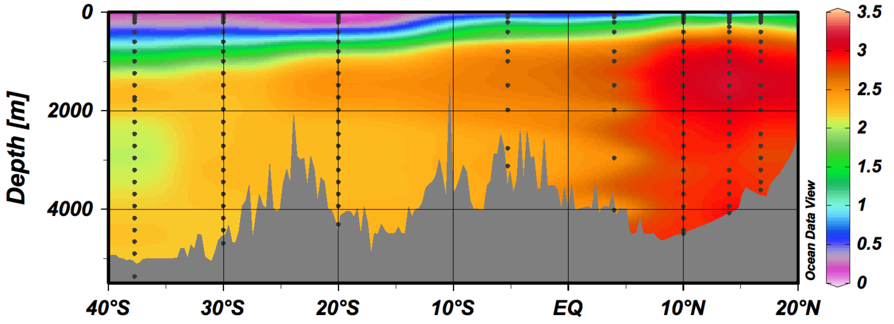

DNi [nmol/kg]


DCu [nmol/kg]


DZn [nmol/kg]


DCd [nmol/kg]

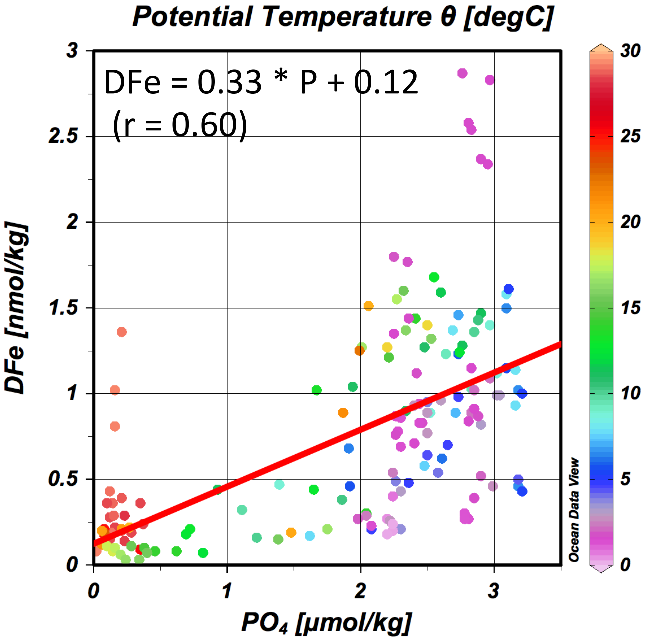

$Si(OH)_4$ [μmol/kg]

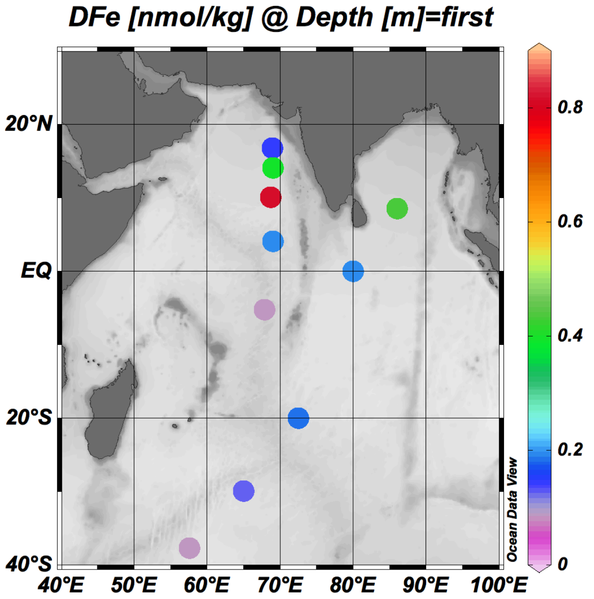

PO_4 [μmol/kg]

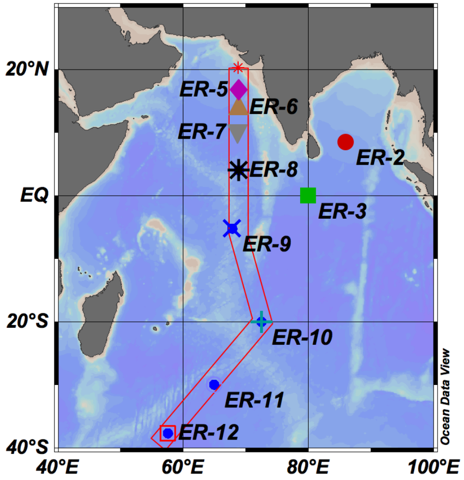
- dNi, dCu and dZn showed the strongest correlation with Si (*r* = 0.81-0.97)
- dCd showed the strongest correlation with P (*r* = 0.97)

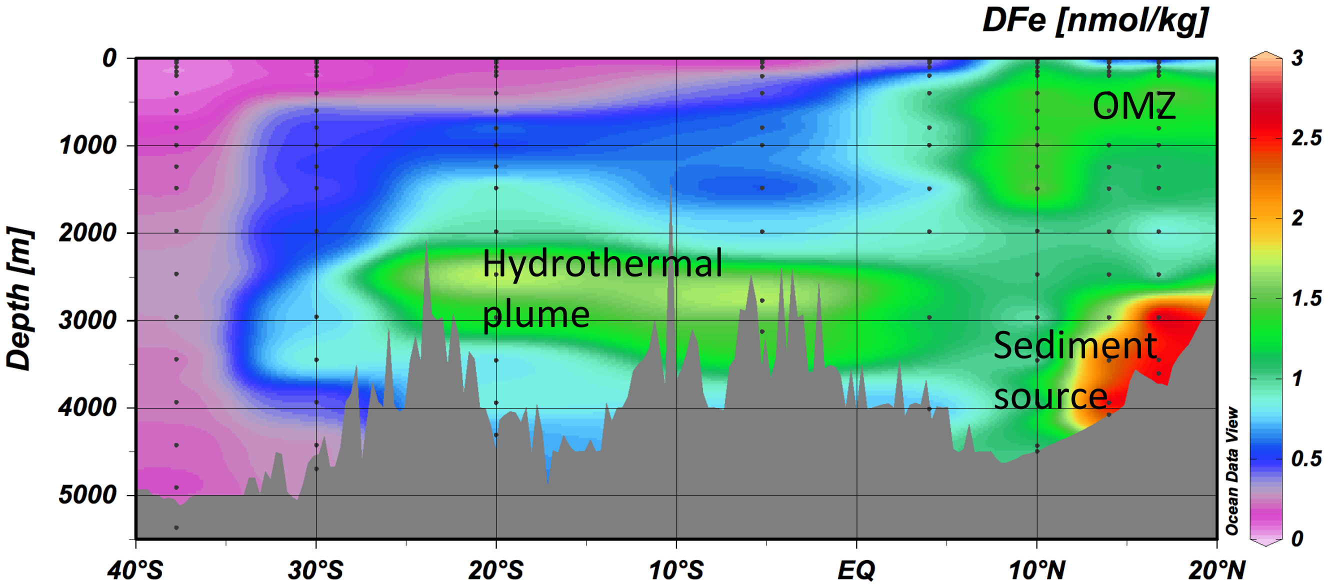
Recycled and scavenged-type: dFe

- dFe is depleted in surface water (< 0.8 nmol/kg), co-limiting production
- The distribution of dFe is controlled not only by biogeochemical cycling but also by local inputs and scavenging









Our presentations in Goldschmidt 2016

- Zheng, Linjie: 12d/241/Tu
  - Distributions of Dissolved Trace Metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) along 160°W in the Pacific Ocean

- Takano, Shotaro: 12d/14:00/We
  - Distributions of Nickel, Copper and Zinc Isotopes in the North Pacific Ocean

- Tsujisaka, Makoto: 12i/203/Th
  - Determination of the Stable Isotope Ratio of Molybdenum and Tungsten in Marine Sediments