Ocean – Trace Metals – Climate Coupling

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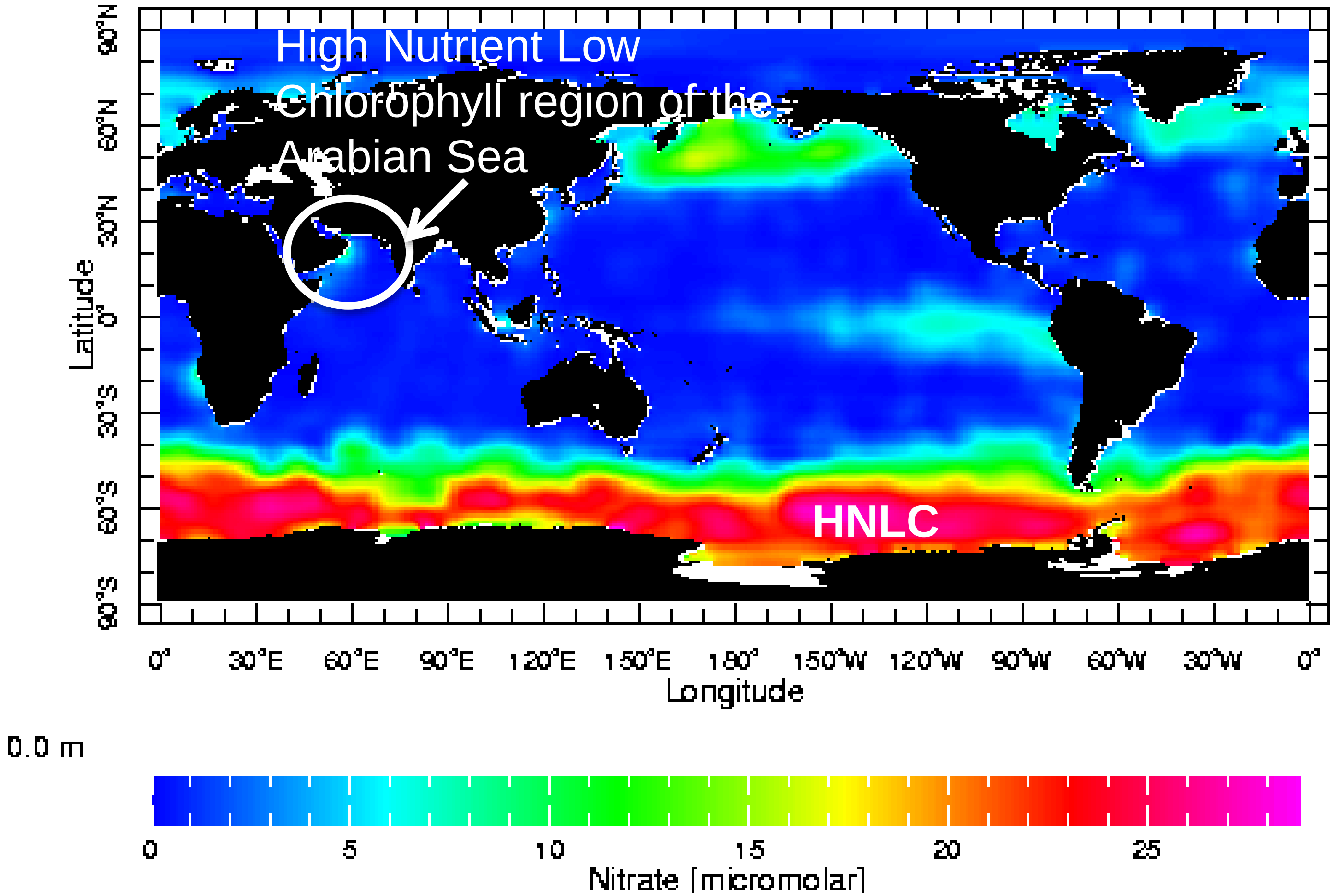
An International Study of the Marine Biogeochemical Cycles of Trace Elements and their Isotopes

Government of India
Ministry of Earth Sciences

TROPMET BHU 27 Oct 2018

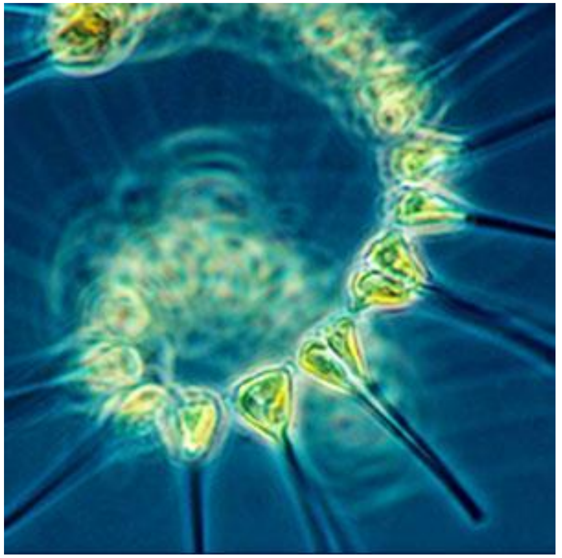
➢One of the major discoveries of last decade was the presence of HNLC (High Nutrient Low Chlorophyll) region in world Ocean.

➢The low productivity was found to be a result of deficiency of key trace elements, e.g.: Fe



- Trace elements serve as micronutrients and regulates marine ecosystem dynamics and carbon cycle
- They serve as paleo-oceanographic tracers

Ocean Productivity and climate



- Phytoplankton, tiny plants of the sea, are the life-sustaining force of our beautiful blue planet.
- They produce most of the oxygen we respire,
- Consume massive amounts of CO_2, and
- Feed ocean creatures

Importance of Trace Metals

- Phytoplankton need food to live, grow, and reproduce.
- Mostly carbon, nitrogen, silica and phosphorus.
- They also require metals like iron (Fe), zinc (Zn), and cadmium (Cd) to activate important cellular processes (such as photosynthesis).

- In seawater, these biologically-utilized metals are often present at extremely low concentrations,
- Photosynthesis is predicted to be limited by metal availability in ~40% of the ocean.
- The global carbon cycle, Earth's climate, our precious oxygen, and food for large population depend on the availability of metals in seawater.

Ocean Carbon Cycle and climate

Absorption of CO_2 from atmosphere

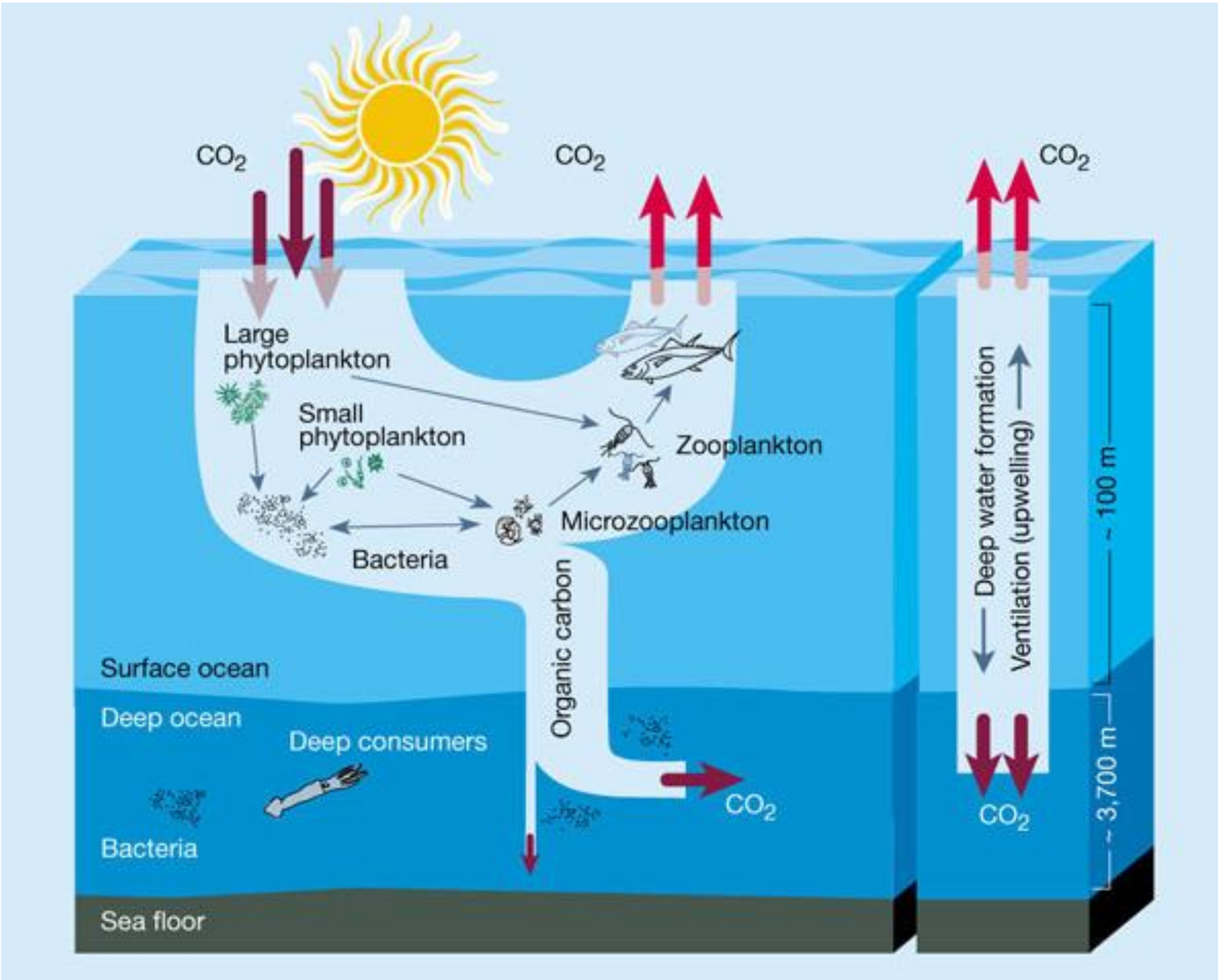
Biological Pump

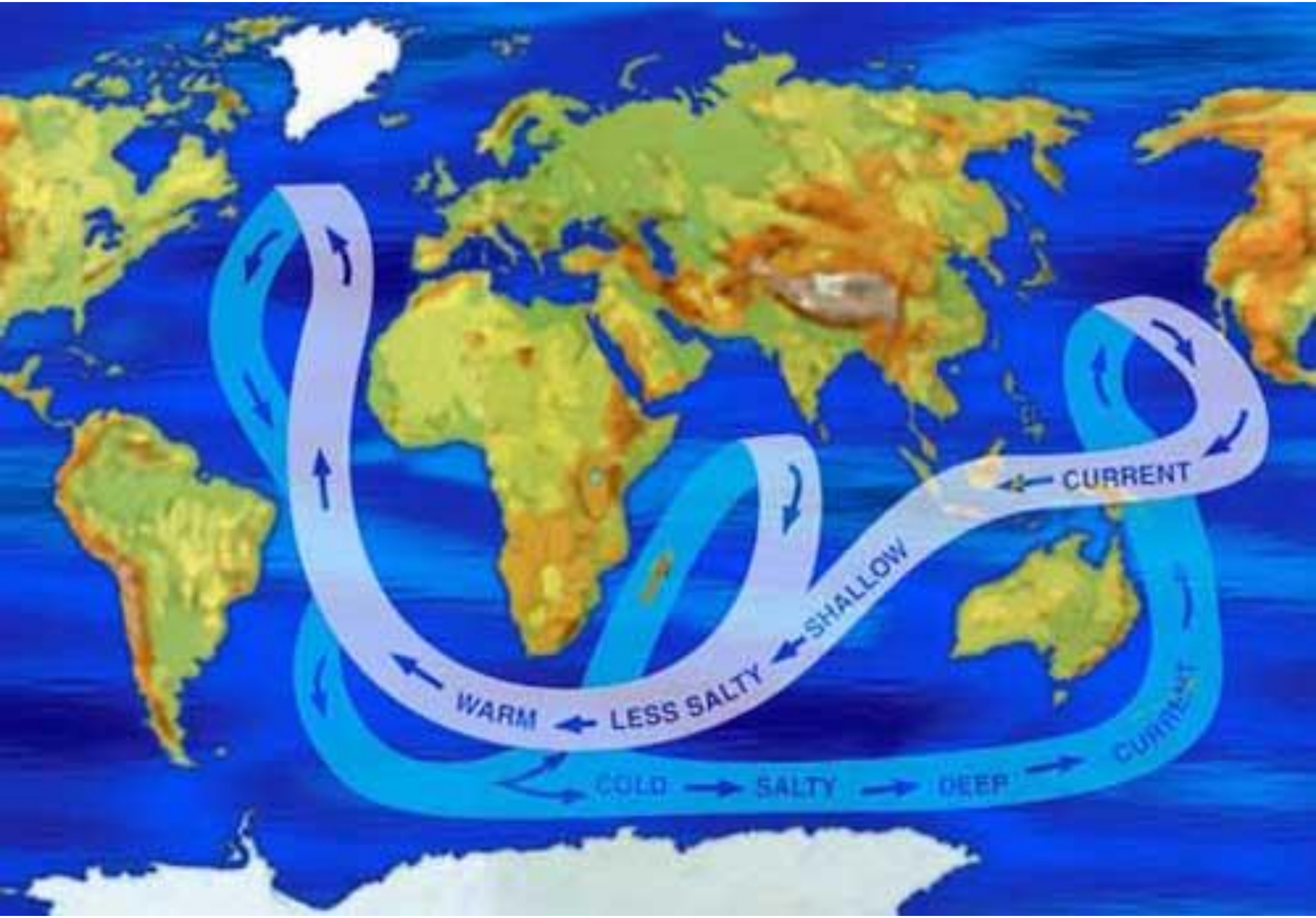
- Primary productivity
- Organic Carbon burial
- Removal of CO_2 from atmosphere

Physical Pump

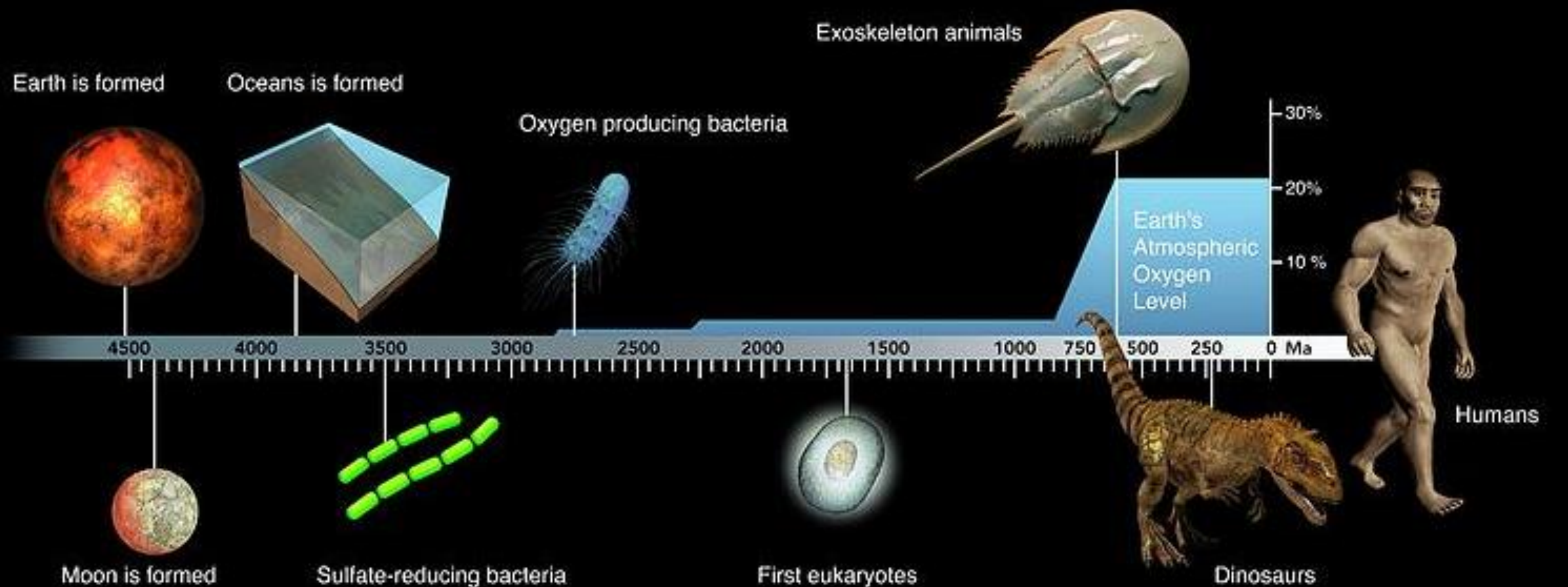
- CO2 solubility
- Transportation to deep water
- Degassing at equator

Ocean Biological Pump

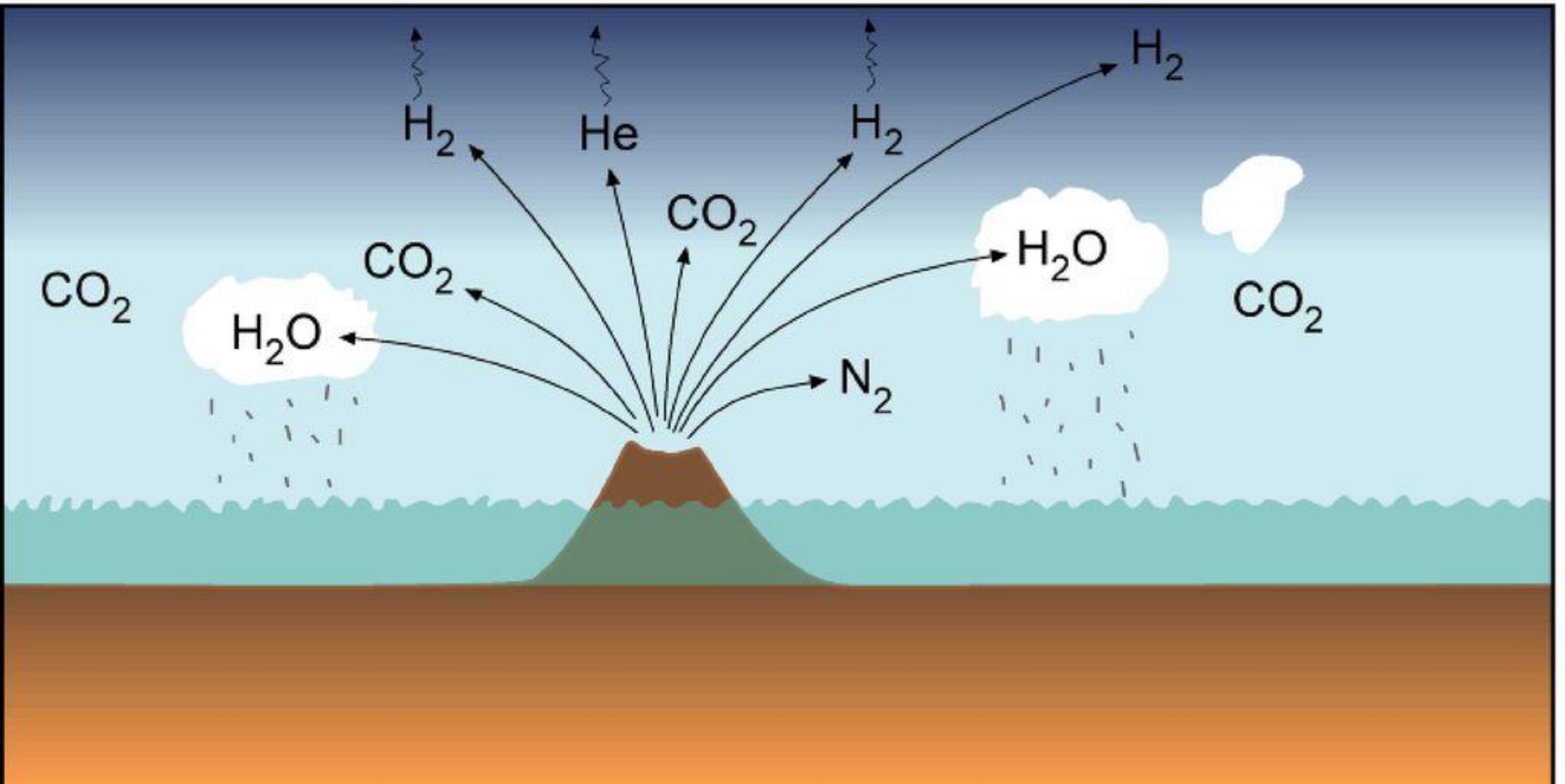



CURRENT
SHALLOW
LESS SALTY
WARM
COLD
SALTY
DEEP
CURRENT

Origin of Earth, Ocean and Atmosphere



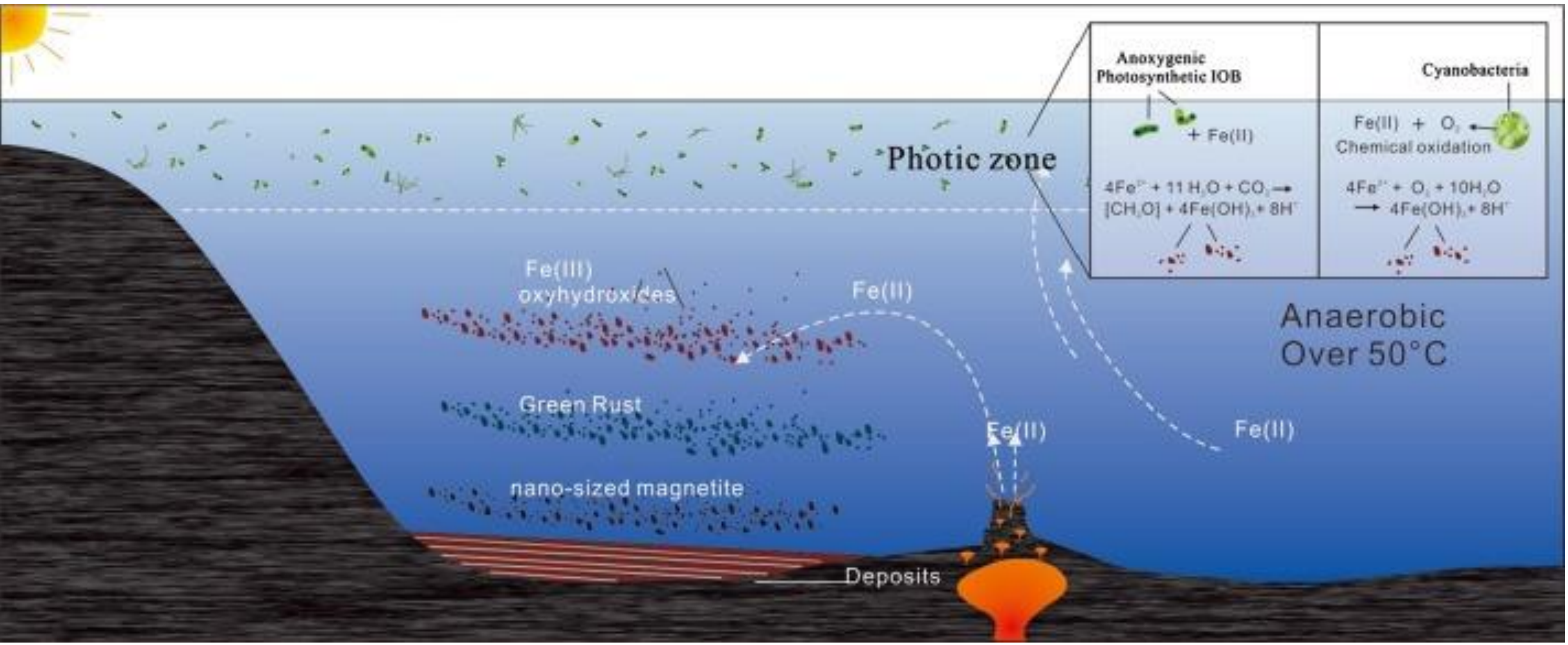
Volcanic **Outgassing** creates atmosphere (CO_2, CH_4, NH_3, H_2O)



Origin of the Oceans

- The earth is 4.6 billion years old
- The water that created the oceans came from:
  - Comets and meteorites: carry lots of water, which transferred to Earth upon impact
  - Volcanism: volcanic gas has mostly water vapor and carbon dioxide
    - The CO_2 and other gases formed the Earth's atmosphere
    - As the Earth cooled, the water vapor condensed, forming the oceans

Source of Fe to the early ocean: Hydrothermal



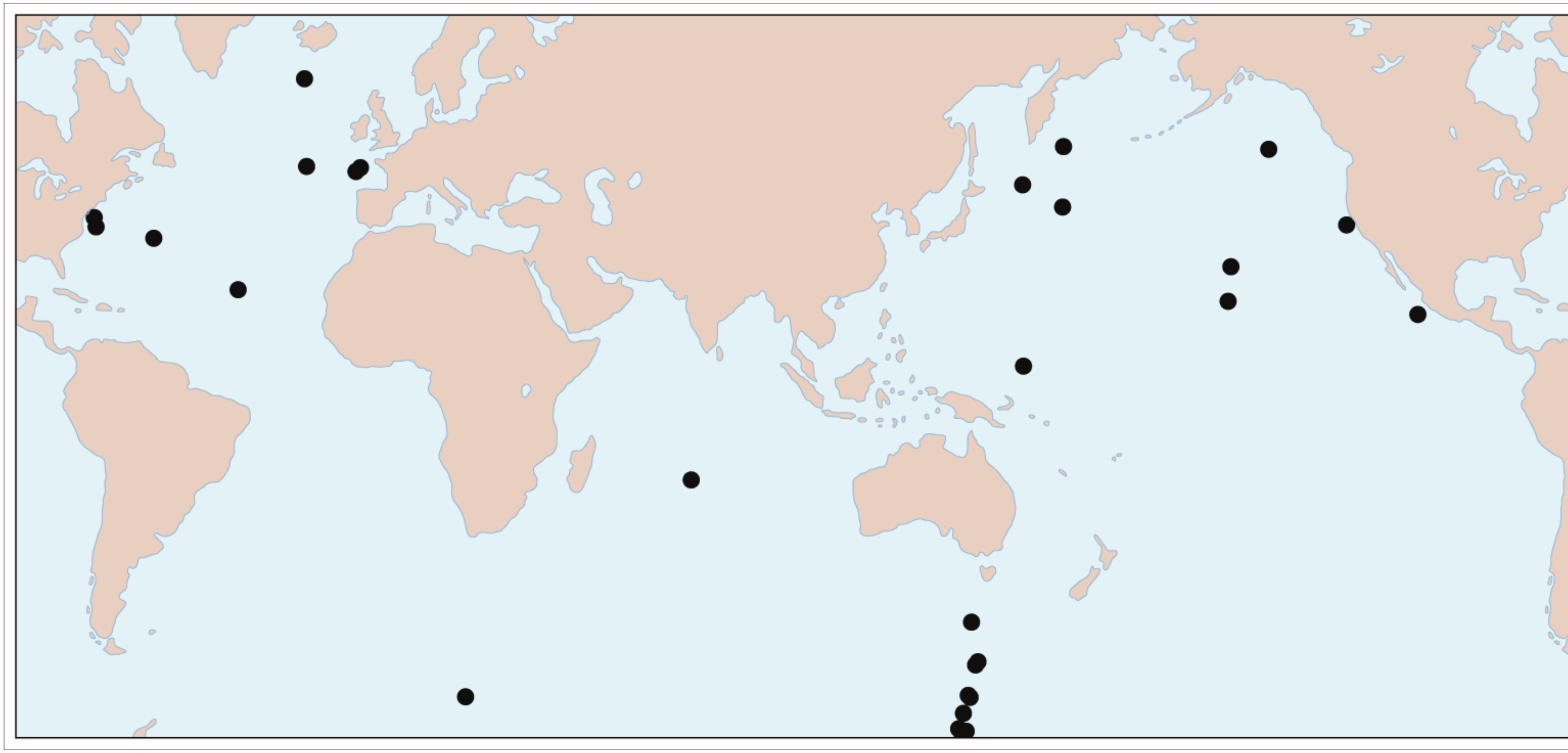
Fe Ocean

Present day oxygen levels
ATMOSPHERIC CHEMISTRY
Oxygen levels rise again to 15% of today's levels
Oxygen levels rise to 1-5% of today's levels
No oxygen in the atmosphere
OCEAN CHEMISTRY
No oxygen, dissolved iron
No oxygen, no iron. Hydrogen sulfide
Mostly oxygenated
4.6 billion Earth forms
3.8 billion First life in the oceans
2.7 – 1.8 billion Evolution of photosynthesising microbes
580 million
575 million First animals appear in the deep oceans
543-490 million Cambrian explosion. Diversification of life
Present day
YEARS

Important biogeochemical processes in the ocean and the trace metals thought to be fundamental to their action.

Biogeochemical process	**Important trace elements**
Carbon fixation	Fe, Mn
CO_2 concentration/acquisition	Zn, Cd, Co
Silica uptake – large diatoms	Zn, Cd, Se
Calcifiers – coccolithophores	Co, Zn
N_2 fixation	Fe, Mo (?V)
Denitrification	Cu, Fe, Mo
Nitrification	Cu, Fe, Mo
Methane oxidation	Cu
Remineralisation pathways	Zn, Fe
Organic N utilisation	Fe, Cu, Ni
Organic P utilisation	Zn
Formation of volatile species	Fe, Cu, V
Synthesis of photopigments	Fe and others
Toxicity	Cu, As (?Cd, Pb)

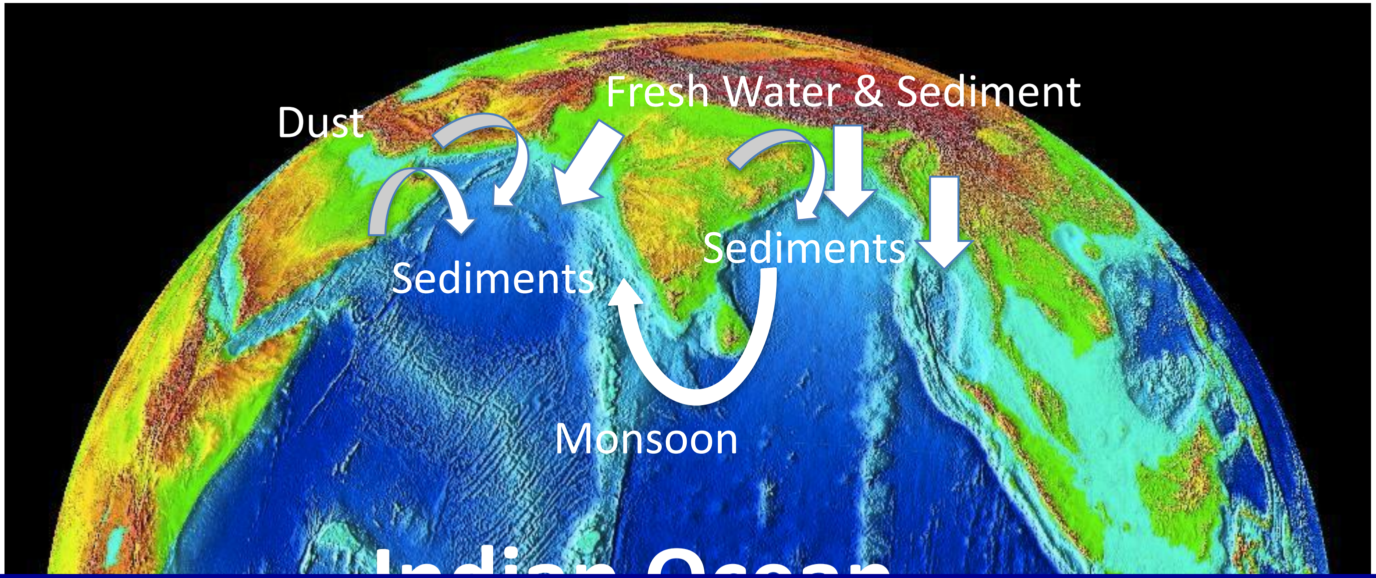
Deep ocean Fe data before GEOTRACES



Fe data is scarce, particularly in the deep ocean, limited understanding of the Fe cycle

Stations with Fe concentrations at depths > 2000 m in 2003
(taken from GEOTRACES Science Plan 2006)

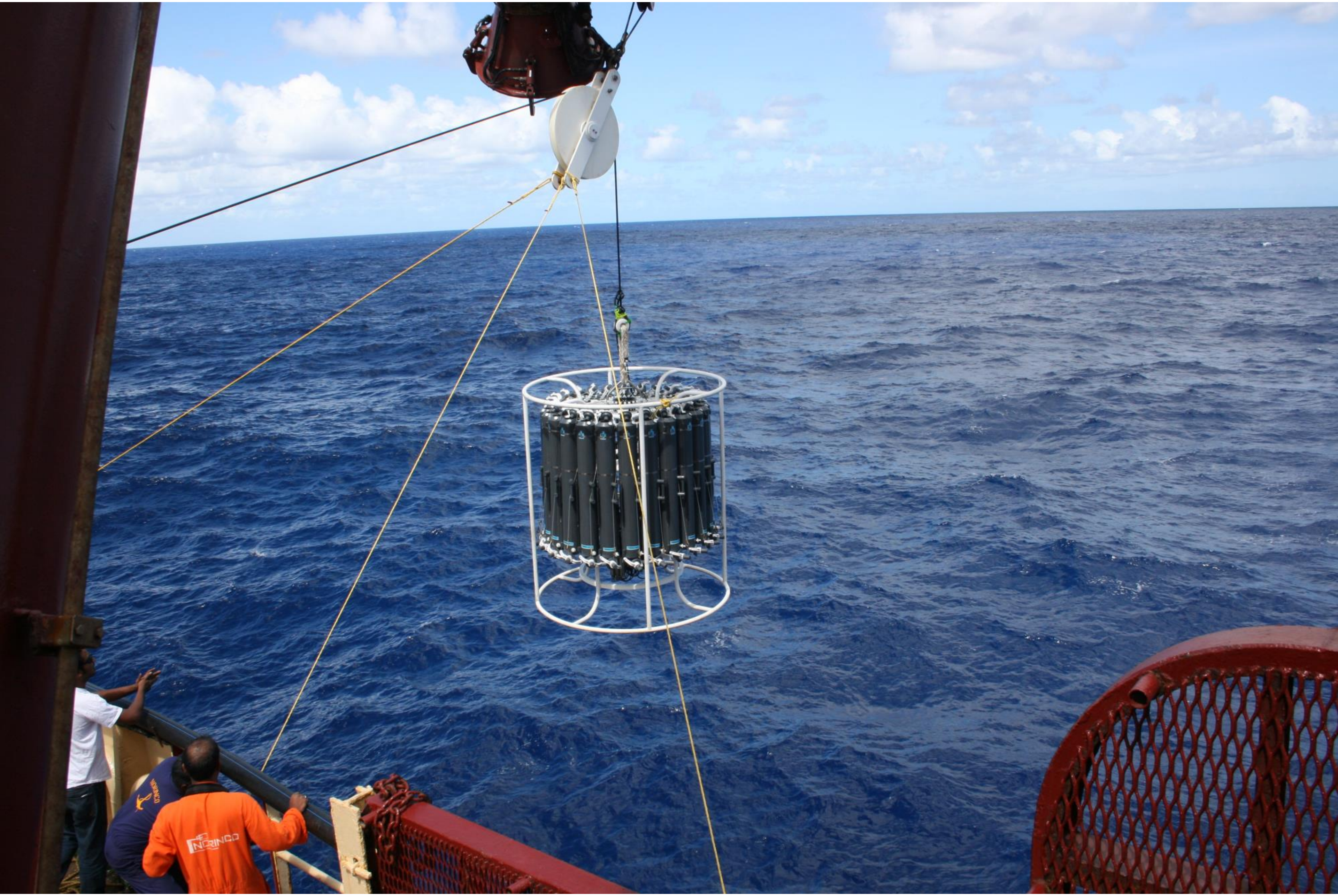
Indian Ocean: A Unique Basin

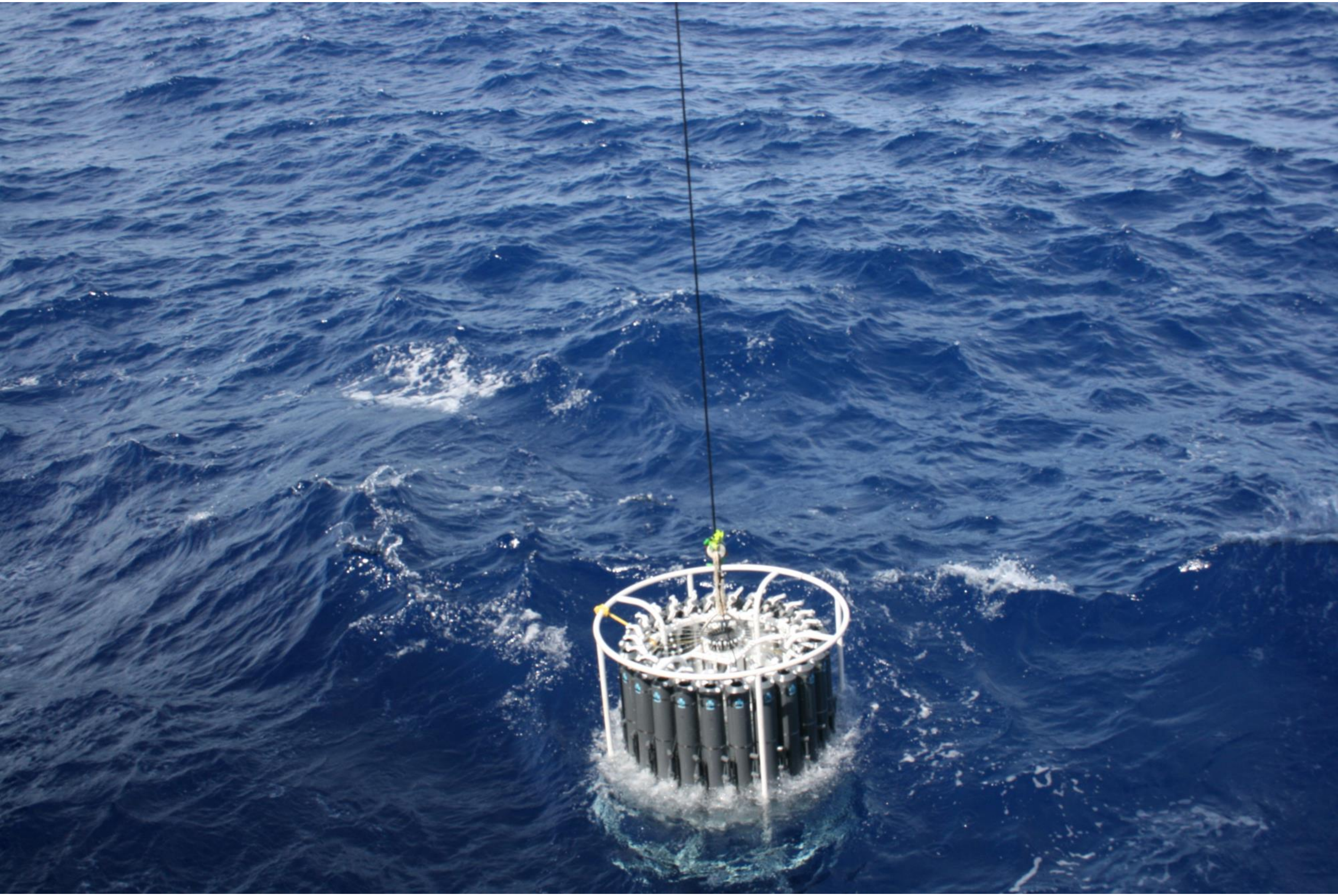


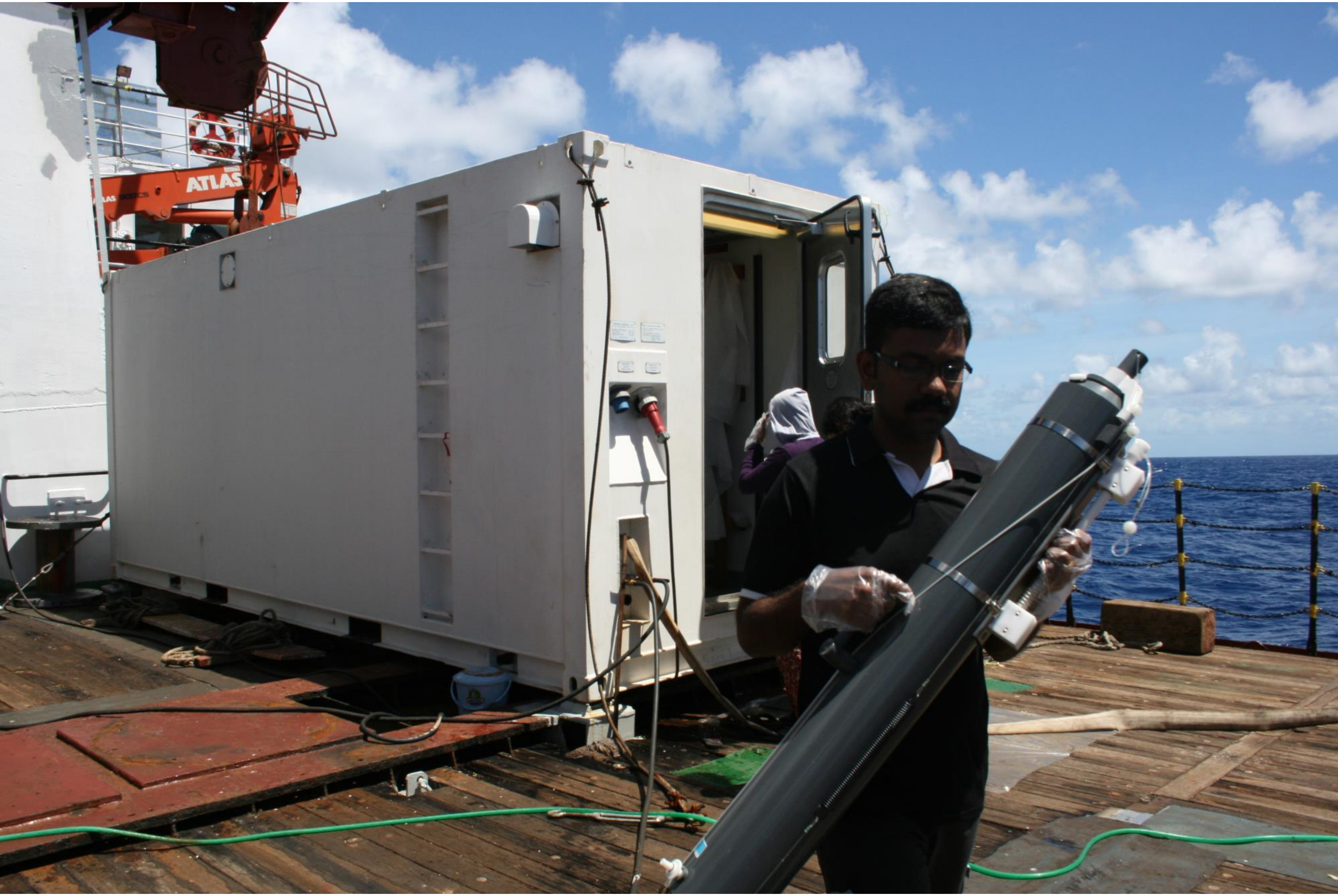
- Low-latitude land boundary to the north
- Low and high latitude exchange through Indonesian Throughflow (ITF) and Agulhas Current
- Three meridional ridges and a triple junction of three spreading centers.
- Subject to strong monsoonal wind forcing that reverses seasonally
- The boundary currents reverse seasonally with monsoon, impacting biogeochemical cycles and ecosystem response of the basin
- High productivity in the Arabian Sea resulting in a major denitrification / suboxic basin
- Bay of Bengal a natural laboratory of river-ocean interactions (water + particulate)
- Dust Input from nearby arid land-masses
- Large repository of detritus and authegenic sediments: archiving paleo-records
- Volcanism

GEOTRACES - India

- Technological Development
- Science






ATLAS


SDOM

FIRST 'GEOTRACES INDIA' MISSION TO STUDY INDIAN OCEAN GETS UNDER WAY | 5

SUNDAY TIMES OF INDIA, GOA
MARCH 3, 2013

Mission to study Indian Ocean begins

To Determine Distribution Of Selected Trace Elements, Isotopes In Marine Env

Krish Fernandes | TNN

Panaji: In a first Indian mission of its kind, a team of largely young researchers on Saturday set off from Mormugao port aboard the oceanographic research vessel (ORV) 'Sagar Kanya' on a 60-day Indian ocean mission to determine the distribution of selected trace elements and isotopes in the marine environment.

The project assumes significance as it will accurately determine many scientific properties of the Indian ocean. Sunil Singh, one of the two chief scientists for the mission, said it had been found that an earlier western study on the Indian ocean that had determined the neodymium levels was incorrect and this mission will attempt to accurately determine the levels of this and other trace elements.

Trace elements and isotopes play important roles in the ocean as nutrients and tracers of the contemporary and the past processes. They regulate ocean processes, such as marine ecosystem dynamics and carbon cycling. For instance, iron is a key micro-nutrient, the scarcity of which limits photosynthesis and nitrogen fixation. Sources, sinks and biogeochemical cycling of trace elements need to be understood to explain the spatial and temporal productivity variations in the global oceans.

The 'Geotraces India' project includes 28 researchers, including 7 women, hailing from 9 scientific research institutes such as the physical research laboratory (PRL) - Ahmedabad, national centre for Antarctic and ocean research (NCAOR), national institute of oceanography (NIO), ISER - Kolkata, universities of Tamil Nadu, Mangalore, Cochin, Pondicherry and Goa.

The Geotraces researchers will be collecting and testing ocean water and sediments at different locations in the ocean as part of the mission and special equipment such as an imported conductivity temperature versus depth (CTD) system to collect samples, and a metal-free clean room for testing will be utilised for the purpose. The mission will take the Sagar Kanya on a path towards Australia and the ship will make a port call at Jakarta in Indonesia on their return to Chennai.

S Rajan, director NCAOR which is a major partner for the mission, said "this is the most ambitious programme launched by NCAOR and PRL."

Ravi Bhushan, chief scientist for the first-leg of the cruise, said, "It is a big challenge, as it is unexpected for India to take up such a mission." He said the young research team augured well for the project as the young researchers will be able to carry on their work in this field in the coming years.

Shailesh Nayak, secretary, Union ministry of earth sciences, said this important programme will lead to new discoveries and new understanding of the processes that will come. It will help dispel the perception that the Indian ocean was a dead ocean as far as global climate goes, he added.

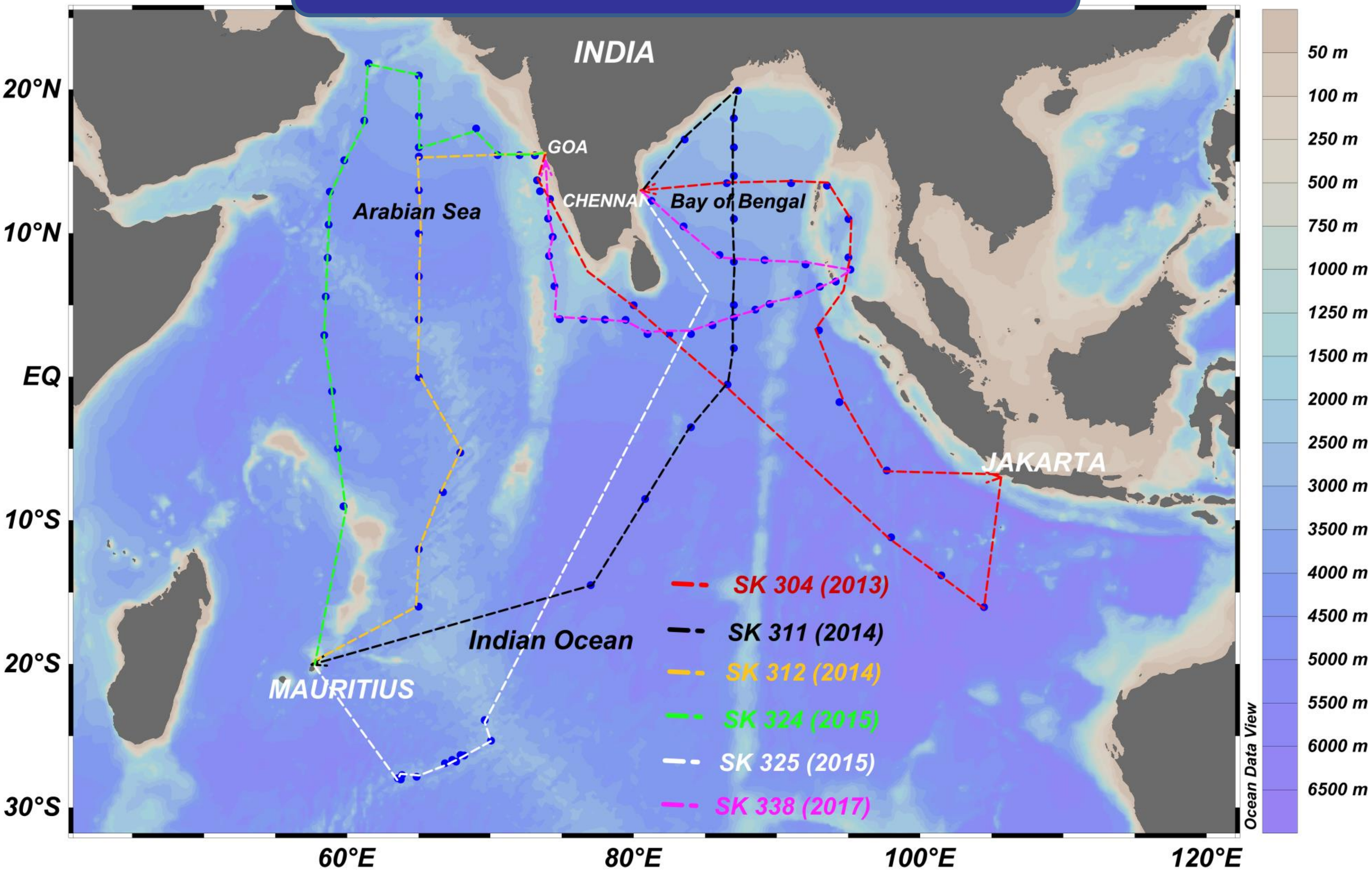
Most of the samples collected during the mission will be brought back for analysis to a NCAOR' completely metal-free clean laboratory that is being setup, said Thamban Meloth, programme director, NCAOR. The world-class facility will be the first of its kind in India and only the fourth in the world, said Nayak.

Latika N, from NCAOR, said she "will be analysing sediment cores for trace metals and see how they can be used as proxies, as well as measure isotopes." For Akhil P S, from Cochin university, the research he will undertake during the mission was part of his doctoral thesis, while M Murugamanthan from Pondicherry university, said he will be carrying out micro-fossil study in the Andaman sea.

Krish Fernandes

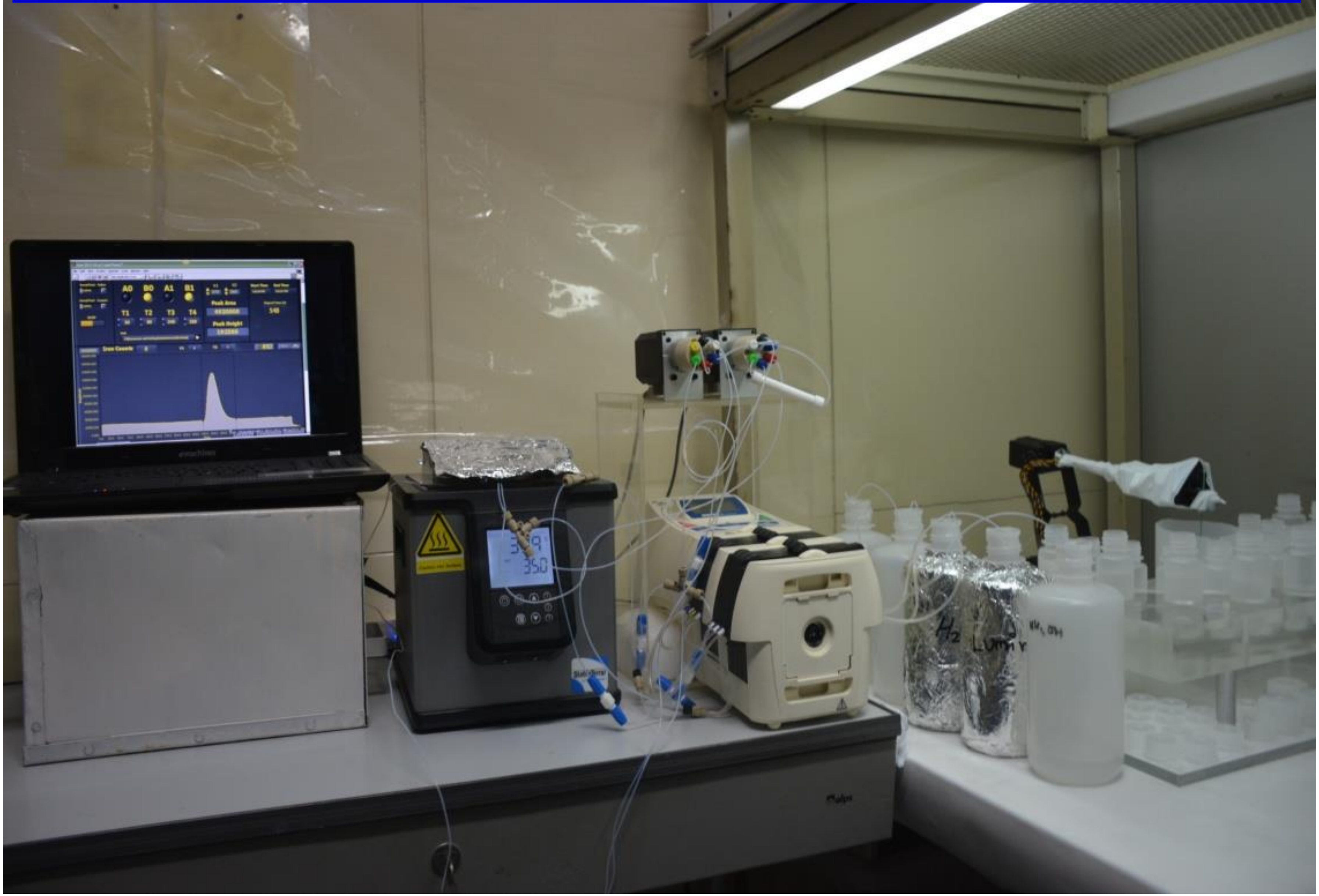
Trace elements and isotopes play important roles in the ocean as nutrients and tracers of the contemporary and the past processes

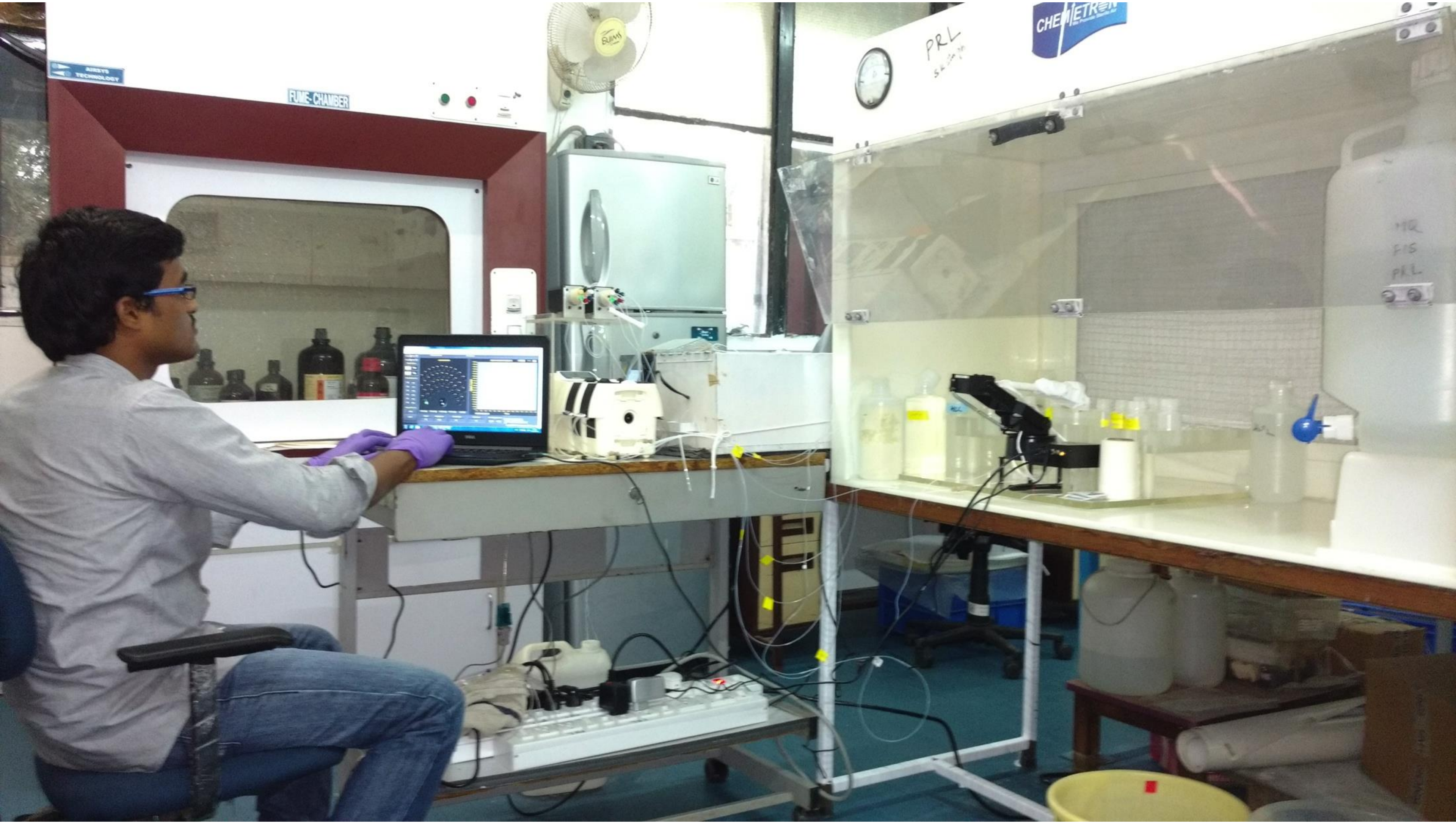
GEOTRACES - INDIA



DFe In Seawater

Flow Injection System for determination of Dissolved Fe at ppt level





ONLY 5-6 Labs worldwide have capability to measure seawater Fe

SAFe and GEOTRACES Standards

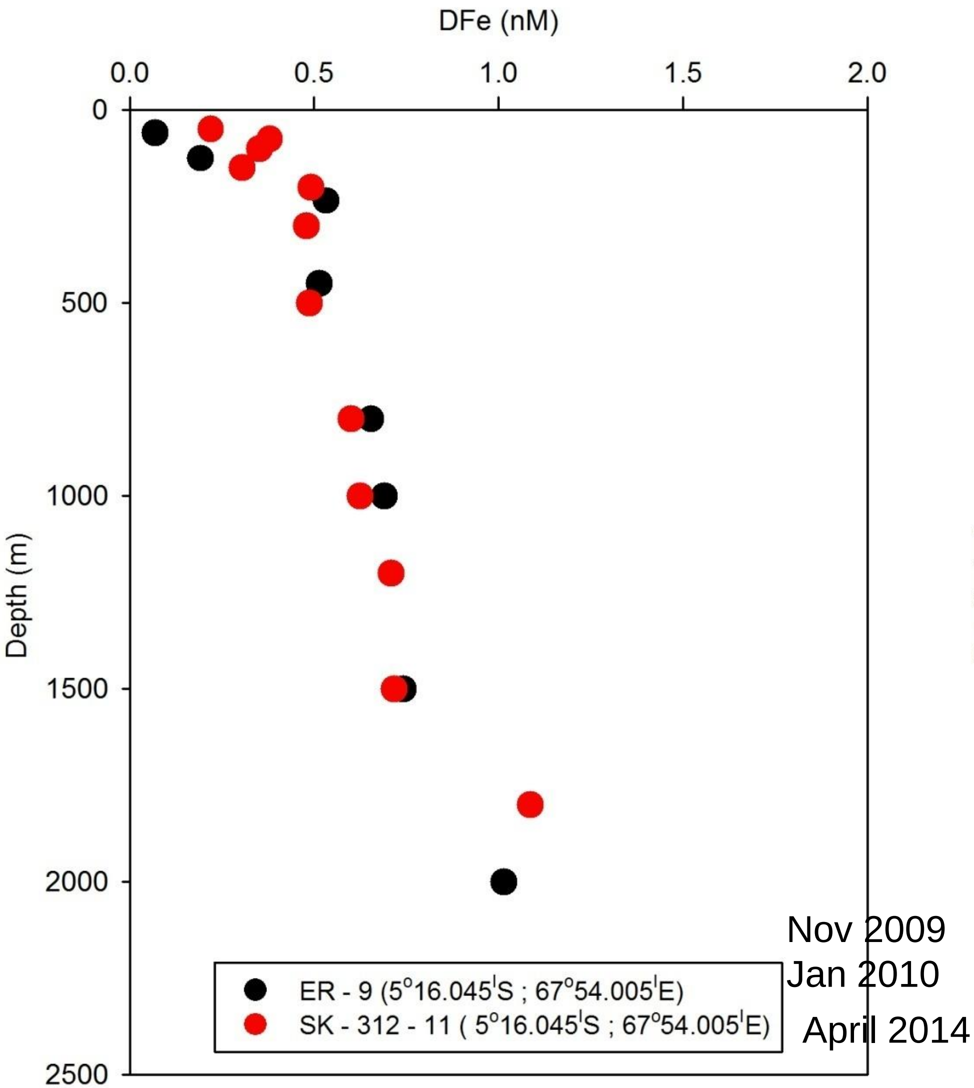
✓University of California Santacruz provided reference standards for iron in seawater.

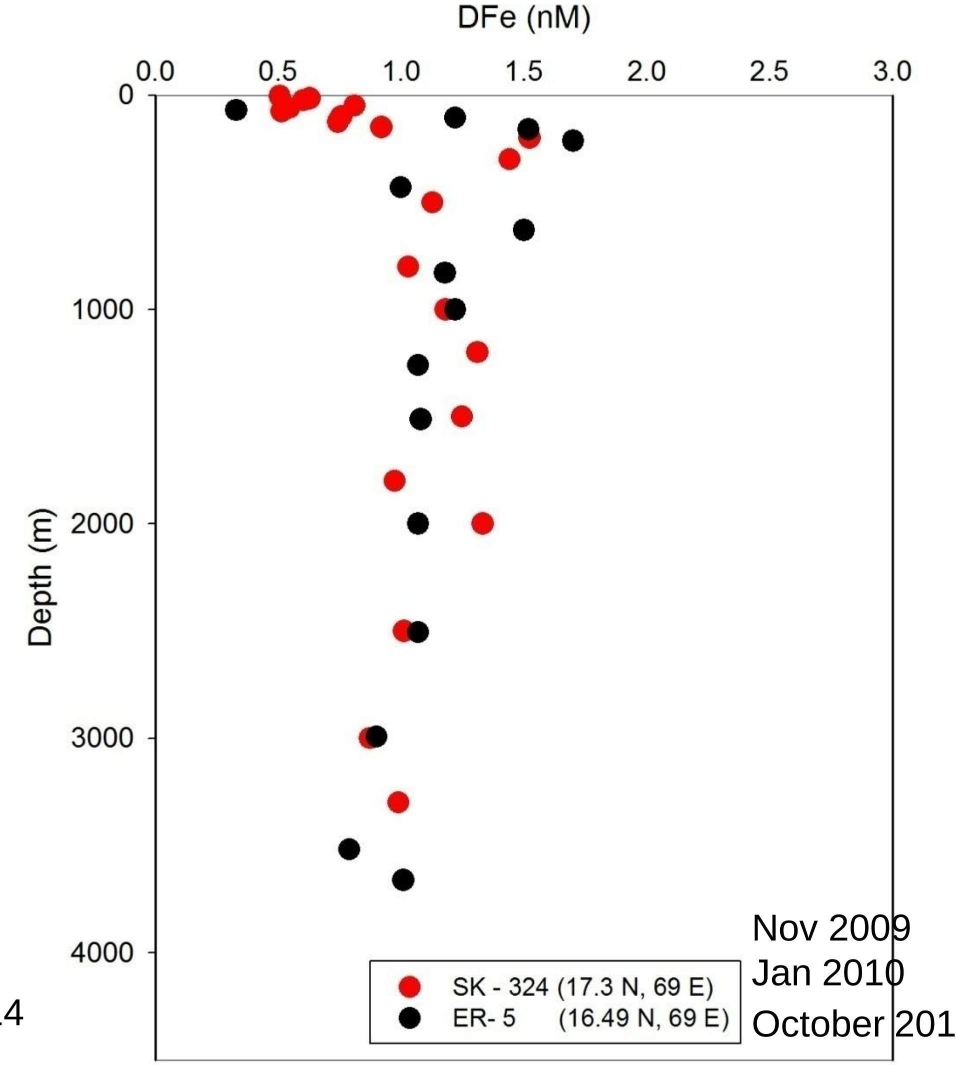
✓Samples were collected at North Atlantic,North Pacific Ocean (30° N, 140° W).

Std Name	Consensus Value	PRL Value
GS	0.546 ± 0.046 nM	0.53 ± 0.03 nM (n =15)
GD	1 ± 0.1 nM	0.97 ± 0.07 nM (n =7)
SAFe - D_1	0.67 ± 0.04 nM	0.65 ± 0.03 nM (n = 7)
SAFe - D_2	0.91 ± 0.1 nM	0.93 ± 0.04 nM (n = 9)

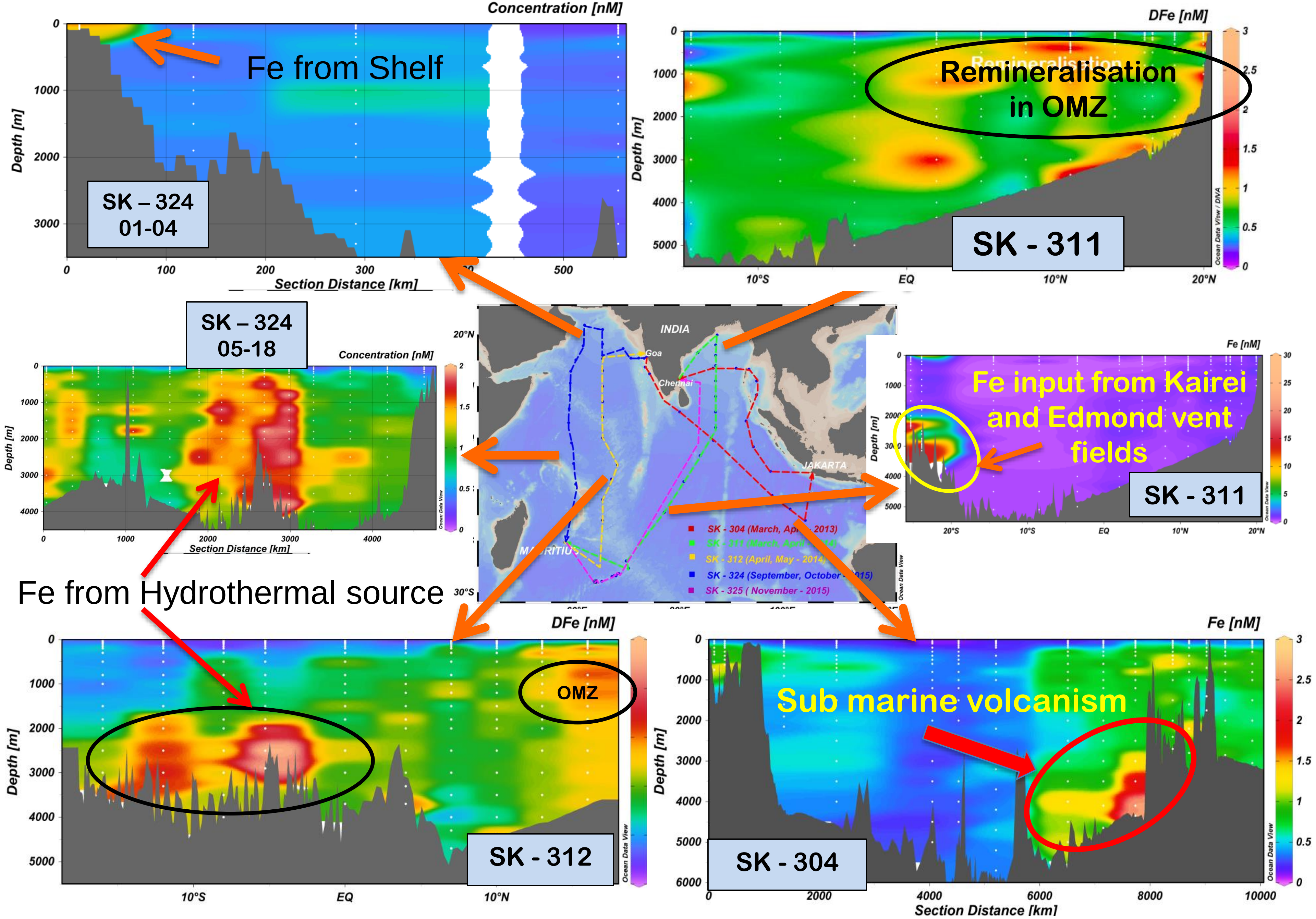
GS – Geotraces Surface, GD – Geotraces deep
SAFe – Sampling and analysis for Iron

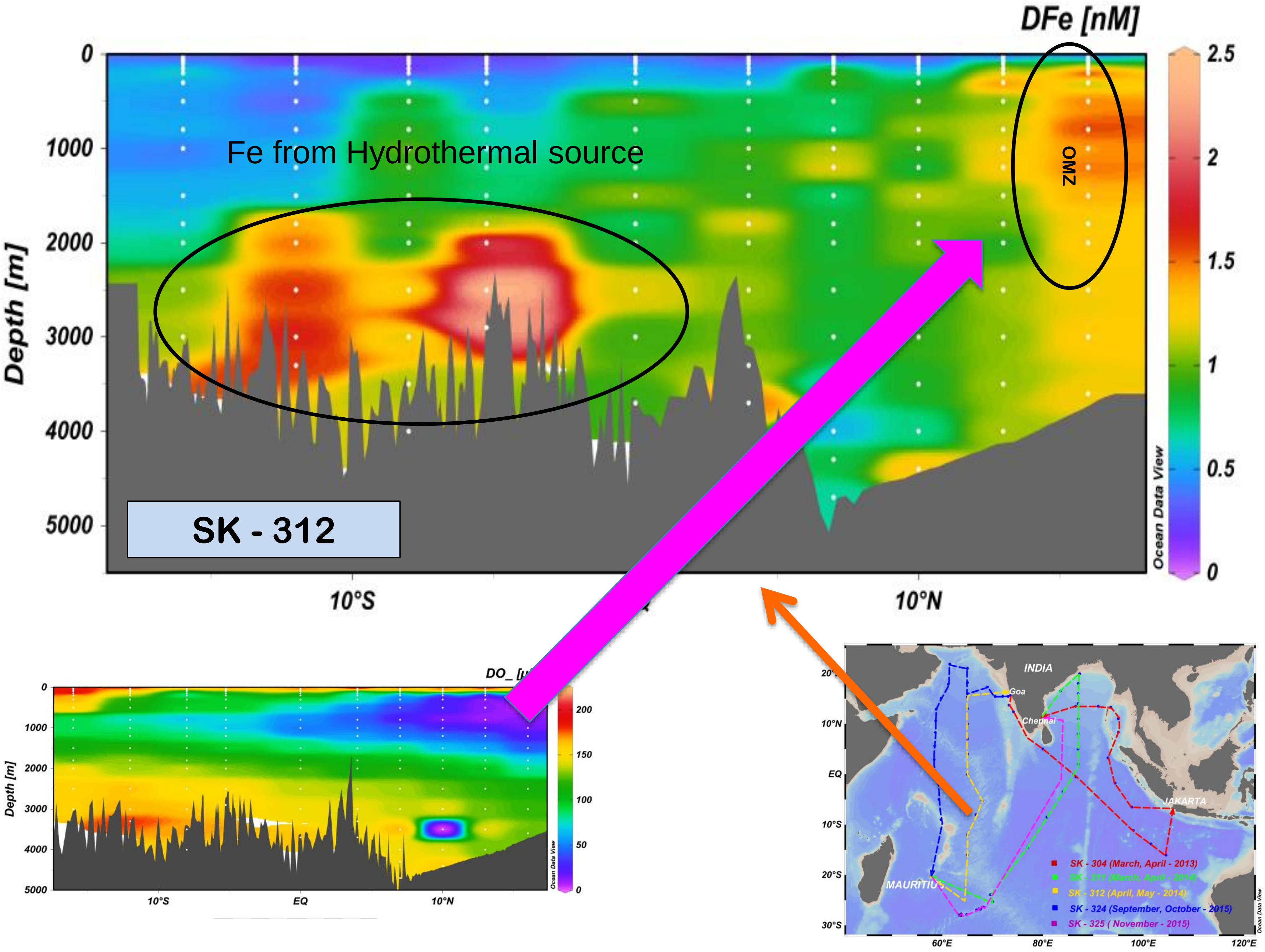
Japanese Cross over

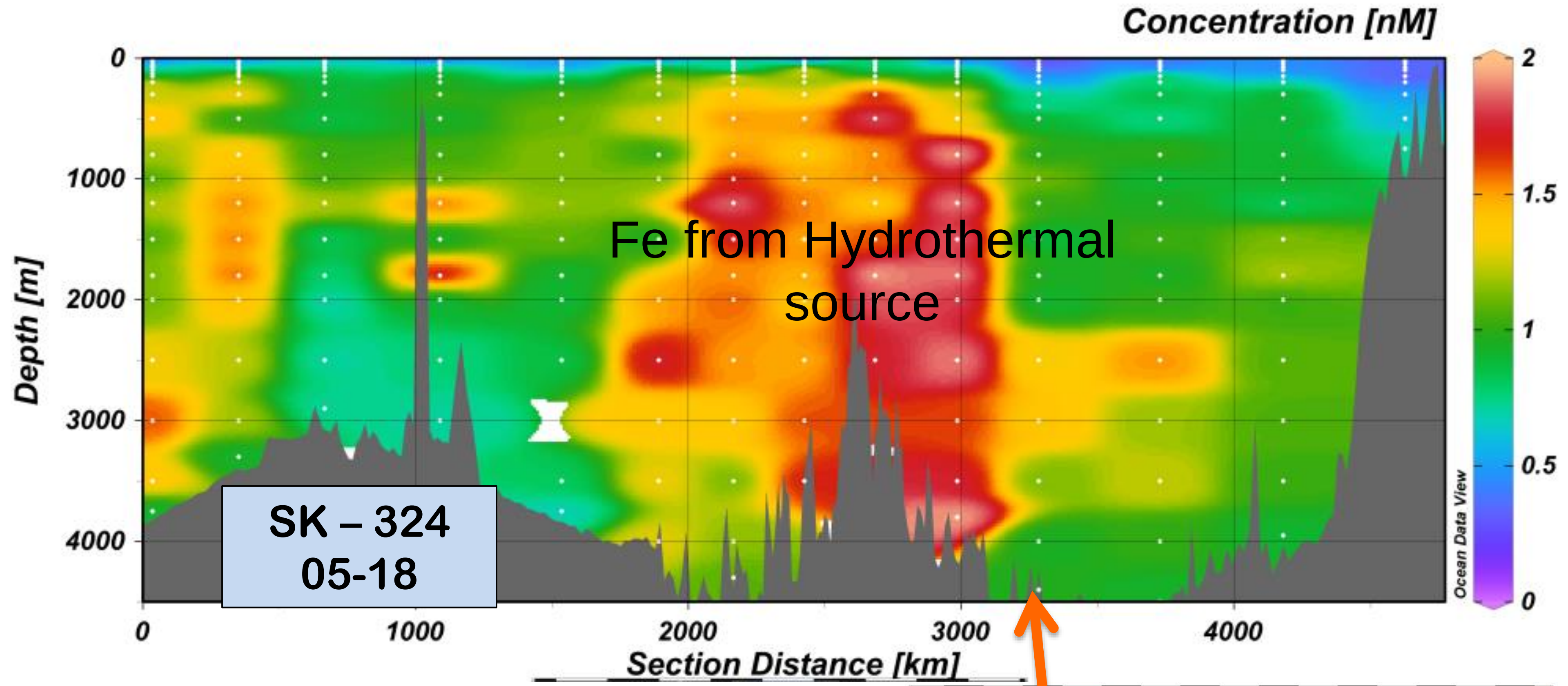


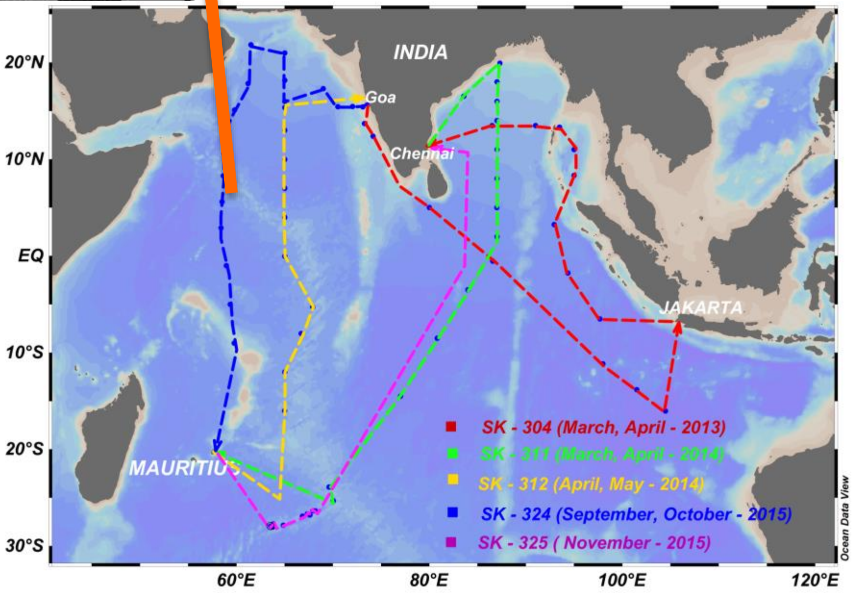


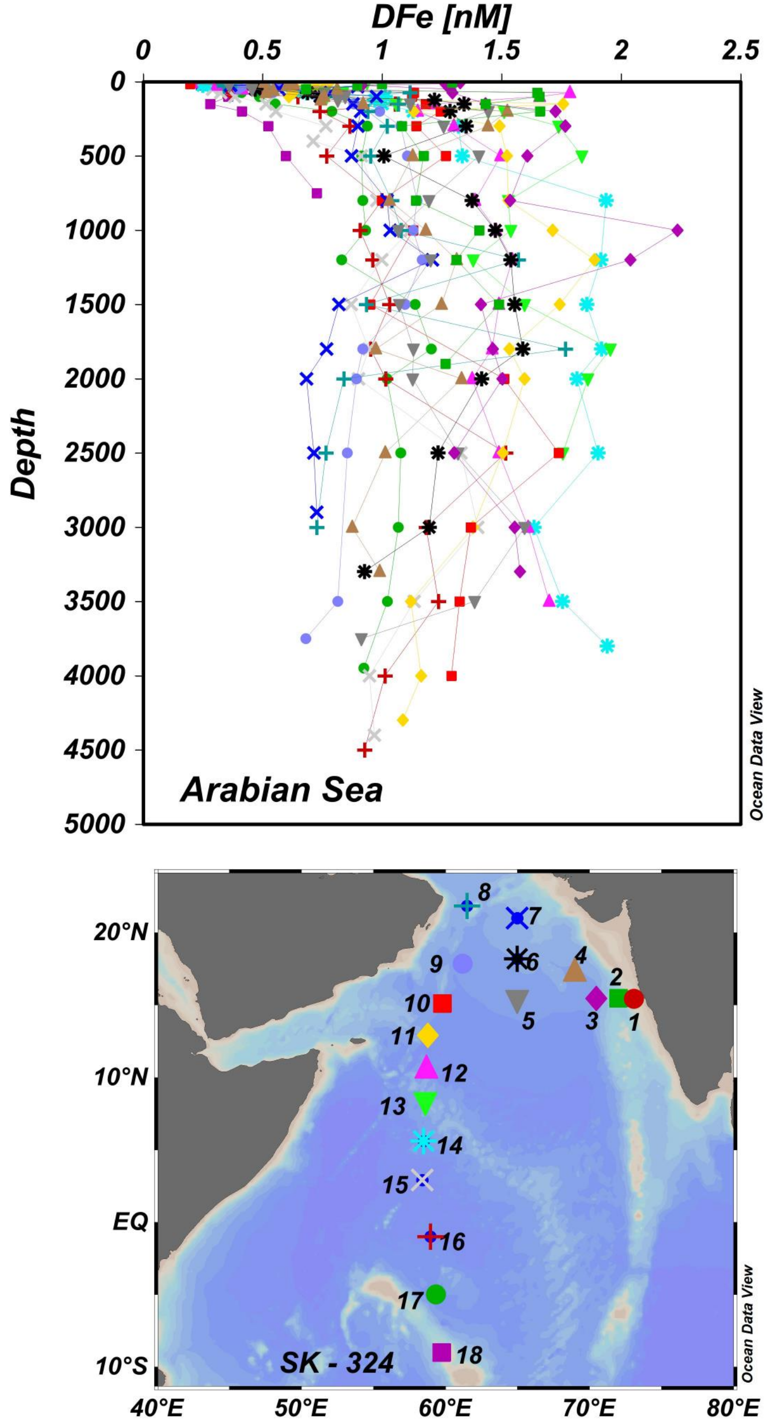
Sources of Dissolved Fe in the Indian Ocean and productivity



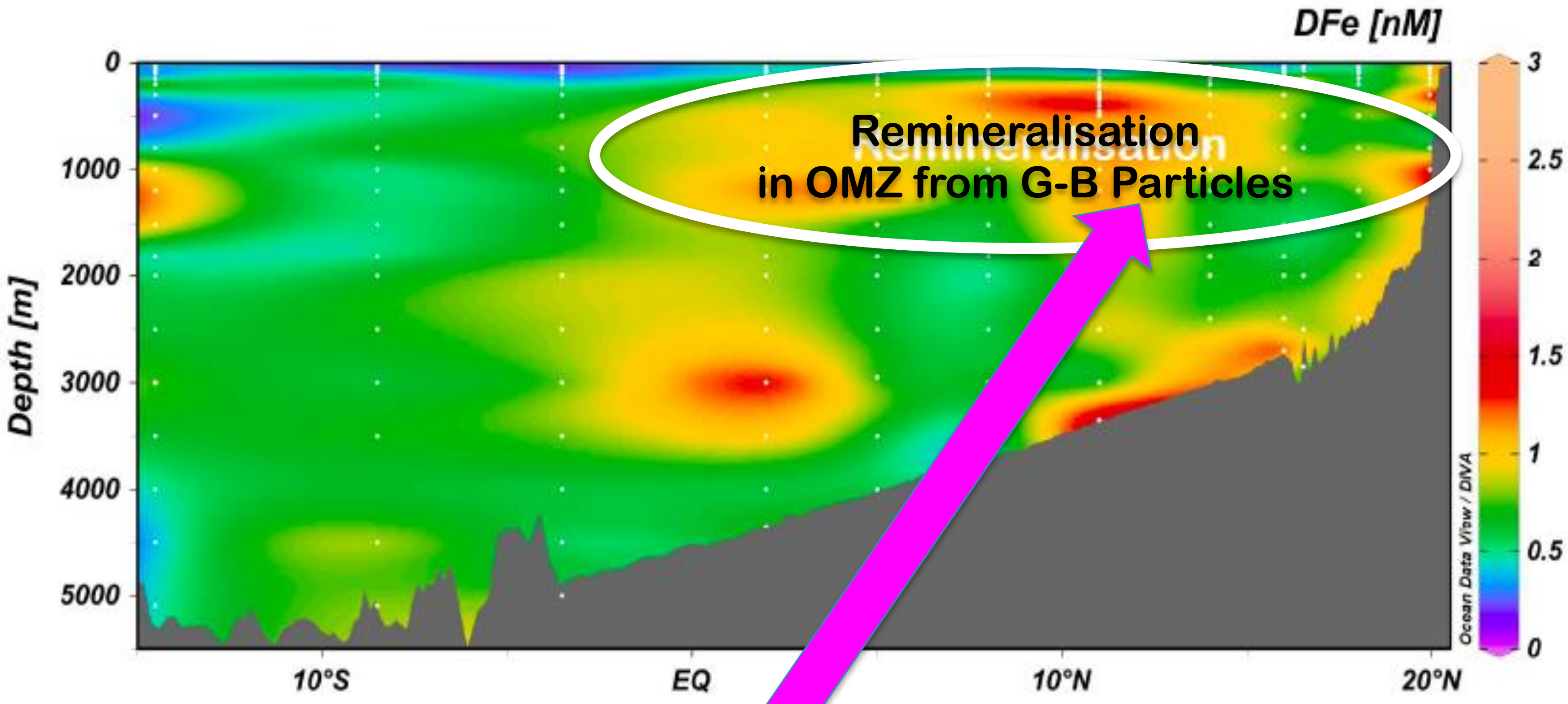

DFe [nM]
Depth [m]
0
1000
2000
3000
4000
5000
10°S
10°N
2.5
2
1.5
1
0.5
0
Ocean Data View
Fe from Hydrothermal source
OMZ
SK - 312
DO_ [µ
200
150
100
50
0
10°S
EQ
10°N
INDIA
Goa
Chennai
JAKARTA
MAURITIUS
20°N
10°N
EQ
10°S
20°S
30°S
60°E
80°E
100°E
120°E
SK - 304 (March, April - 2013)
SK - 311 (March, April - 2014)
SK - 312 (April, May - 2014)
SK - 324 (September, October - 2015)
SK - 325 (November - 2015)

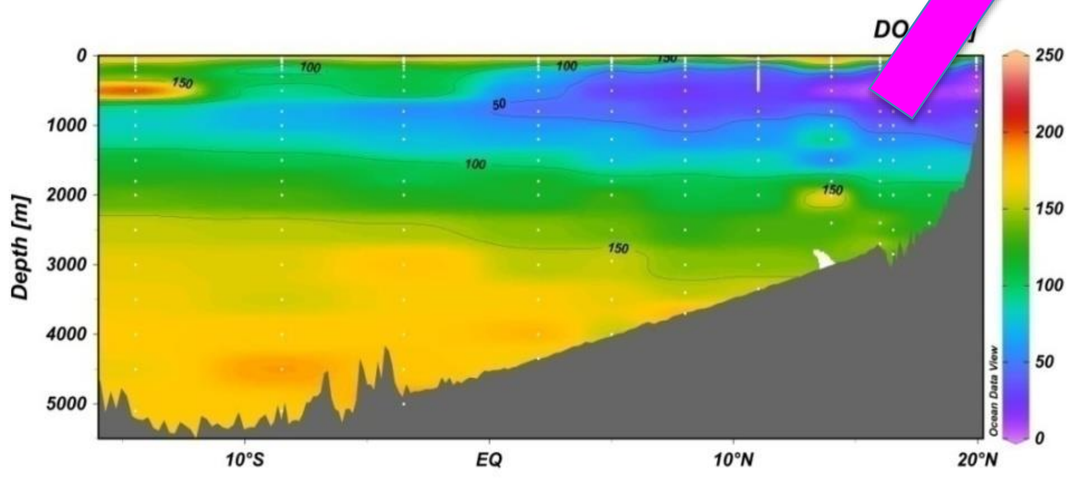

Concentration [nM]
Depth [m]
Section Distance [km]
Fe from Hydrothermal source
SK – 324
05-18
Ocean Data View

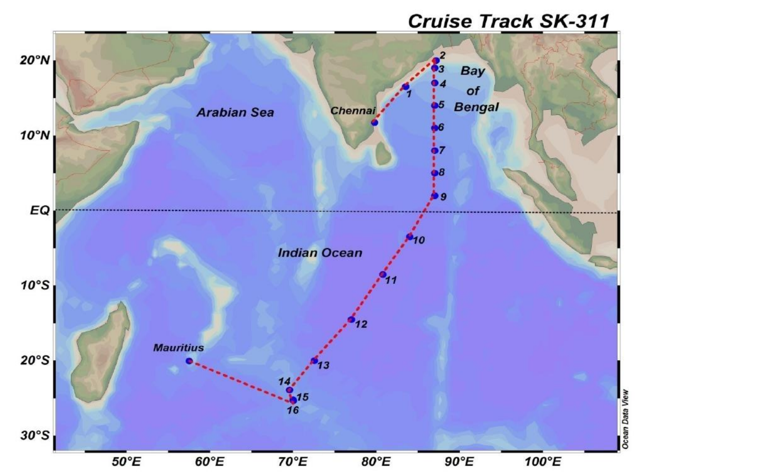

INDIA
Goa
Chennai
JAKARTA
MAURITIUS
SK - 304 (March, April - 2013)
SK - 311 (March, April - 2014)
SK - 312 (April, May - 2014)
SK - 324 (September, October - 2015)
SK - 325 (November - 2015)
Ocean Data View


DFe [nM]
0
0.5
1
1.5
2
2.5
Depth
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Arabian Sea
Ocean Data View
20°N
10°N
EQ
10°S
40°E
50°E
60°E
70°E
80°E
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
SK - 324
Ocean Data View

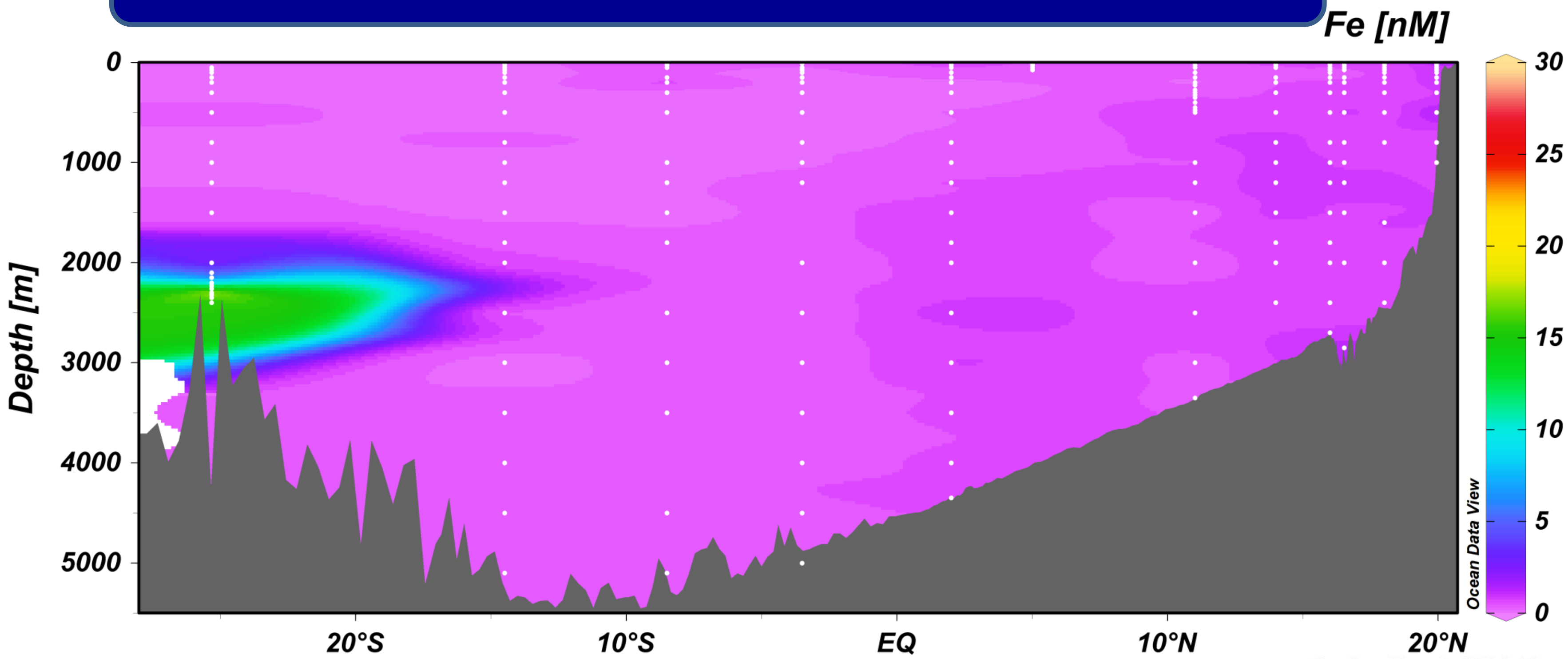
Dissolved Fe in the Bay of Bengal

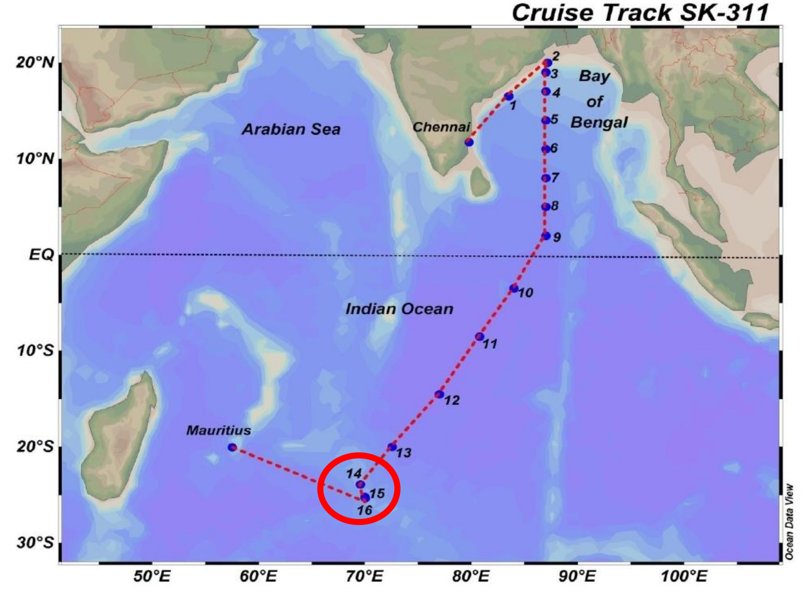






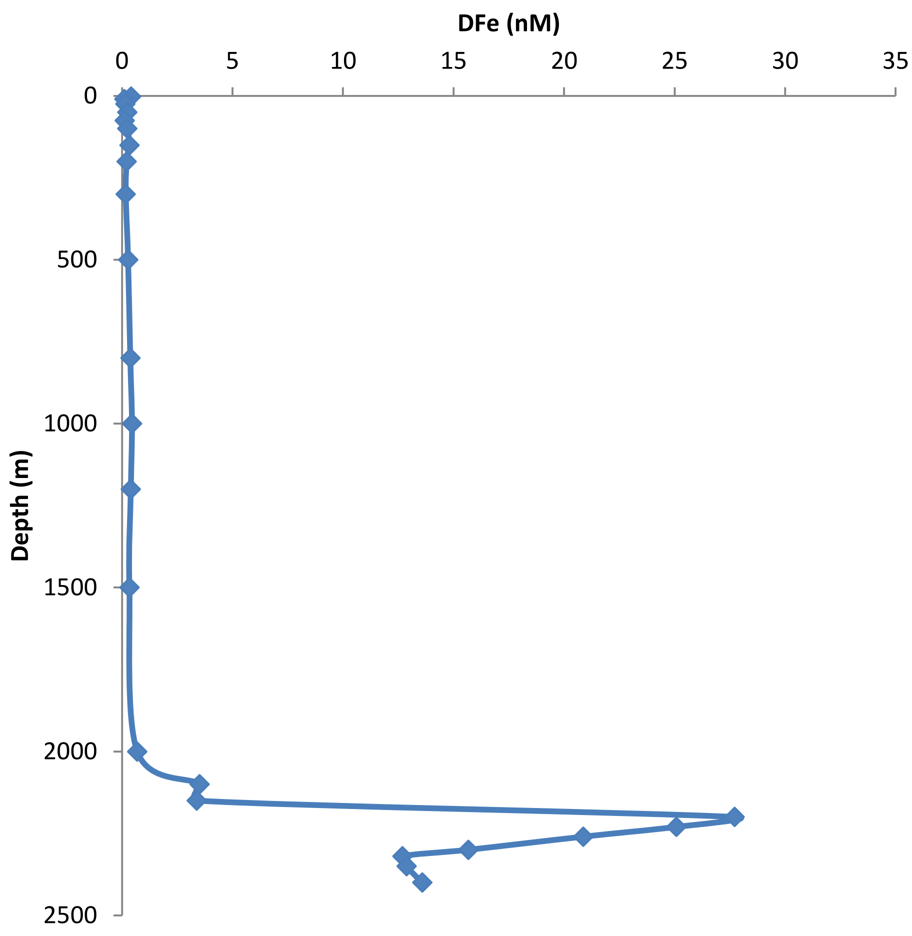
SK – 311 including Hydrothermal station

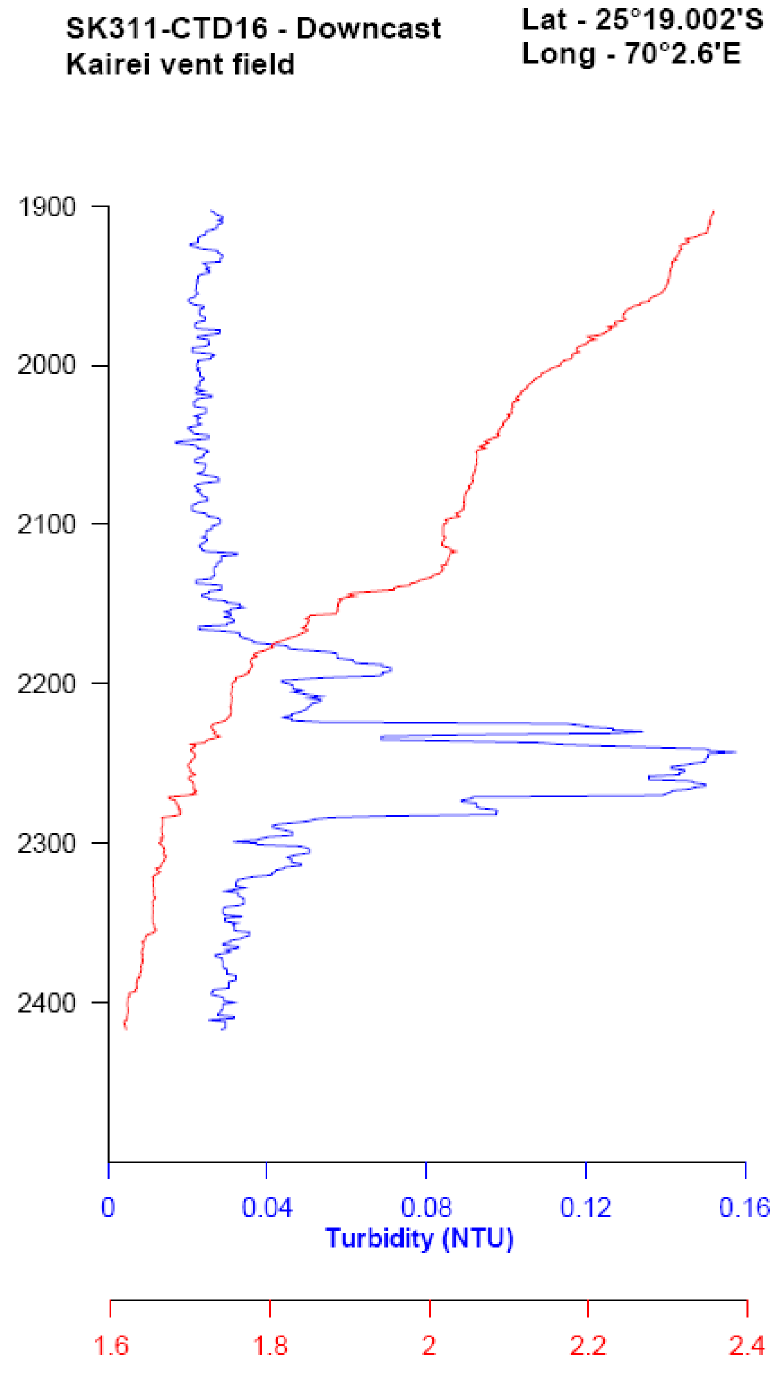




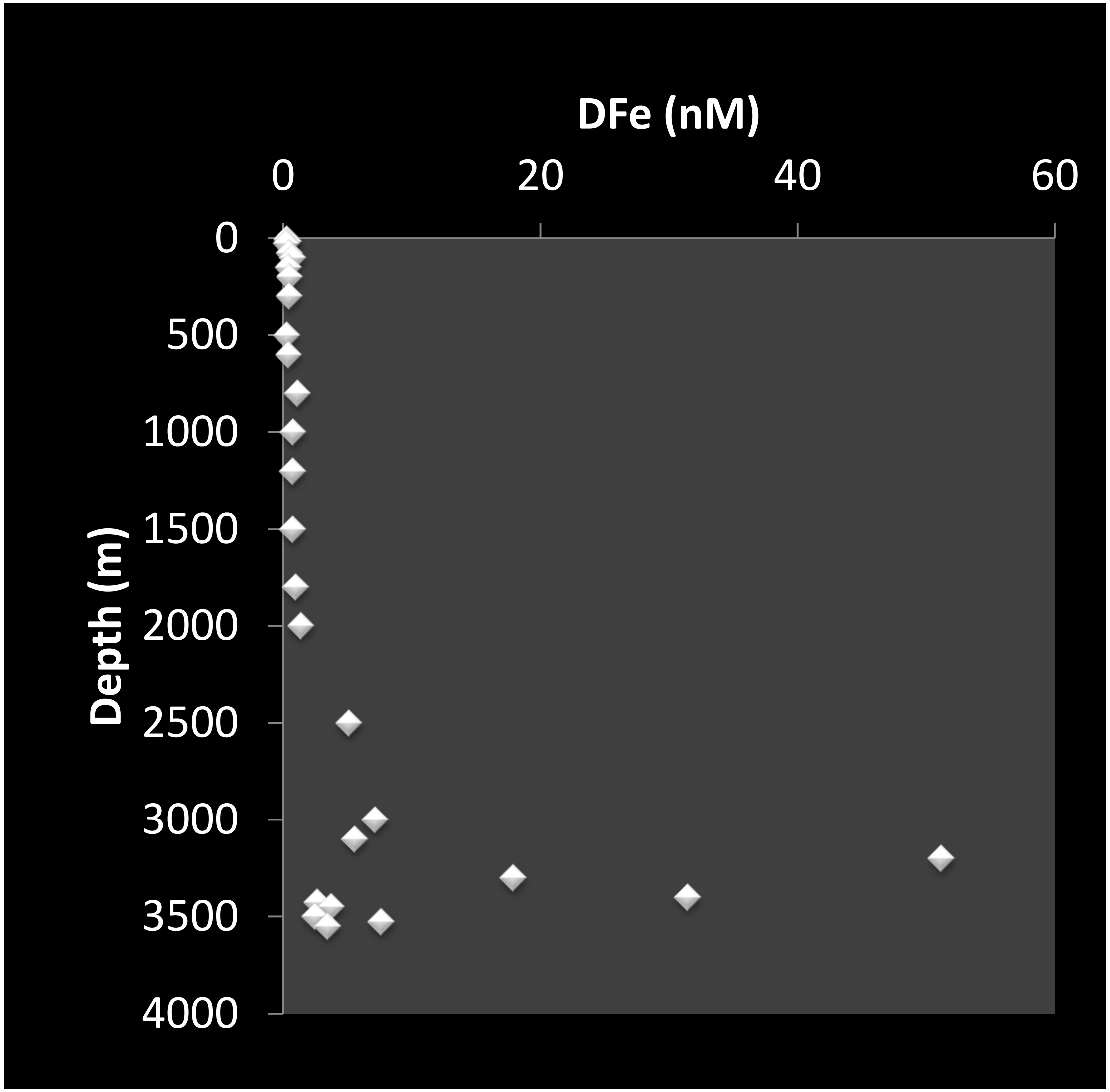
- Hydrothermal Source

SK – 311
Hydrothermal station



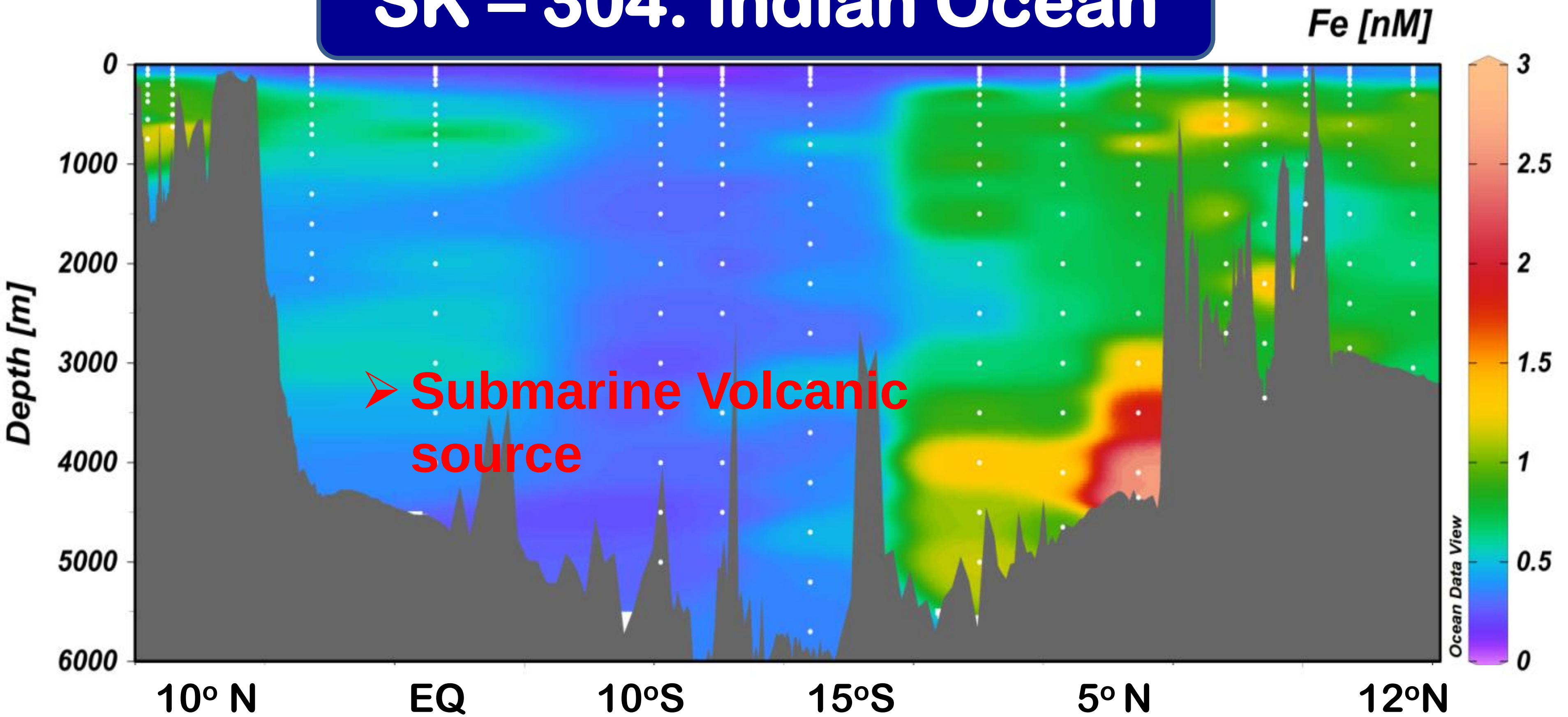


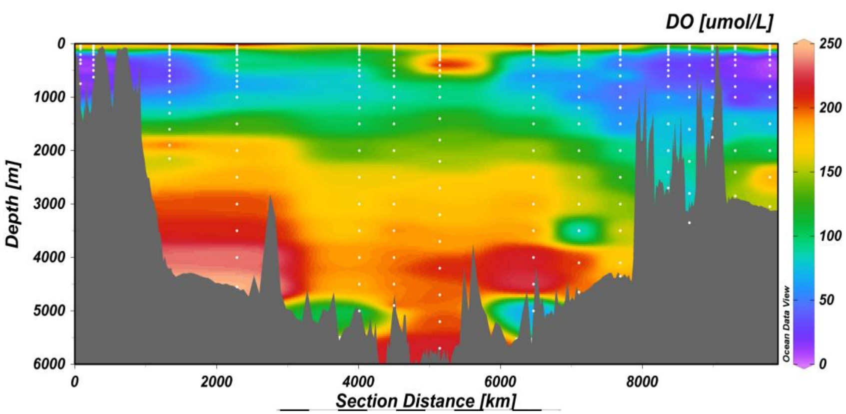
SK – 325 - 02

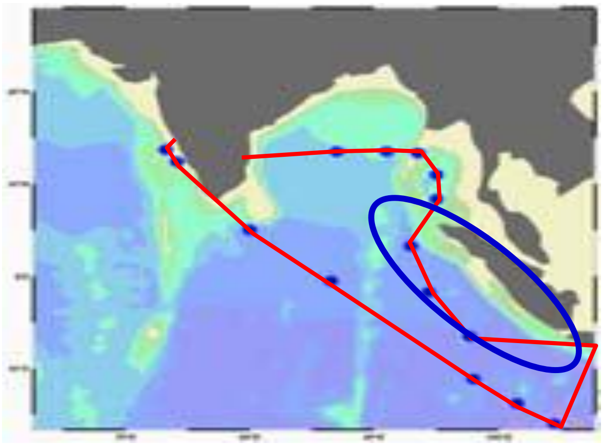


DFe (nM)
0
20
40
60
Depth (m)
0
500
1000
1500
2000
2500
3000
3500
4000

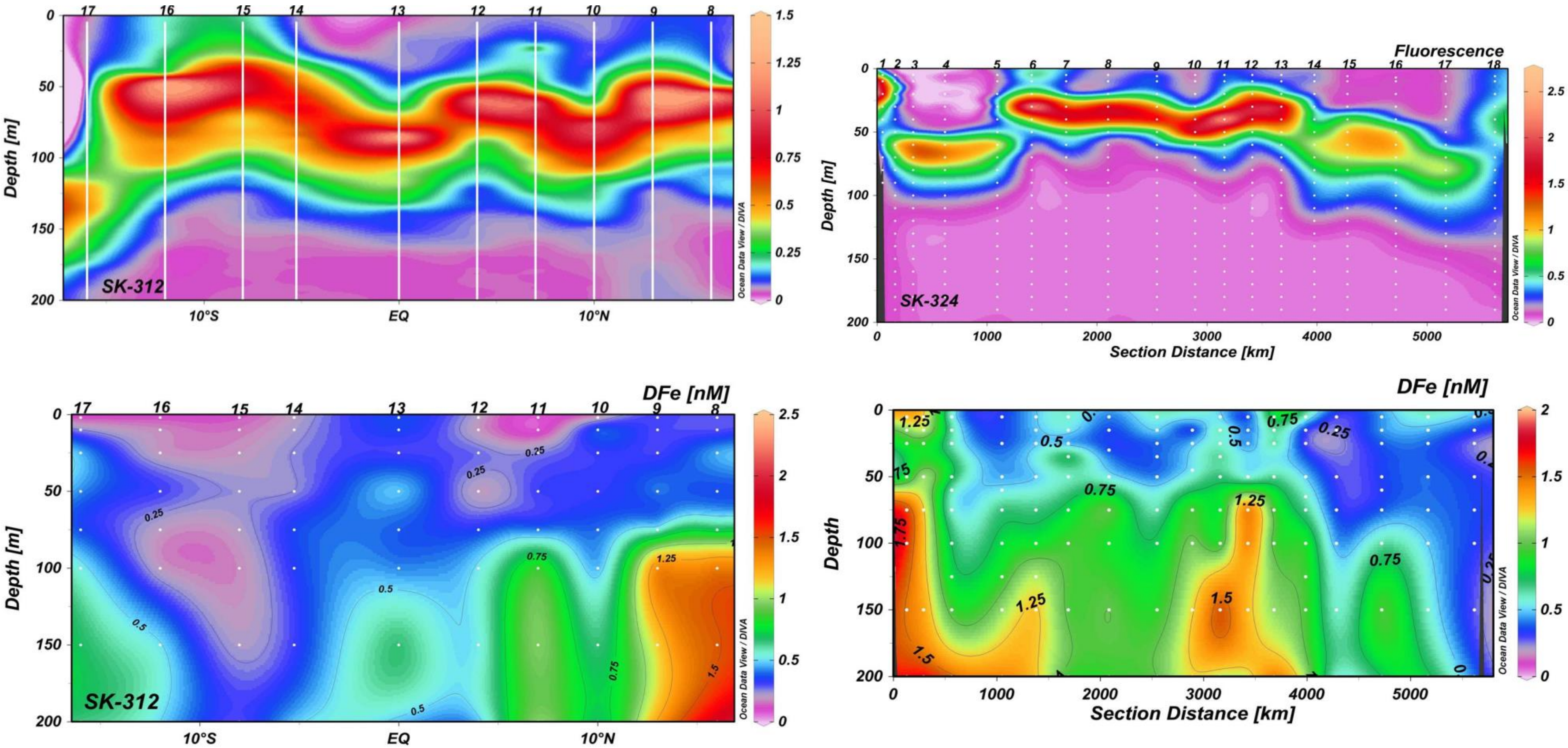
SK – 304: Indian Ocean







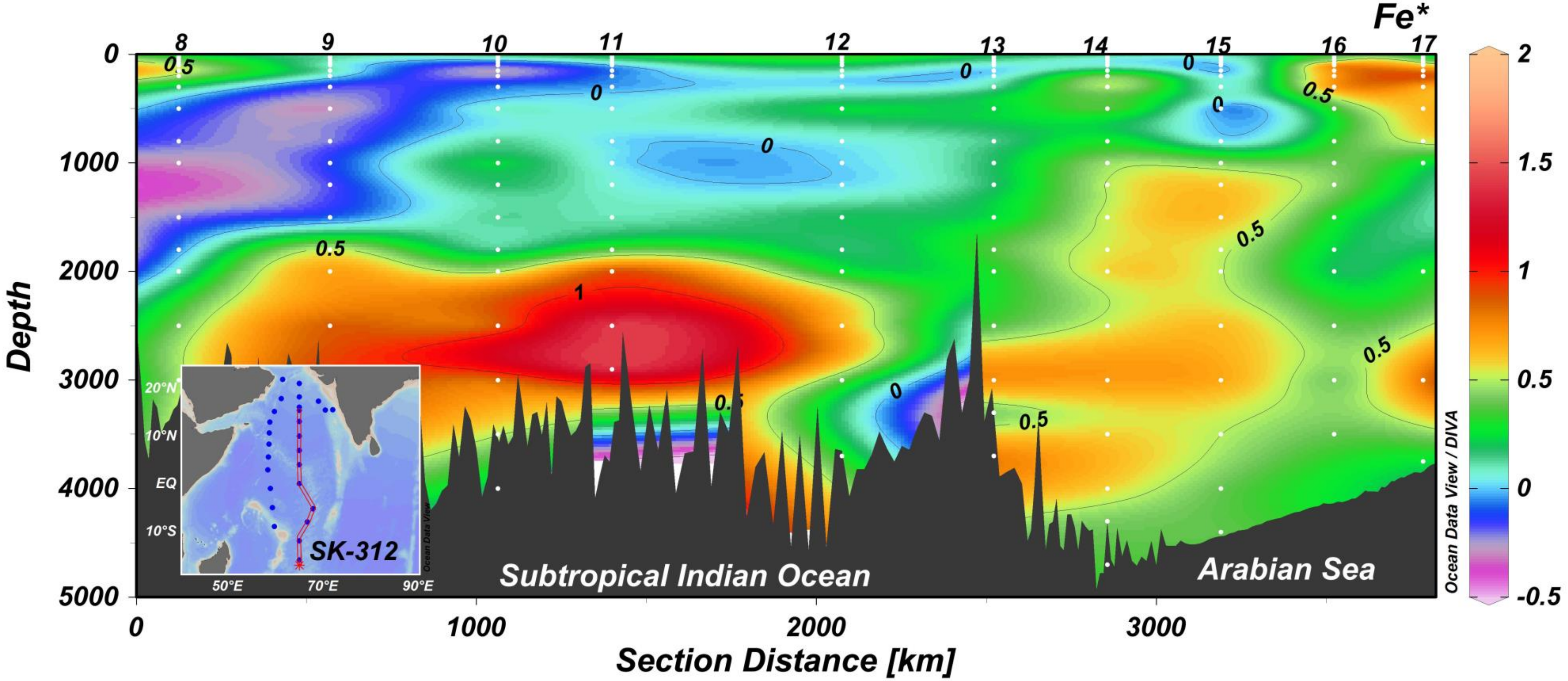
Arabian Sea


Depth [m]
SK-312
10°S
EQ
10°N
Ocean Data View / DIVA
Fluorescence
SK-324
Section Distance [km]
DFe [nM]
Depth

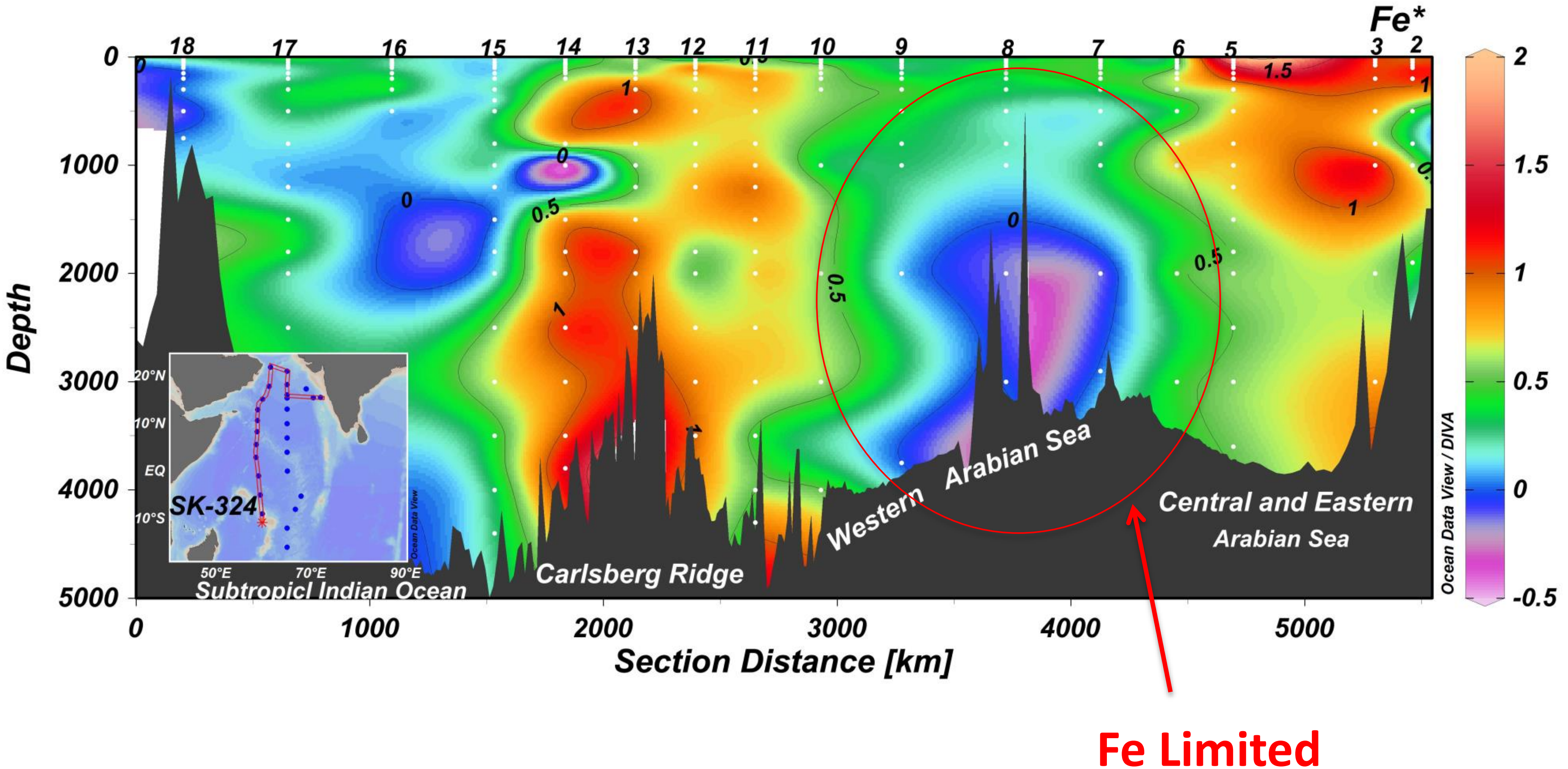
Fe Limitation

$$Fe^* = [DFe] - R_{Fe:P}\,[PO_4^{-3}]$$

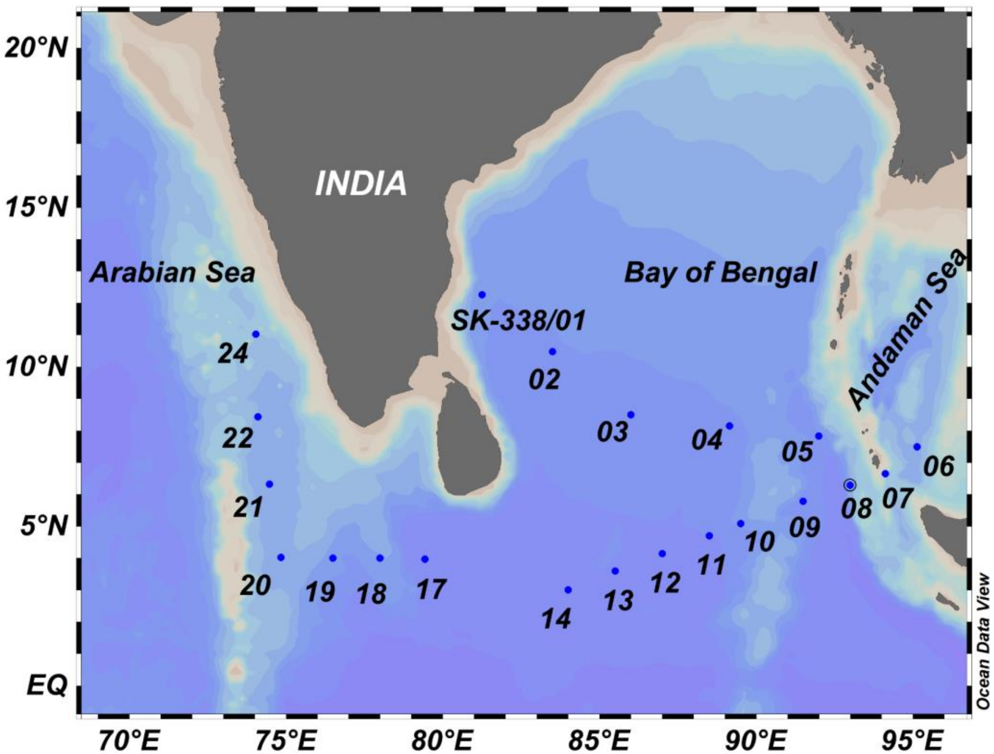
where $R_{Fe:P}$ implies the average biological uptake ratio of Fe over Phosphate

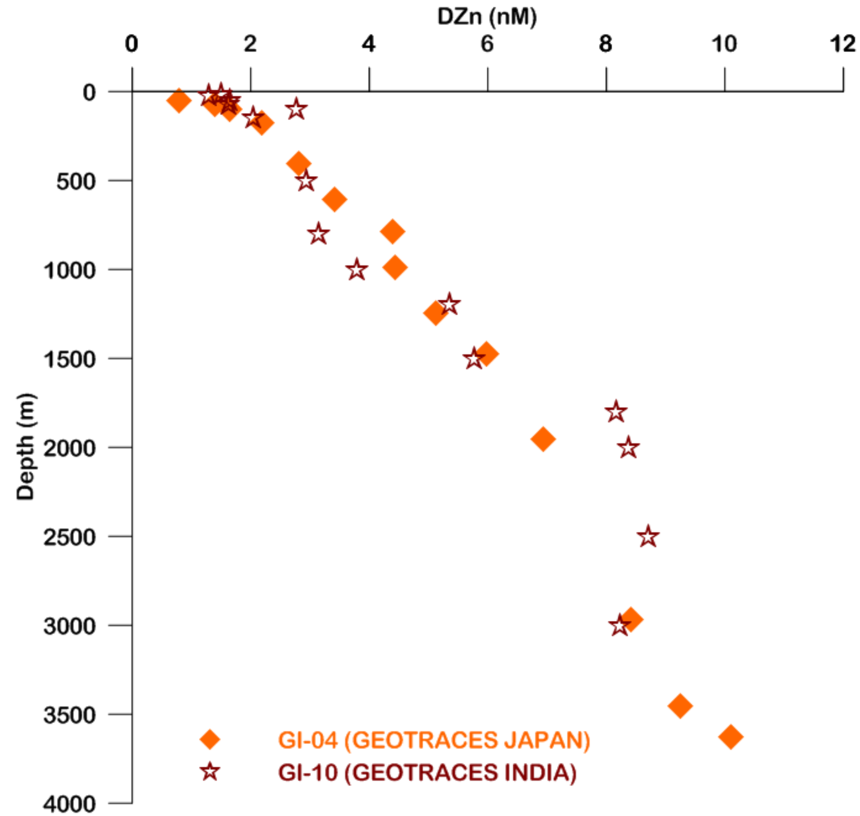


Fe Limitation



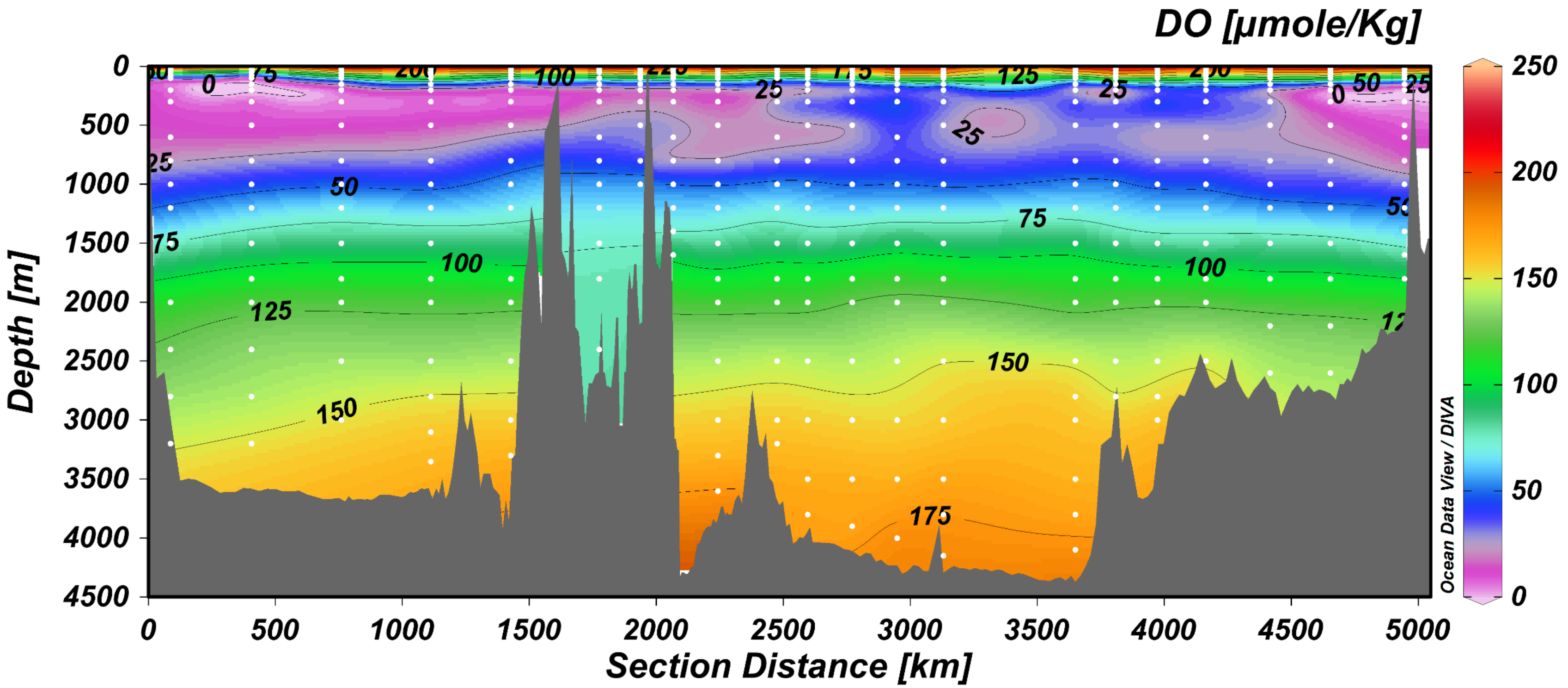
Dissolved Zn





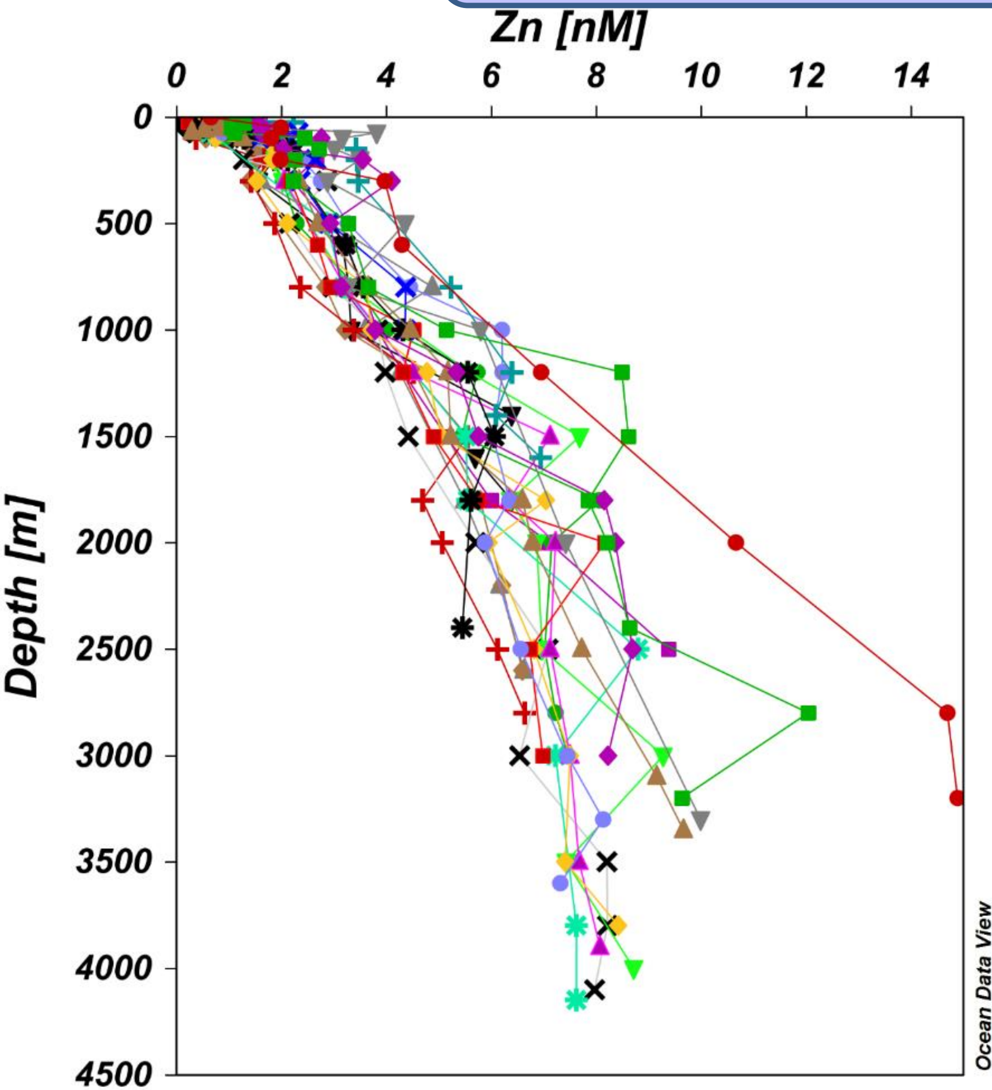
GEOTRACES GI-10 cruise track sampled in Northern Indian Ocean during January-March 2017 (Left). Comparison of DZn data from crossover station (Right). DZn is measured onboard using Flow injection system by fluorometric detection.

Section plot for dissolved oxygen



The DO values are high in the surface compared to subsequent depths. Persistent OMZ exists in the Northern Indian Ocean in between depths of 100 – 1000m. The DO values in the intermediate waters is less than 50 µM.

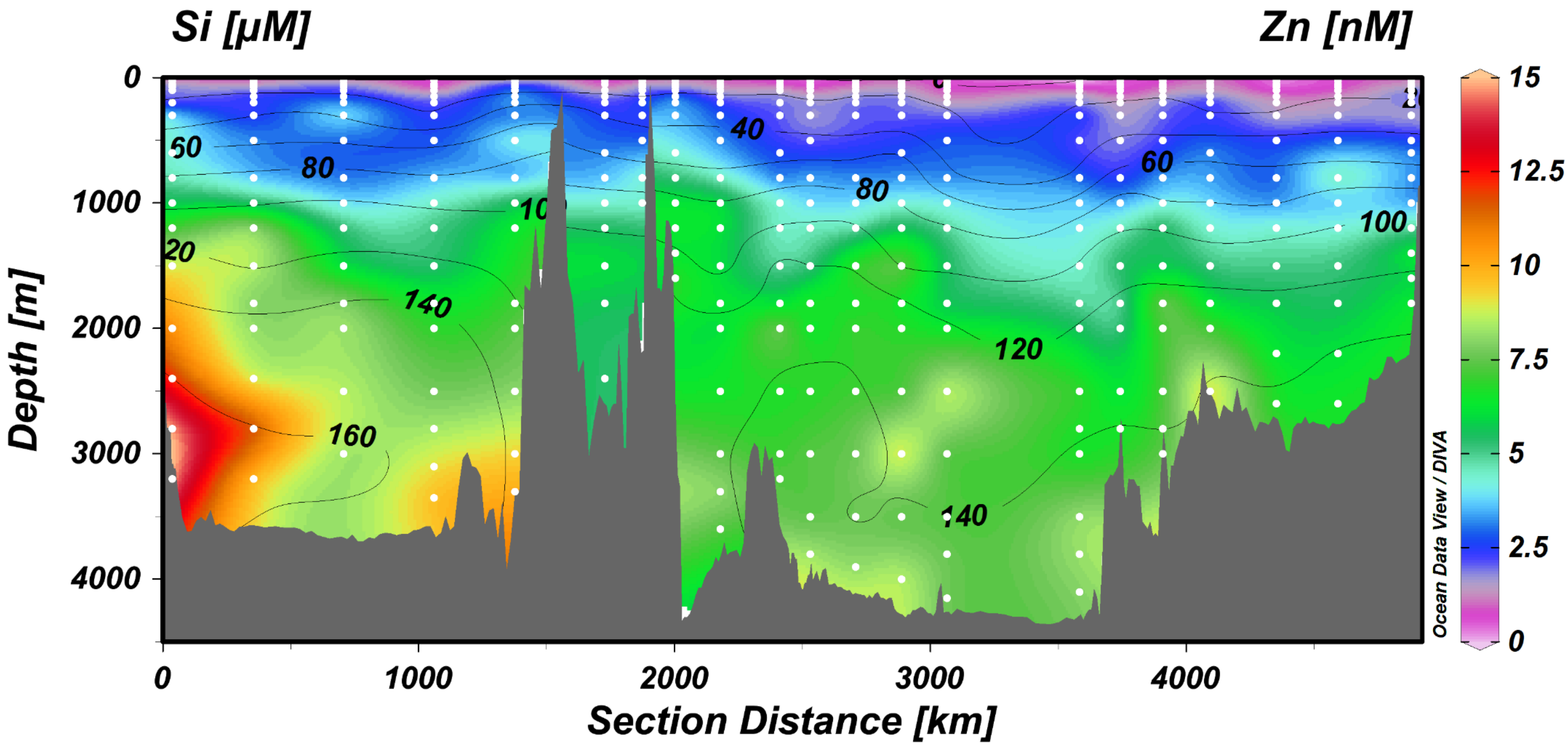
Zinc vertical profiles



Zinc shows nutrient type profile in all the stations with surface low and increases with respect to the depth. The profiles show oceanographically consistent with respect to the major nutrients Phosphate, Silicate and Nitrate.

S.No	Water depth (m)	DZn (nM)
1	0 to 100	0.98 ± 0.50 (n =105)
2	100 to 1000	2.99 ± 1.07 (n =98)
3	> 1000	6.97 ± 1.81 (n = 114)

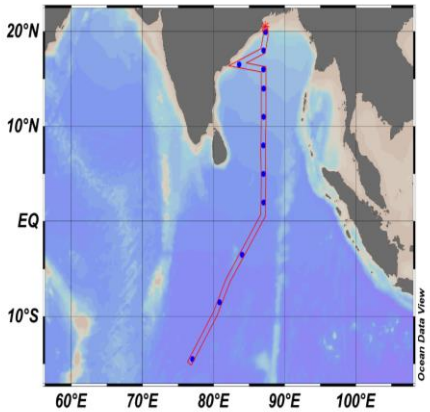
Section plot for DZn with overlying Si contour lines

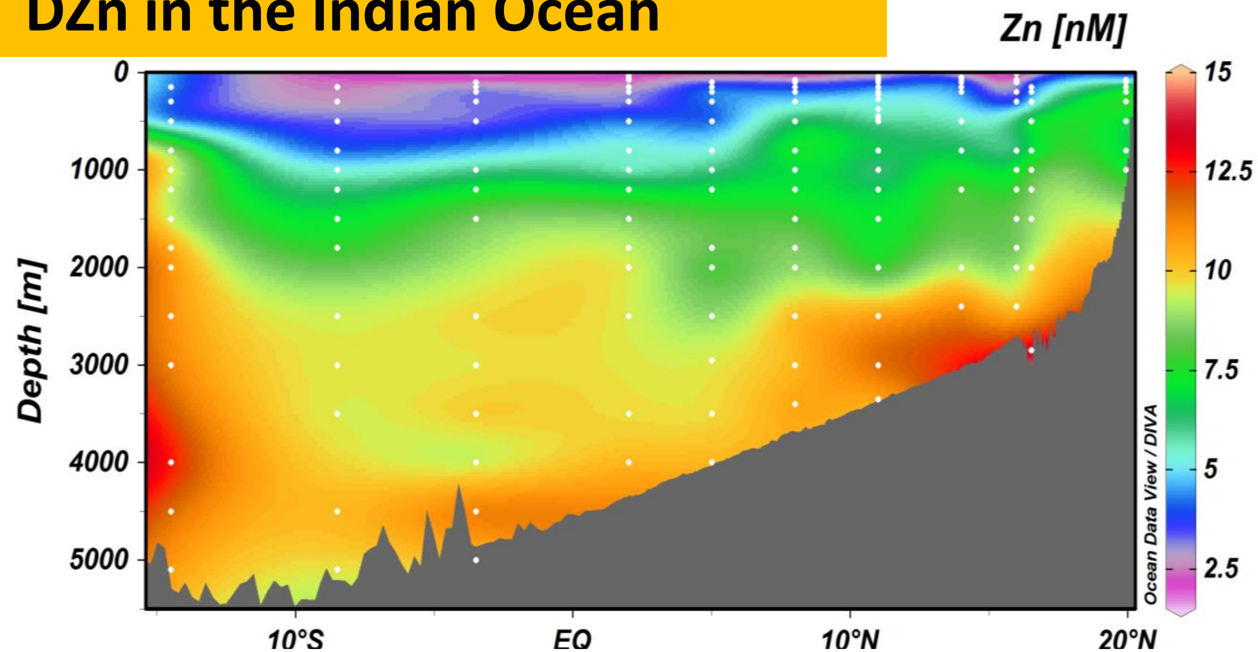


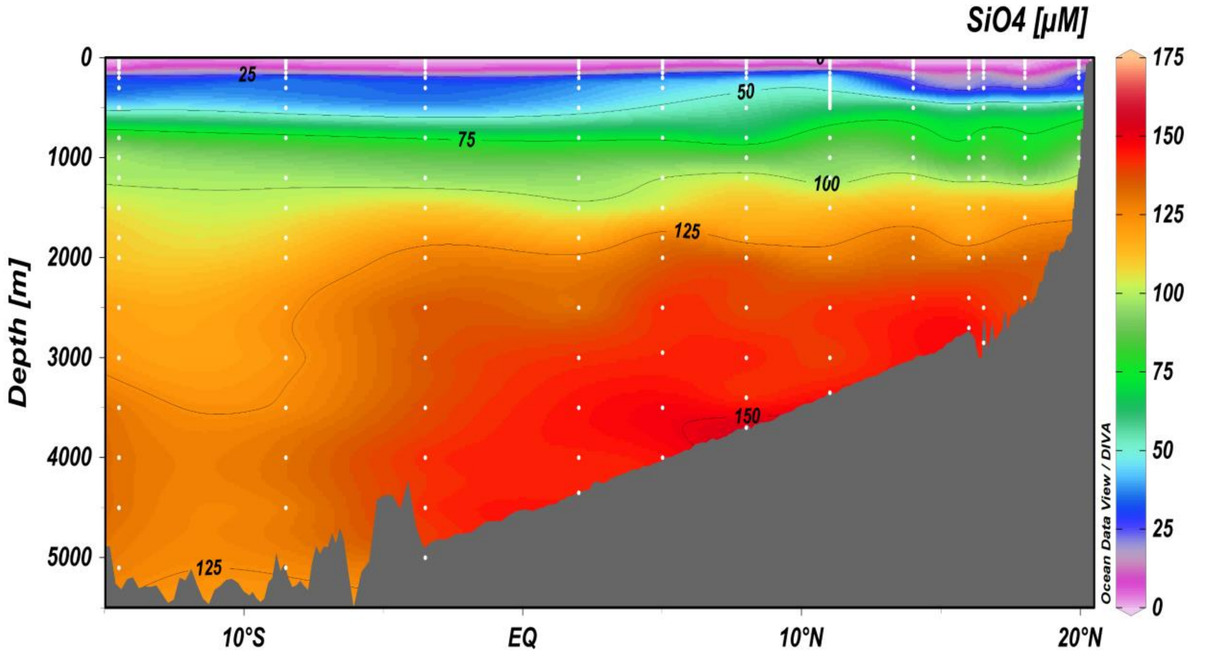
A strong and significant correlation has been observed between DZn and Si in the Northern Indian Ocean. Increase in the Si concentrations has been observed in the intermediate waters where as increment does not seen in the case of Zn.

DZn in the Indian Ocean

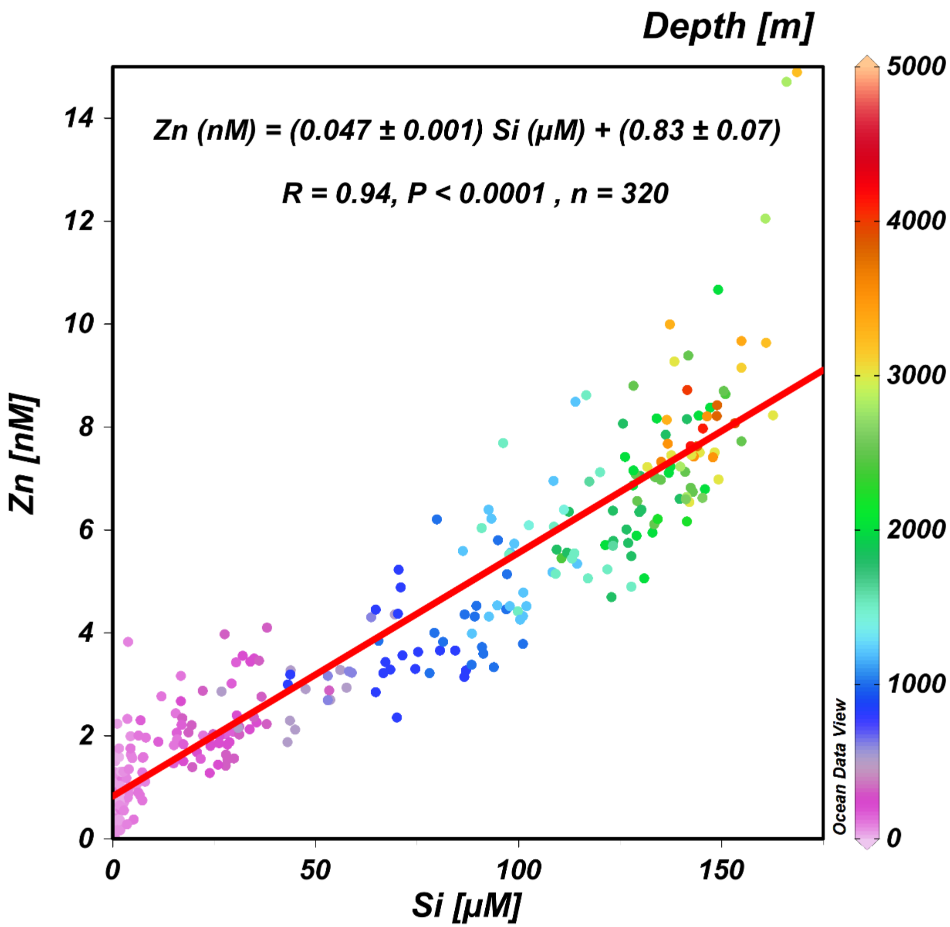
SK 311

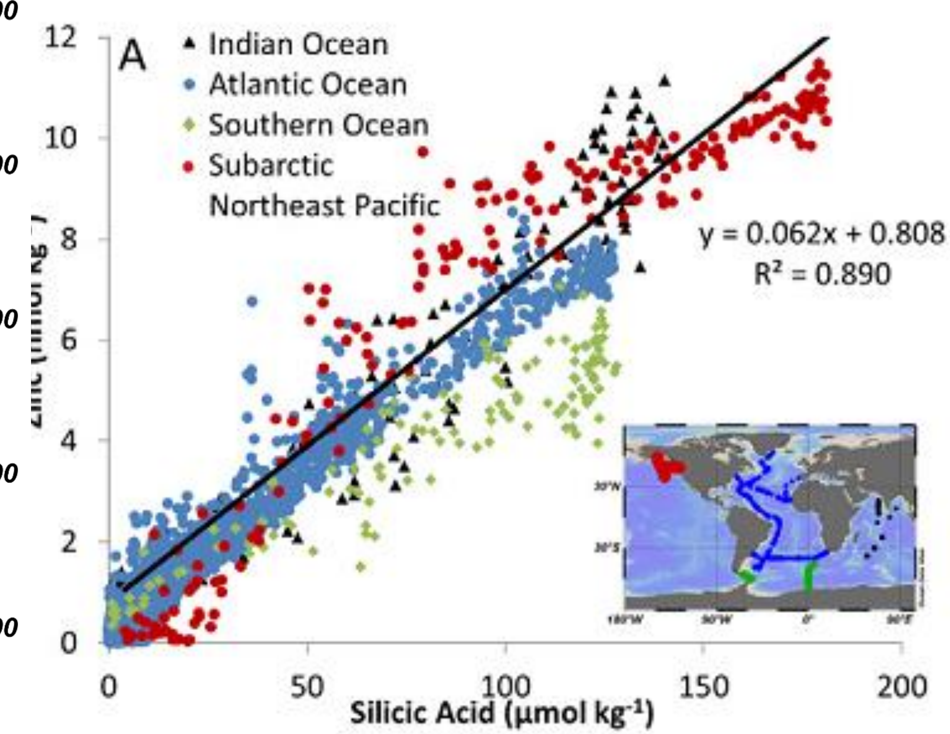




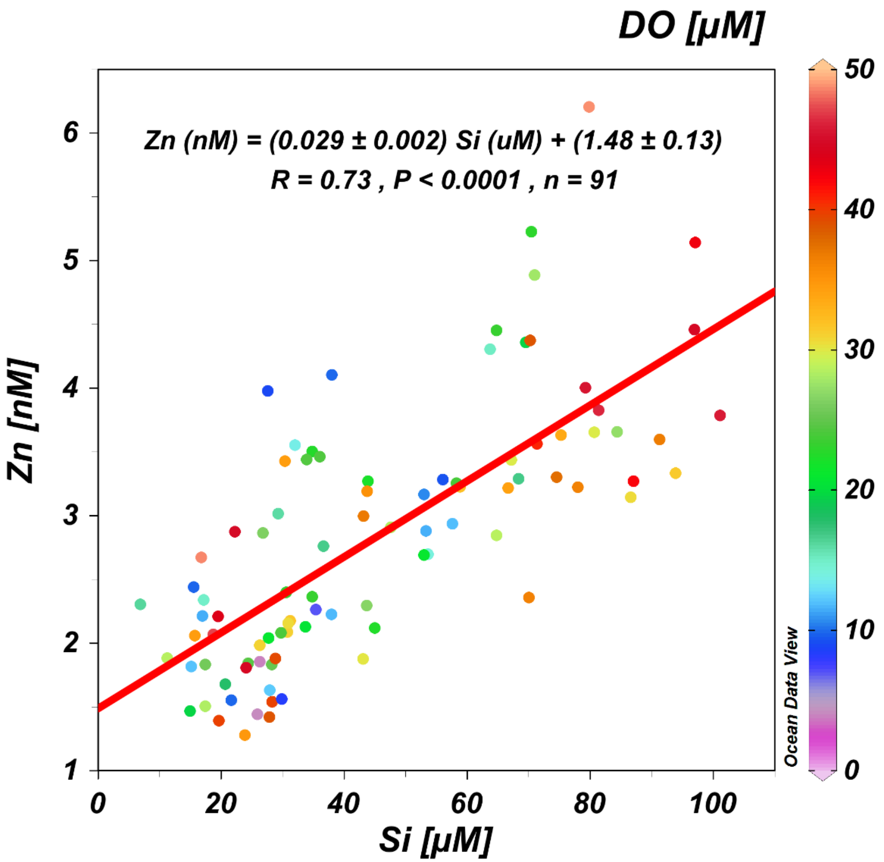


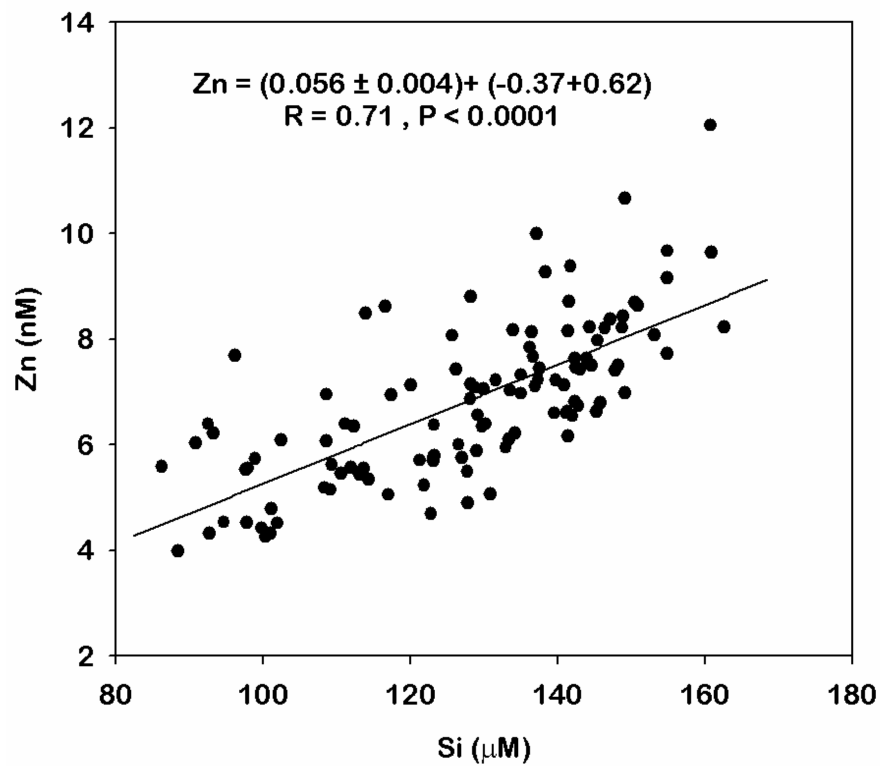
DZn vs. Si in full water column





DZn vs. Si in OMZ and deeper water



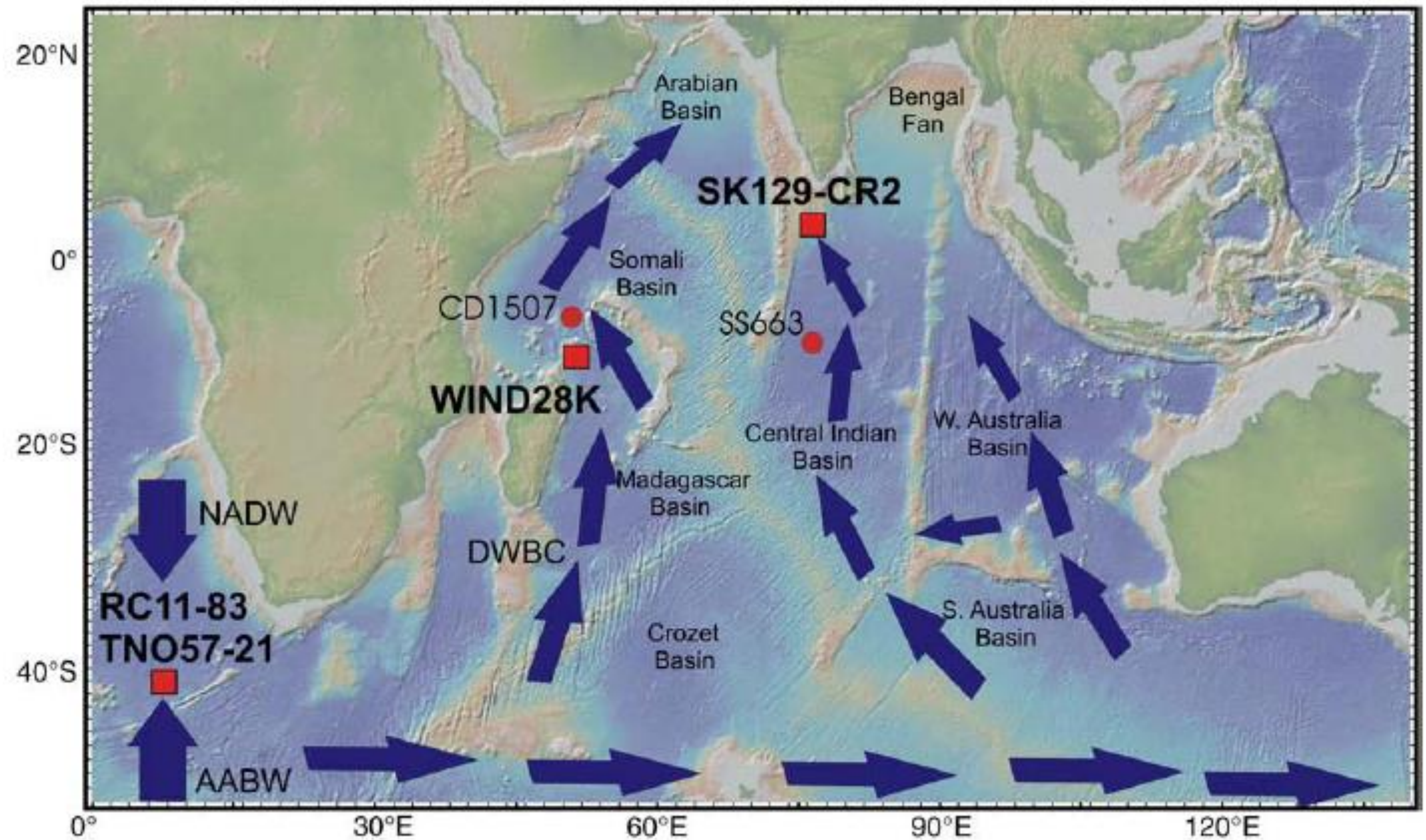


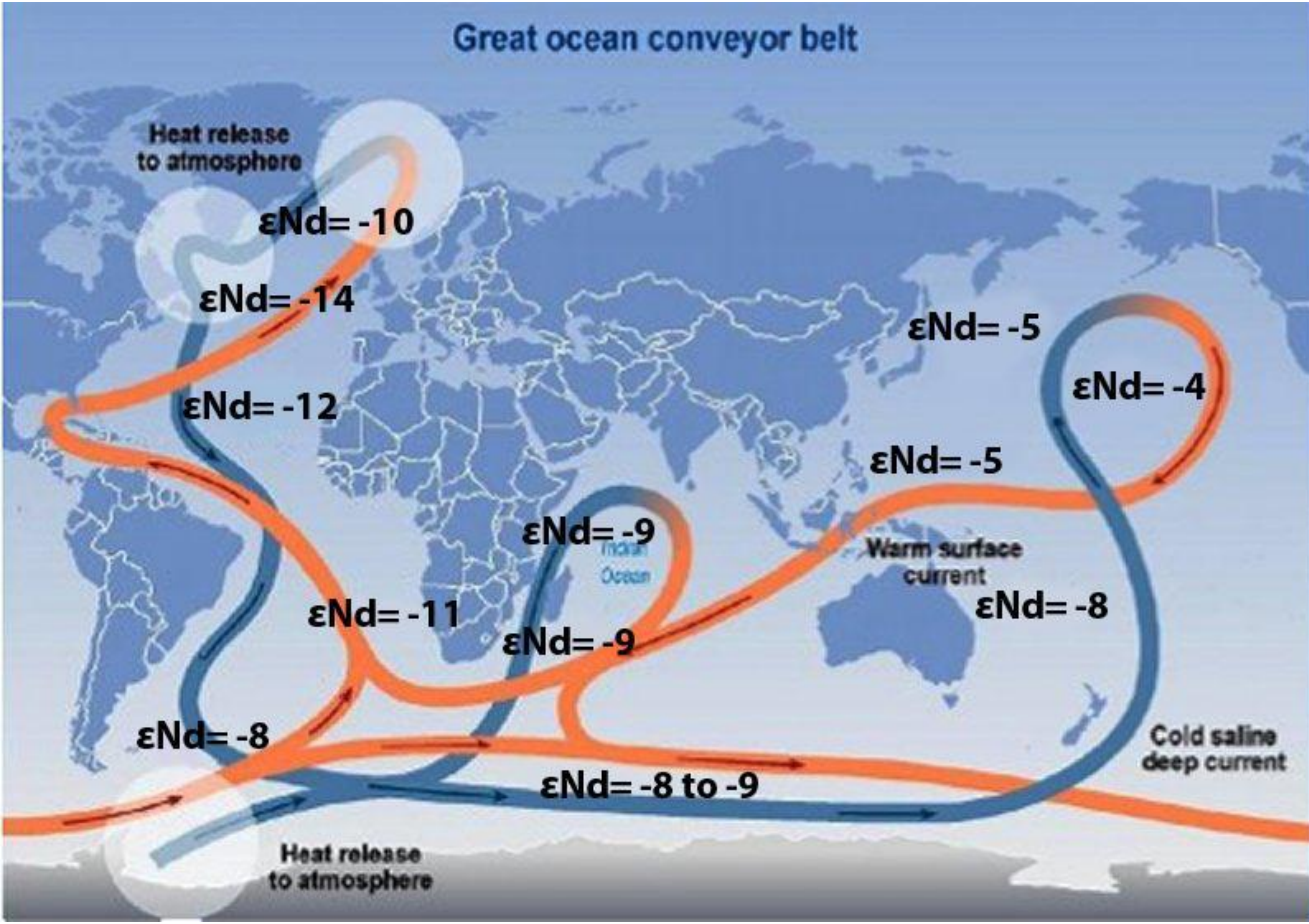
Contrasting slopes for DZn vs. Si is observed between OMZ samples (Between 100-1000m) and deeper water samples (Below 1000m) suggesting that Zn removal from the OMZ region over Si.

❖OMZ acting as a significant water column sink for DZn in the Northern Indian Ocean by some unidentified process.

Thanks

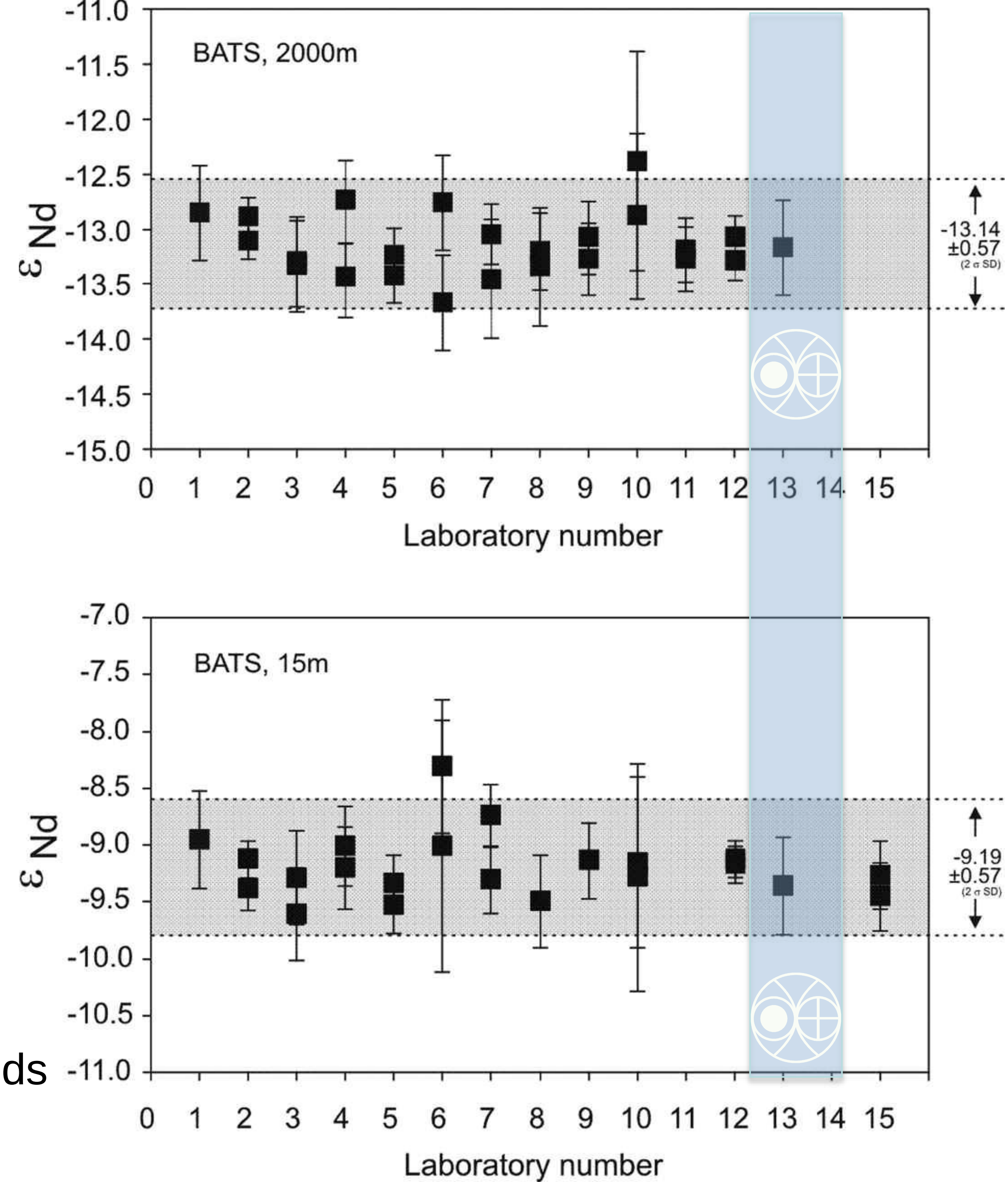
ε_{Nd} as tracer of ocean circulation: Water Masses in the Indian Ocean


20°N
0°
20°S
40°S
0°
30°E
60°E
90°E
120°E
Arabian Basin
Bengal Fan
SK129-CR2
Somali Basin
CD1507
SS663
WIND28K
Central Indian Basin
W. Australia Basin
Madagascar Basin
NADW
DWBC
RC11-83
TNO57-21
Crozet Basin
S. Australia Basin
AABW



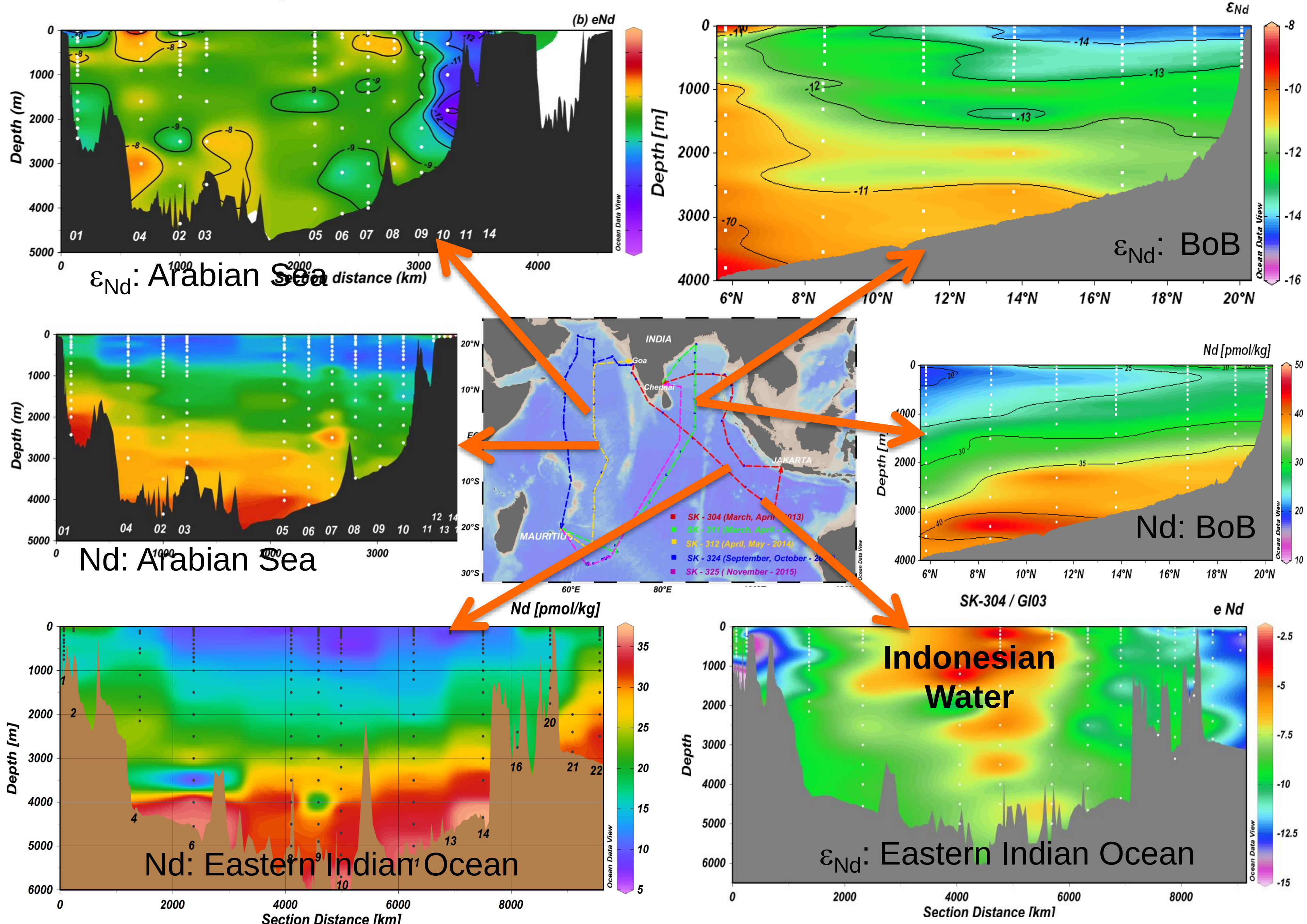
Great ocean conveyor belt
Heat release to atmosphere
εNd= -10
εNd= -14
εNd= -12
εNd= -5
εNd= -4
εNd= -5
εNd= -9
Indian Ocean
Warm surface current
εNd= -8
εNd= -11
εNd= -9
εNd= -8
Cold saline deep current
εNd= -8 to -9
Heat release to atmosphere

International Intercalibration for Nd isotope measurement



Limnol. Oceanogr.: Methods 10, 2012, 234–251

Nd isotope as water mass tracer in the Indian Ocean



Inverse Model Calculation

$$\sum_{i=1}^{9} f_{ij} = 1$$

$$\sum_{i=1}^{9} f_{ij} x_i = x_j$$

$$\sum_{i=1}^{9} f_{ij} Nd_i + Nd_j^{excess} = Nd_j$$

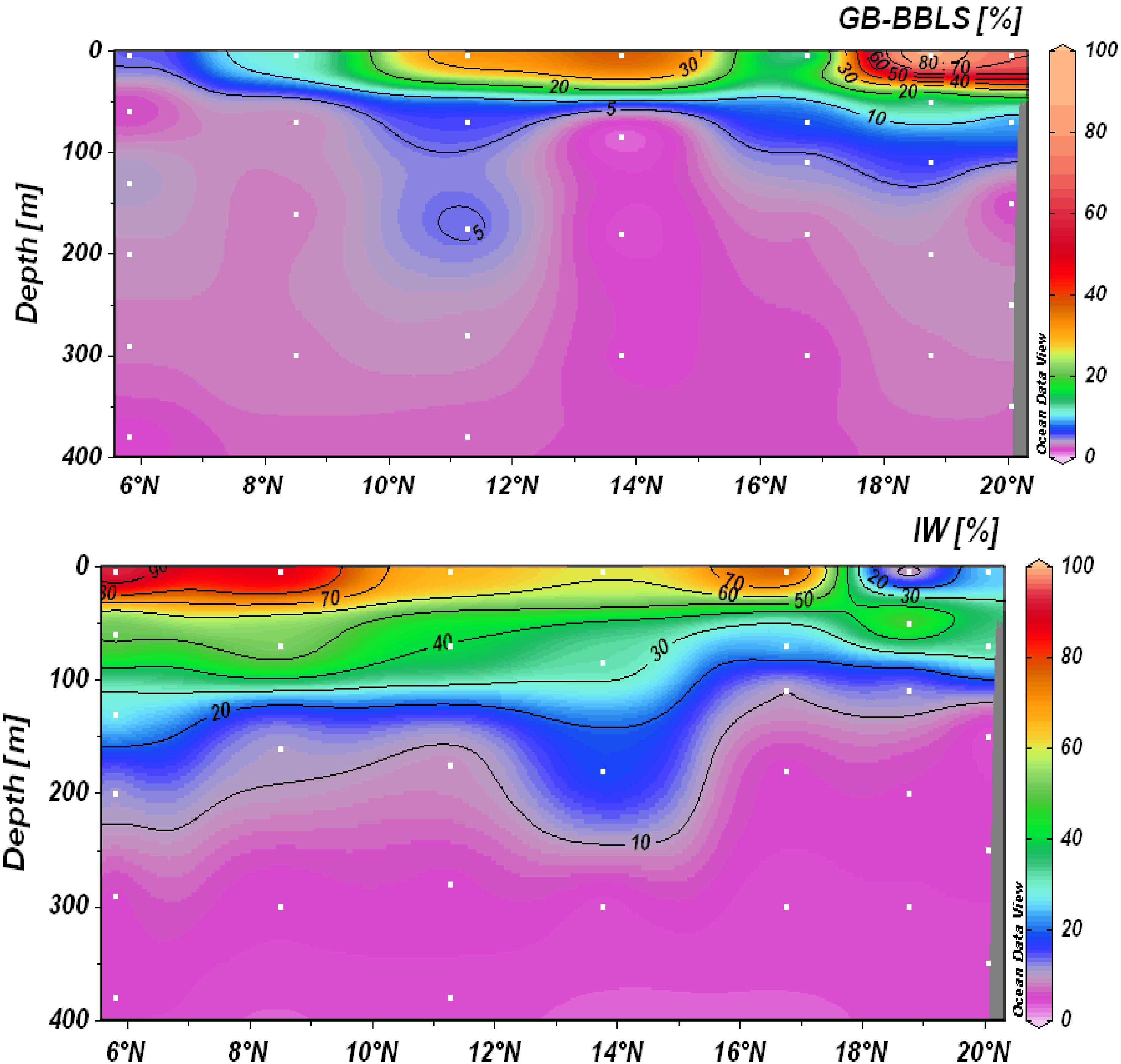
$$\sum_{i=1}^{9} f_{ij} Nd_i \varepsilon_{Nd_i} + Nd_j^{excess} \varepsilon_{Nd_j^{excess}} = Nd_j \varepsilon_{Nd_j}$$

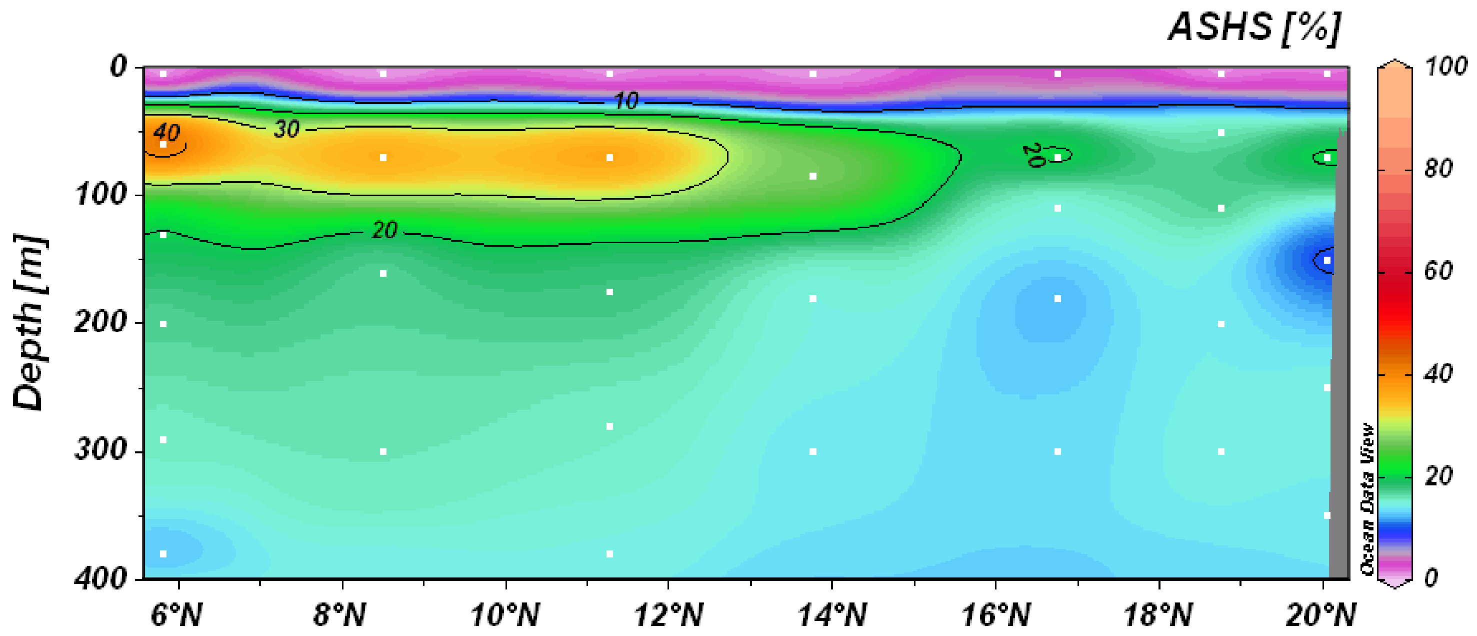
where,

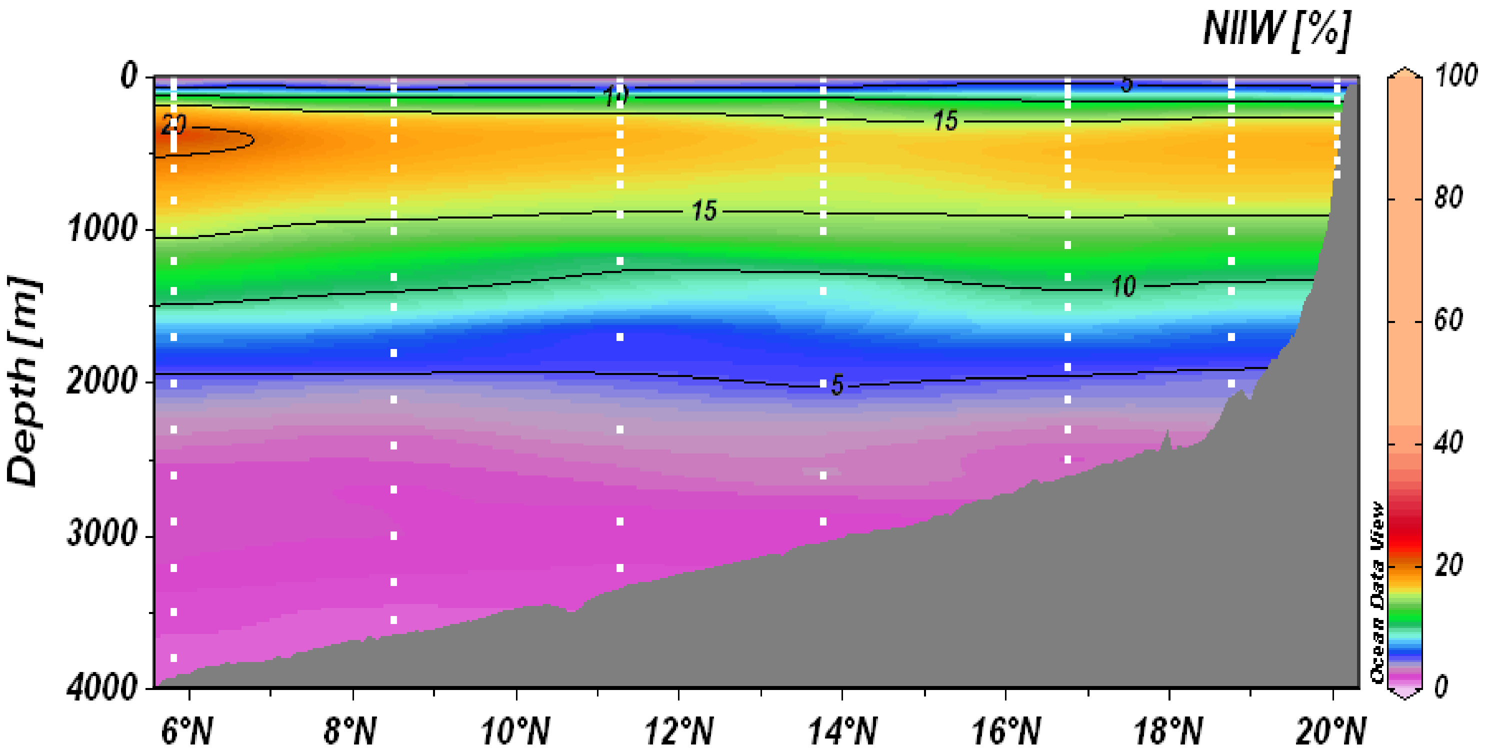
f_{ij} : the fraction of the 'ith' water mass in 'jth' sample,

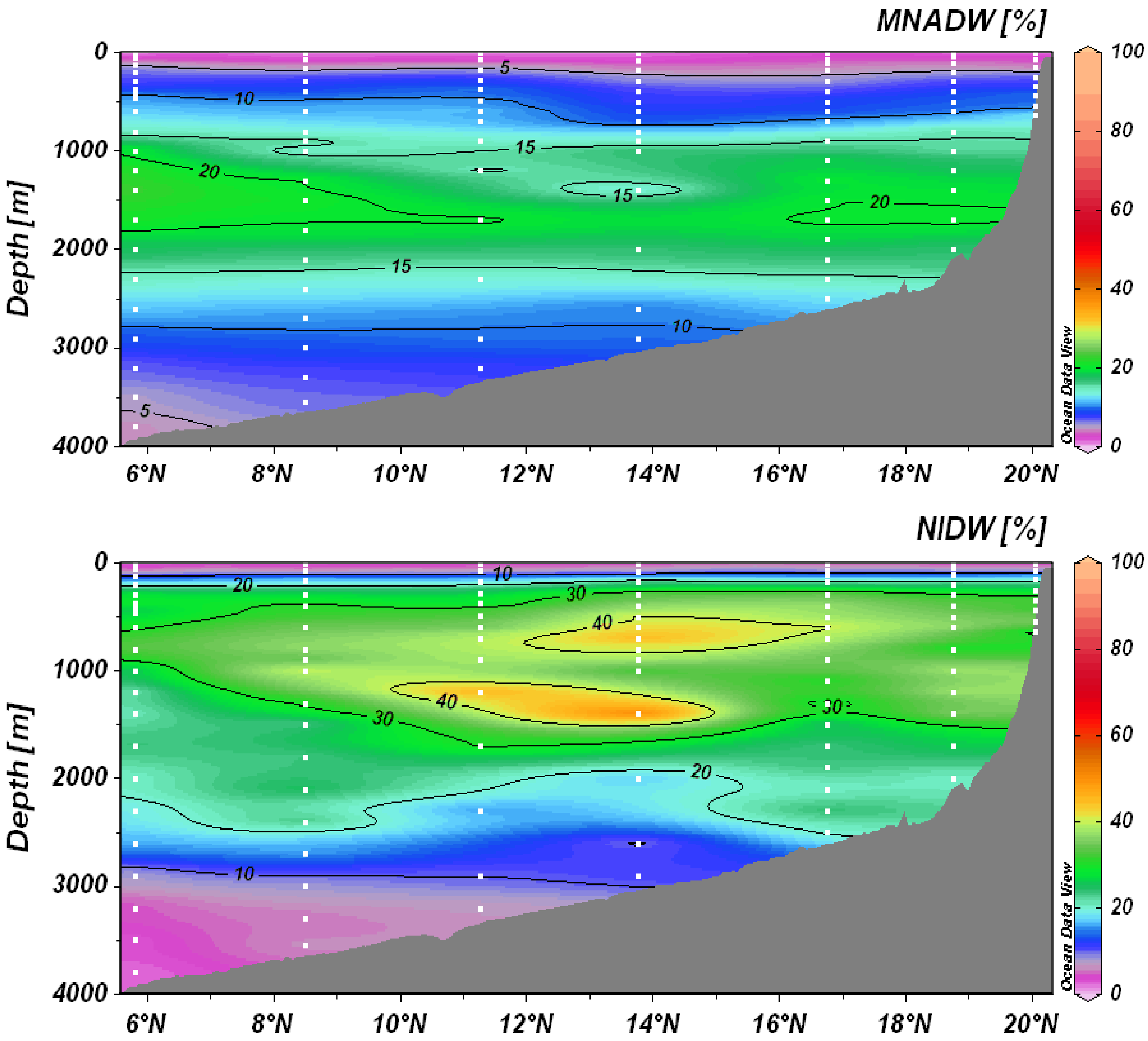
x_i & x_j : either potential temperature or salinity of the 'ith' water mass and 'jth' sample, and

Nd_j^{excess} : excess fraction of dissolved Nd in 'jth' sample over Nd contribution from different water masses, respectively.

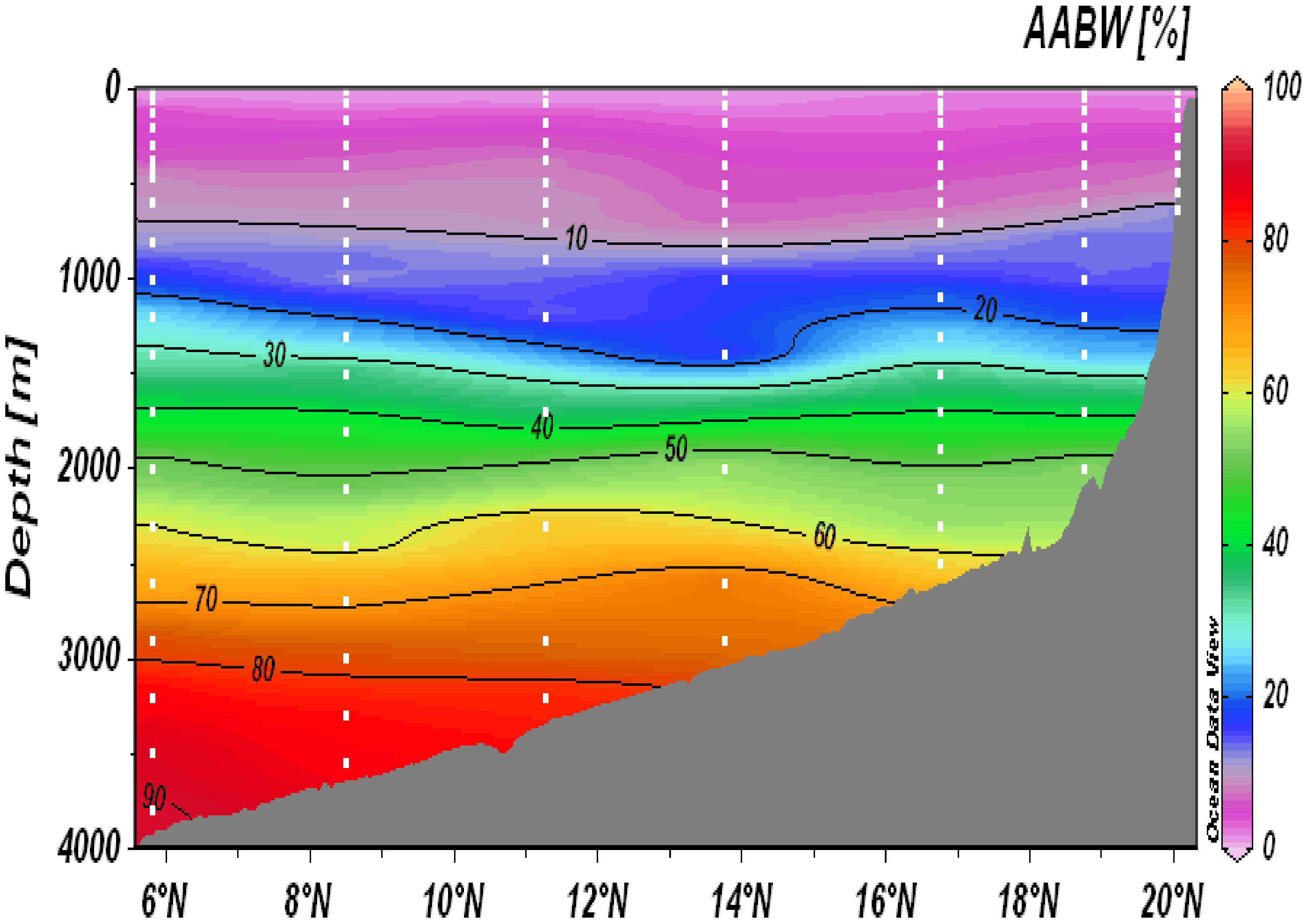

GB-BBLS [%]
Depth [m]
0
100
200
300
400
6°N
8°N
10°N
12°N
14°N
16°N
18°N
20°N
30
20
5
10
60
50
80
70
40
Ocean Data View
IW [%]
90
80
70
60
50
40
30
20
10


ASHS [%]
Depth [m]
0
100
200
300
400
6°N
8°N
10°N
12°N
14°N
16°N
18°N
20°N
10
30
40
20
100
80
60
40
20
0
Ocean Data View

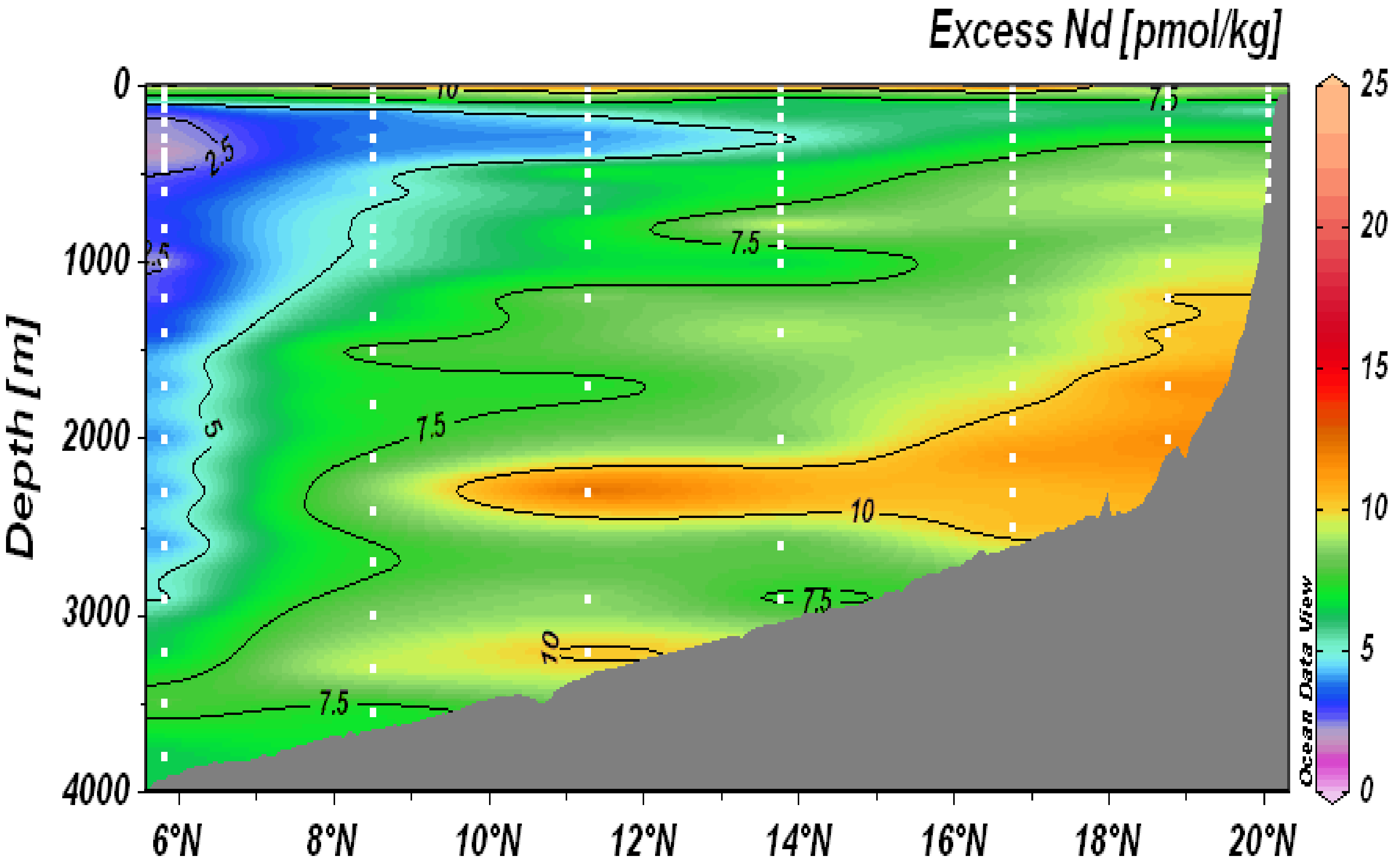

NIIW [%]
Depth [m]
0
1000
2000
3000
4000
6°N
8°N
10°N
12°N
14°N
16°N
18°N
20°N
5
15
10
100
80
60
40
20
0
Ocean Data View



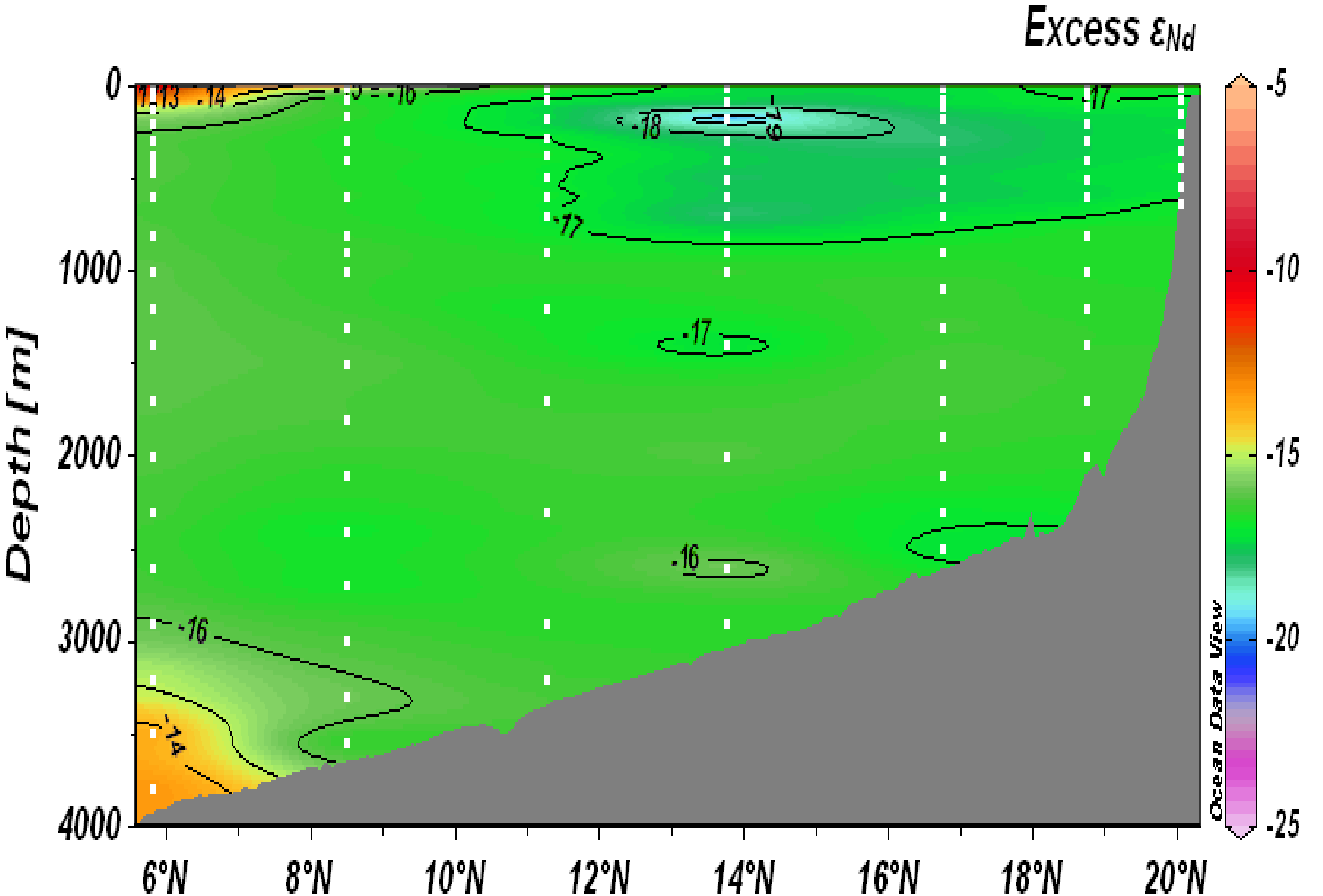
MNADW [%]
Depth [m]
0
1000
2000
3000
4000
6°N
8°N
10°N
12°N
14°N
16°N
18°N
20°N
5
10
15
20
100
80
60
40
20
0
Ocean Data View
NIDW [%]
10
20
30
40



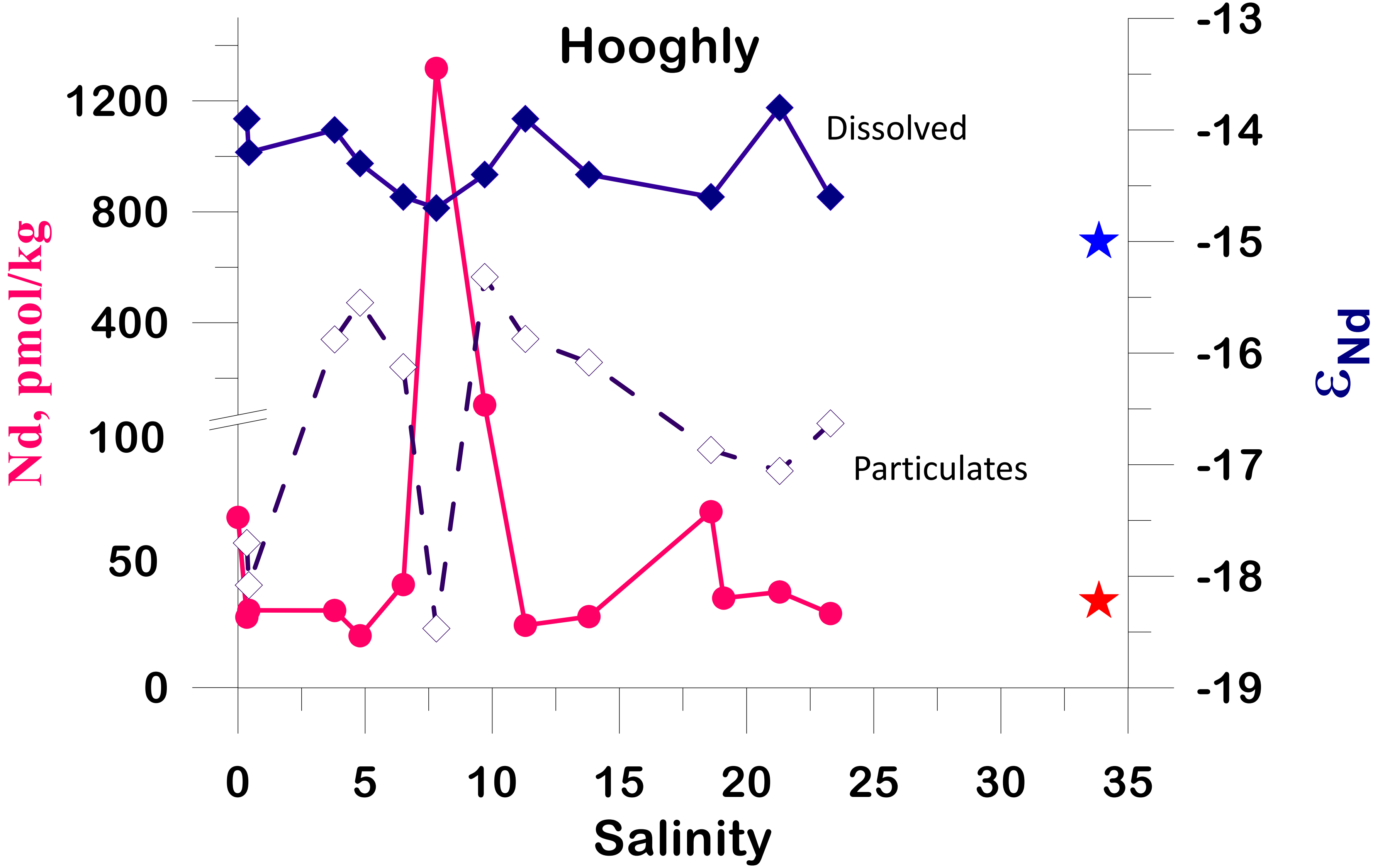
AABW [%]
Depth [m]
0
1000
2000
3000
4000
6°N
8°N
10°N
12°N
14°N
16°N
18°N
20°N
10
20
30
40
50
60
70
80
90
100
80
60
40
20
0
Ocean Data View



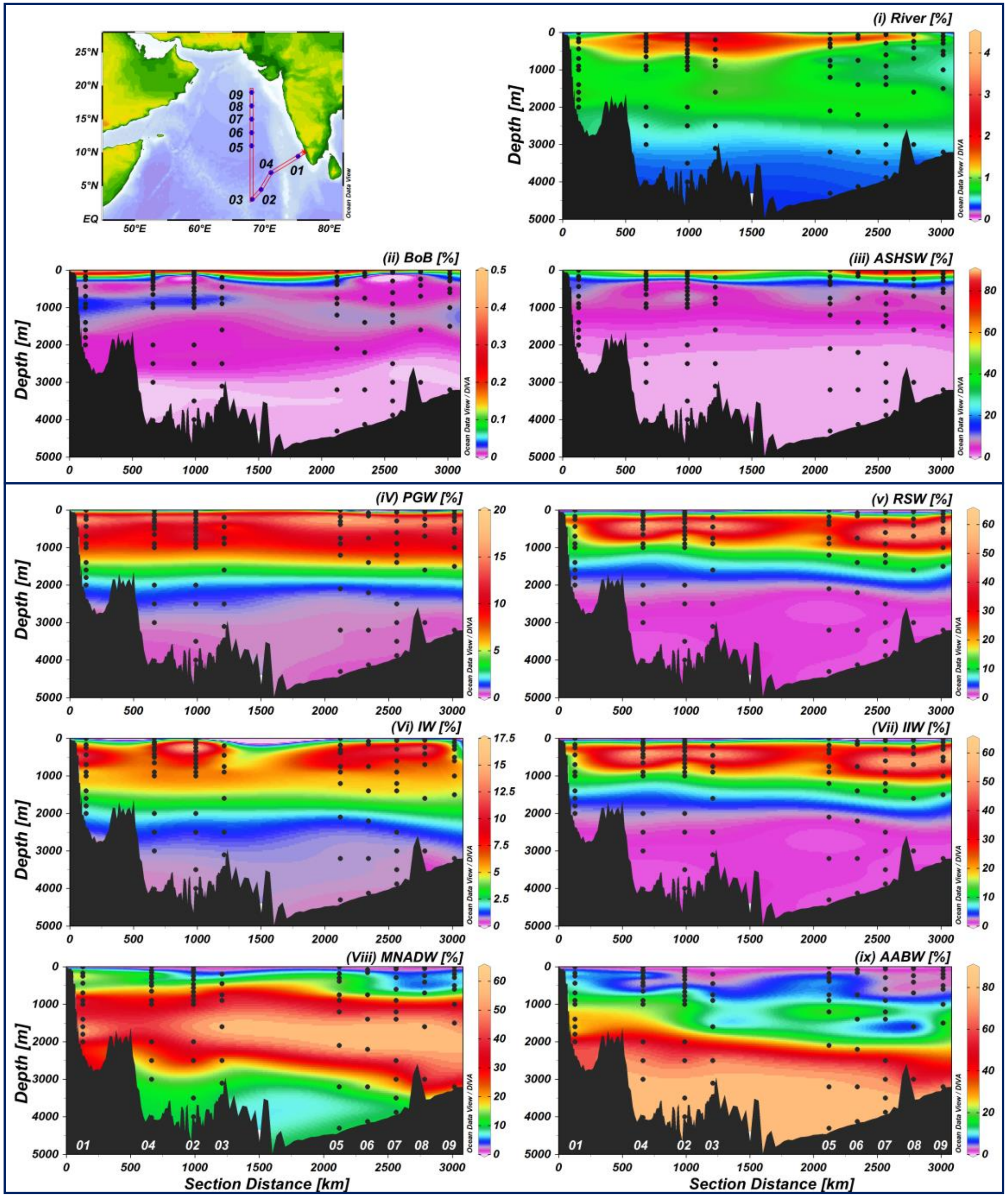
➢**Excess Nd is derived from sinking detrital material or slope sediments**



Excess εNd
Depth [m]
0
1000
2000
3000
4000
6°N
8°N
10°N
12°N
14°N
16°N
18°N
20°N
-5
-10
-15
-20
-25
-13
-14
-16
-17
-18
-19
Ocean Data View

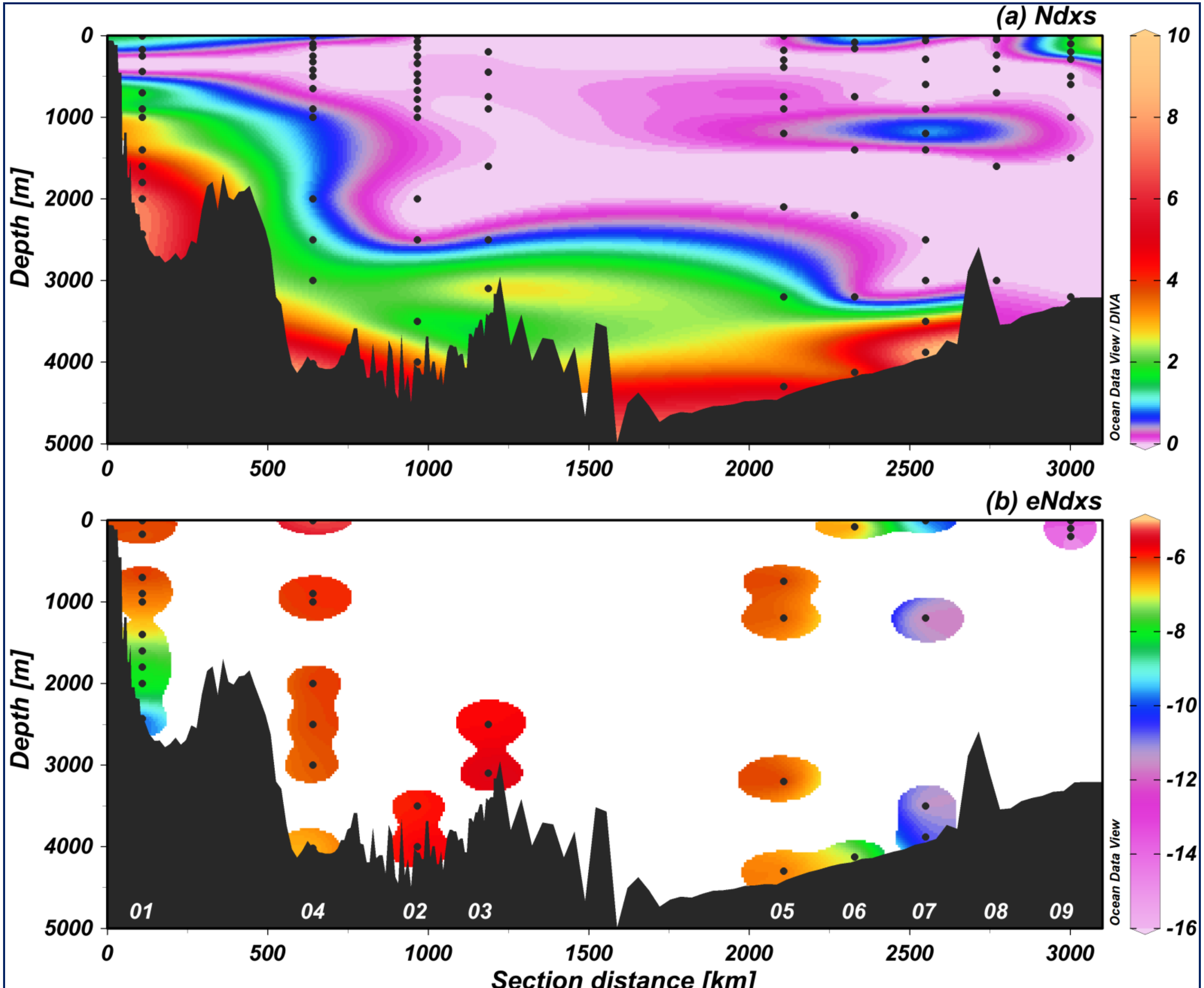

Hooghly
Dissolved
Particulates
Nd, pmol/kg
εNd
Salinity
1200
800
400
100
50
0
-13
-14
-15
-16
-17
-18
-19
0
5
10
15
20
25
30
35

Arabian Sea

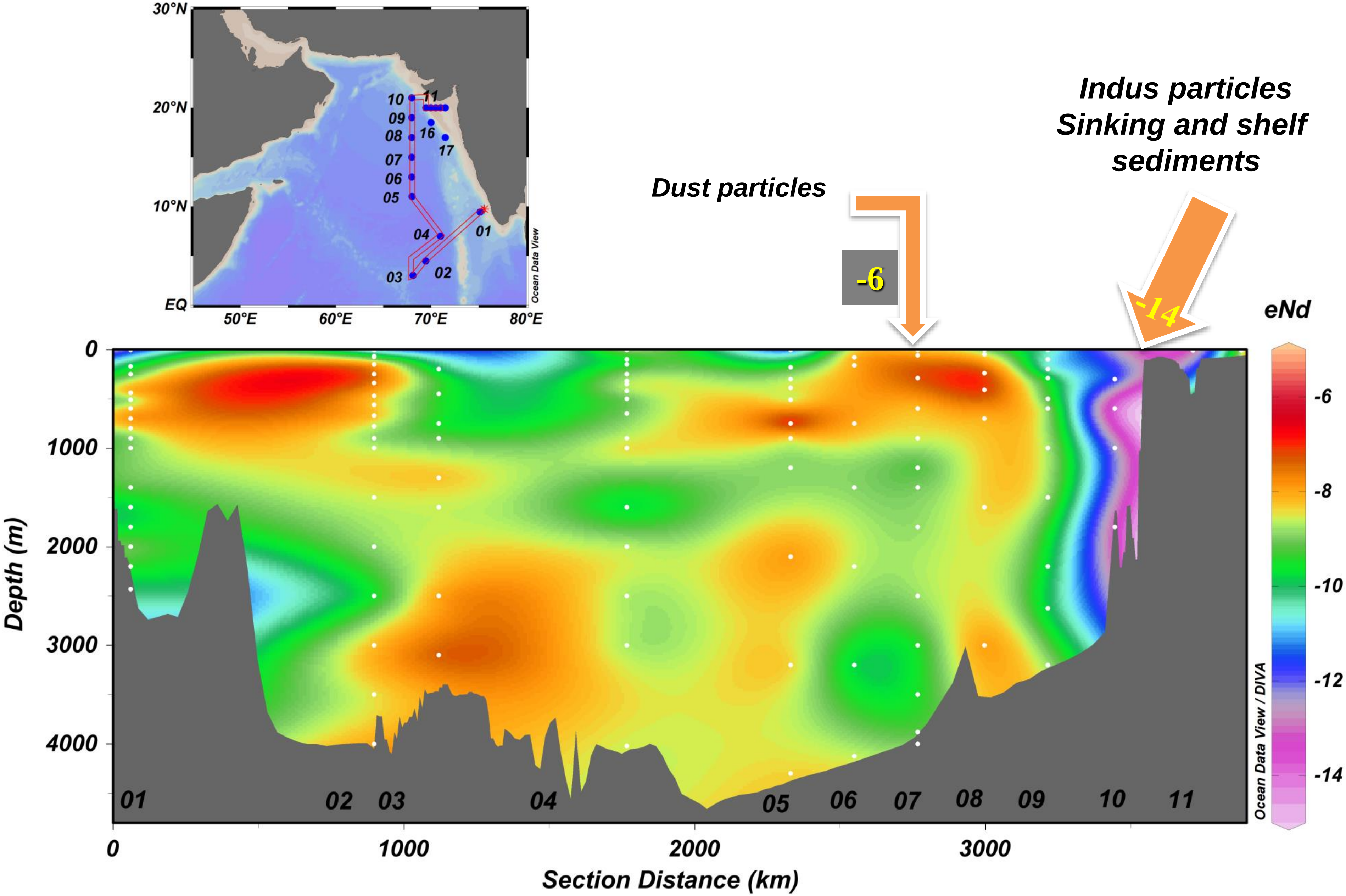


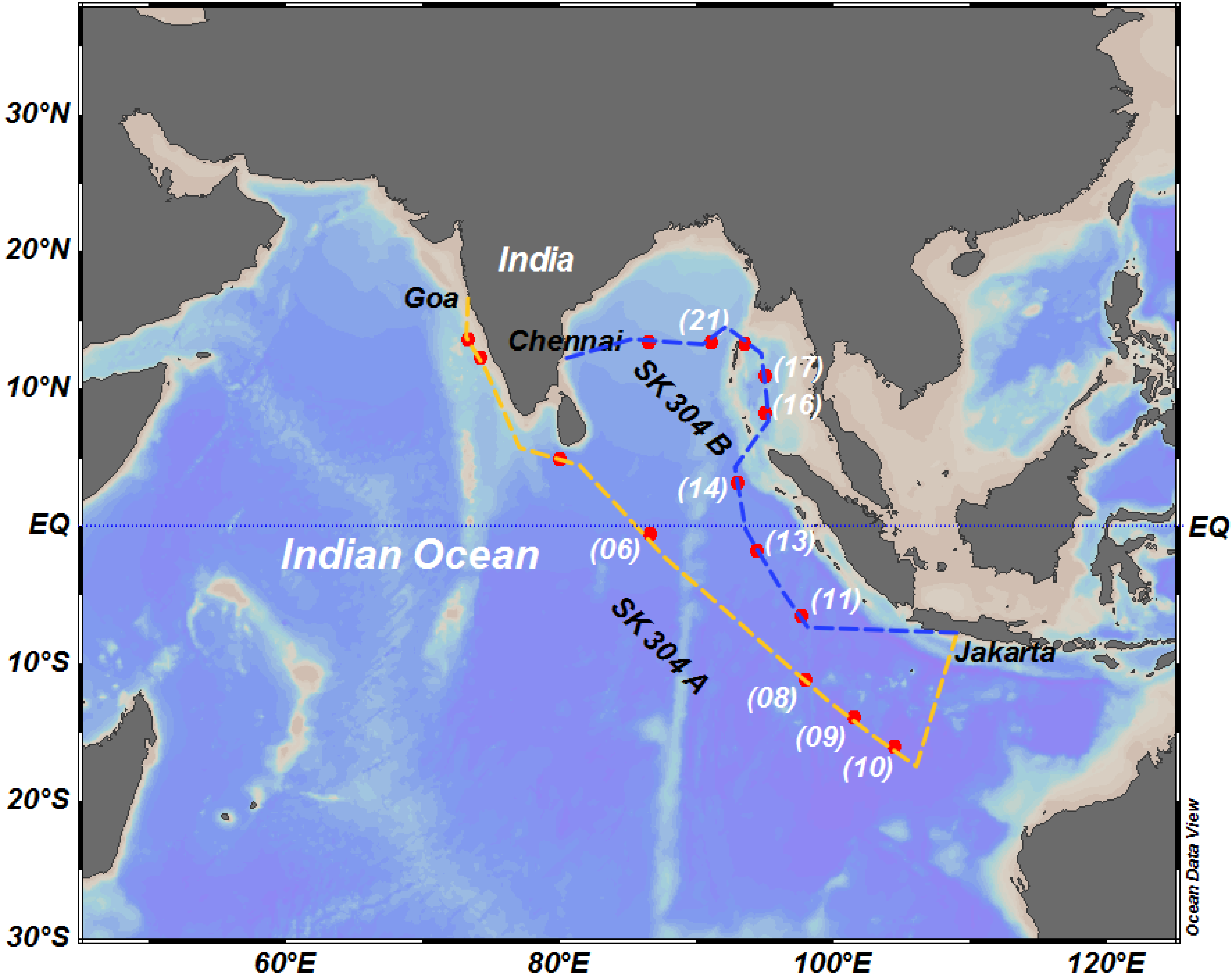
(i) River [%]
(ii) BoB [%]
(iii) ASHSW [%]
(iV) PGW [%]
(v) RSW [%]
(Vi) IW [%]
(Vii) IIW [%]
(Viii) MNADW [%]
(ix) AABW [%]
Depth [m]
Section Distance [km]
Ocean Data View / DIVA
01 04 02 03 05 06 07 08 09
25°N 20°N 15°N 10°N 5°N EQ
50°E 60°E 70°E 80°E

Excess Nd and their isotope composition



ε_{Nd} distribution in the Arabian Sea water column (2-21º N; 68º E)

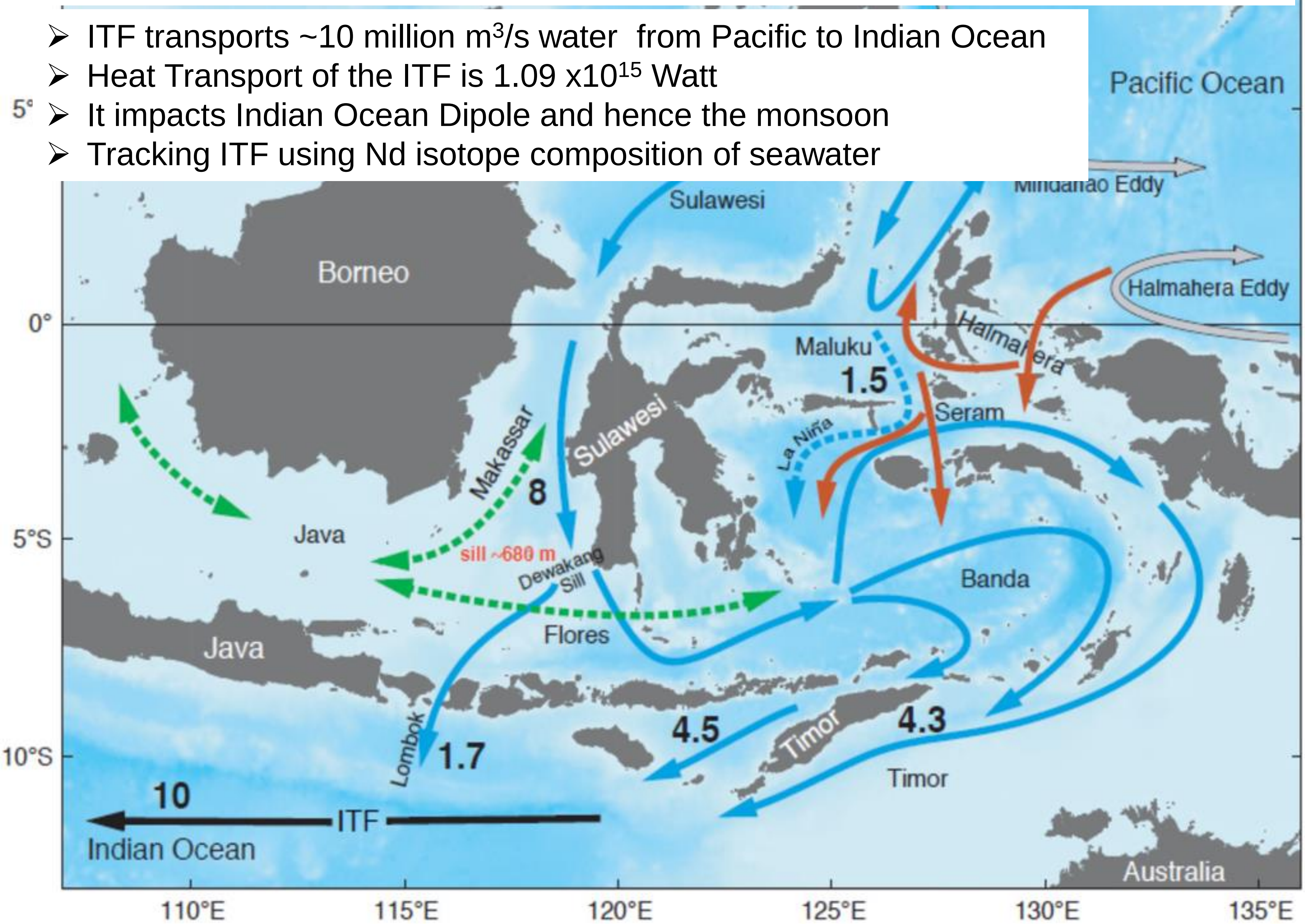


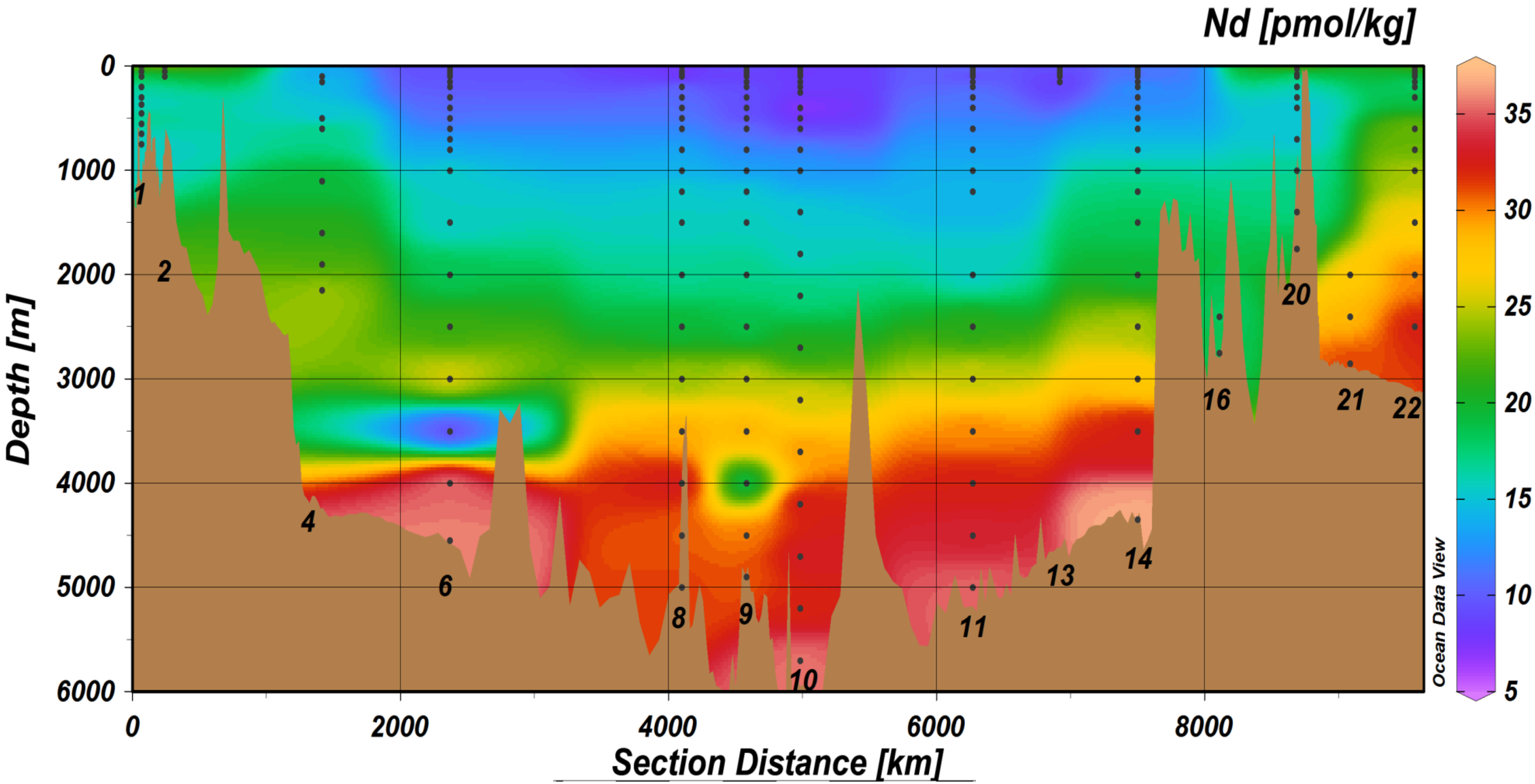


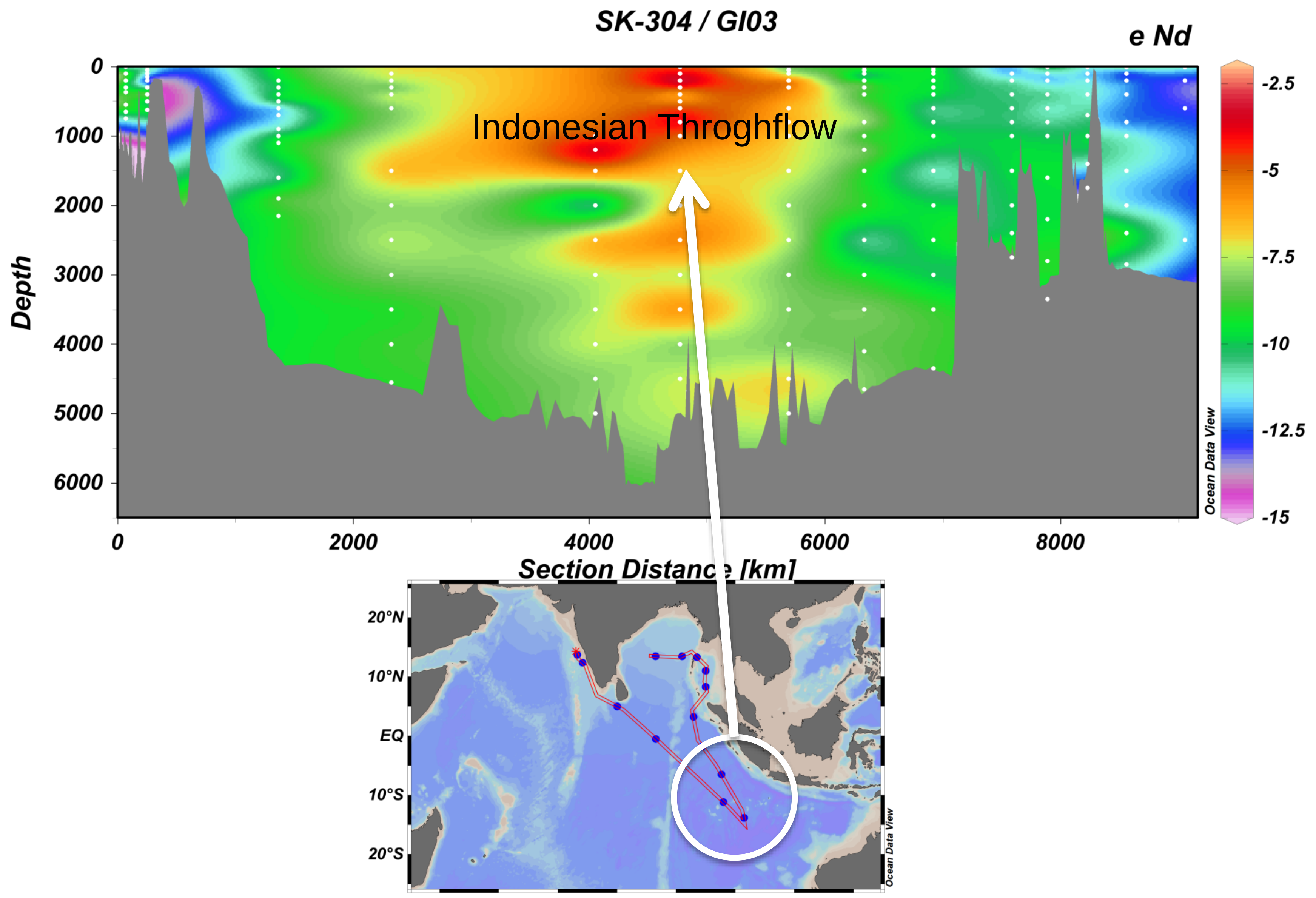
30°N
20°N
10°N
EQ
10°S
20°S
30°S
60°E
80°E
100°E
120°E
India
Goa
Chennai
(21)
(17)
(16)
(14)
(13)
(11)
(06)
(08)
(09)
(10)
SK 304 B
SK 304 A
Indian Ocean
Jakarta
EQ
Ocean Data View

The Indonesian Throughflow (ITF) and Indian Ocean Dipole (IOD)

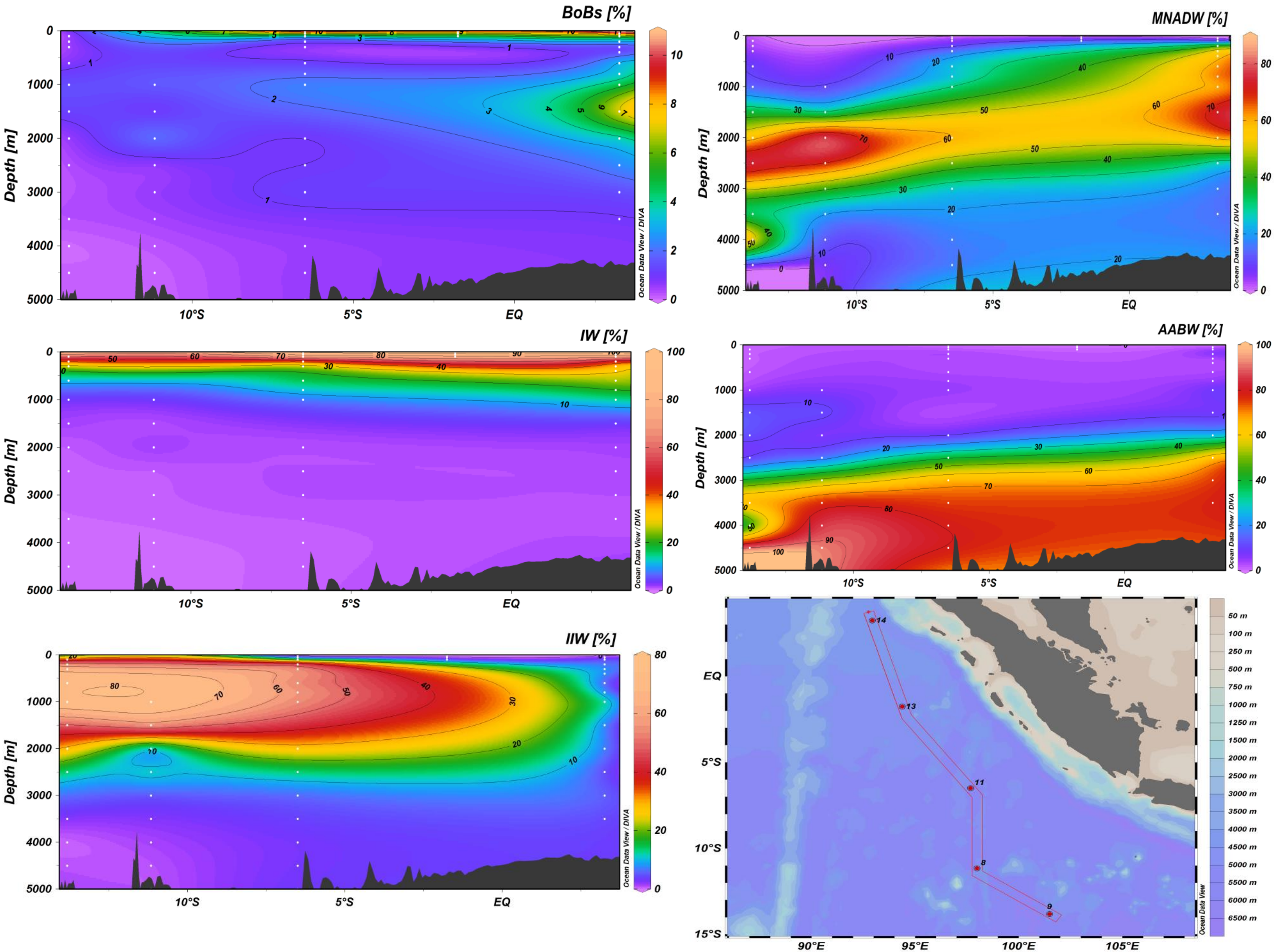
- ITF transports ~10 million m^3/s water from Pacific to Indian Ocean
- Heat Transport of the ITF is 1.09 x10^{15} Watt
- It impacts Indian Ocean Dipole and hence the monsoon
- Tracking ITF using Nd isotope composition of seawater



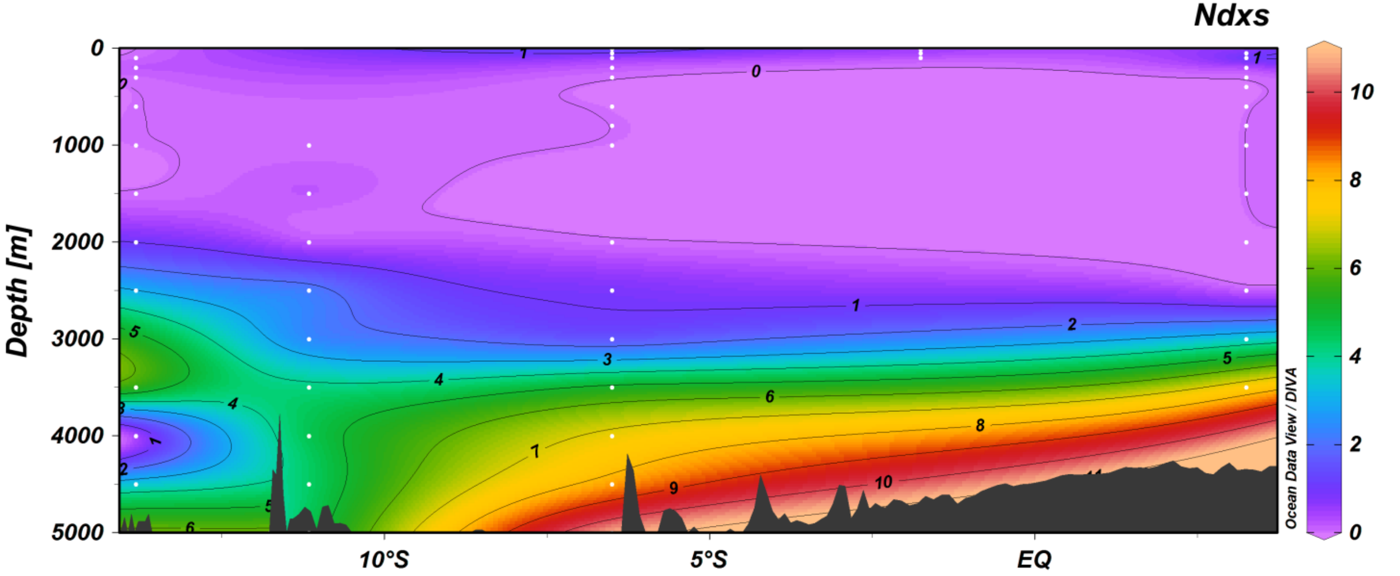

Nd [pmol/kg]
Depth [m]
0
1000
2000
3000
4000
5000
6000
0
2000
4000
6000
8000
Section Distance [km]
1
2
4
6
8
9
10
11
13
14
16
20
21
22
35
30
25
20
15
10
5
Ocean Data View

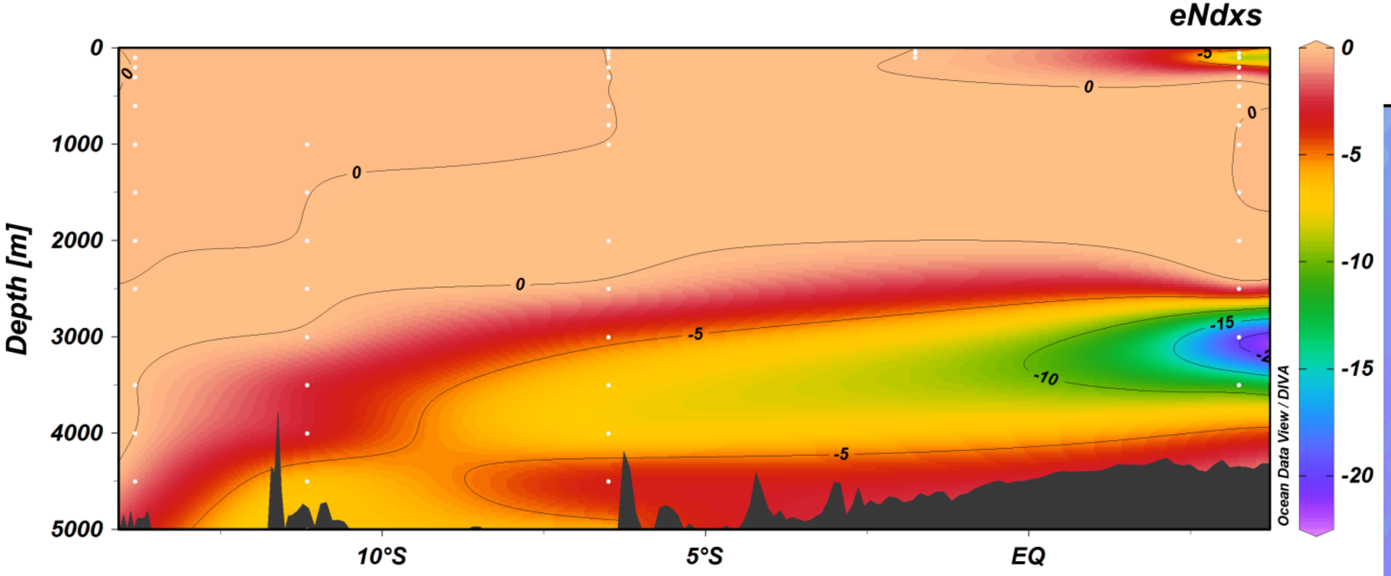


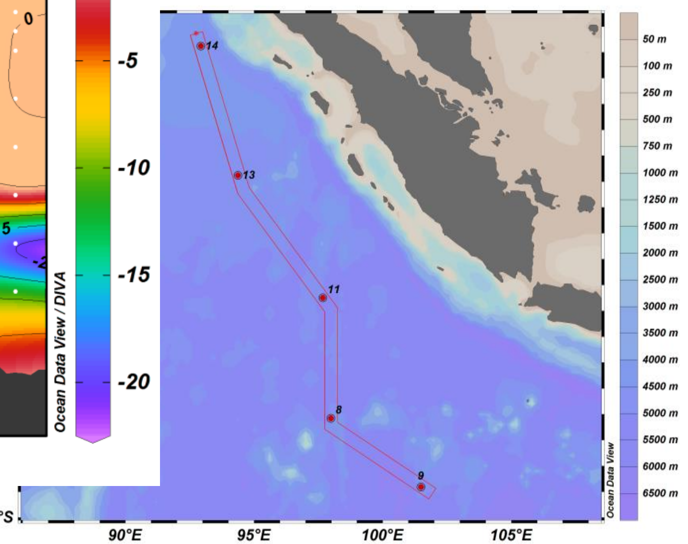
- Results indicate that ε_{Nd} (Nd isotope composition) of water can be used to track Indonesian Throughflow (ITF) as the pacific waters have higher ε_{Nd}
- Impact of ITF on paleo-monsoon can be assessed using ε_{Nd} in forams from sediments and corals


BoBs [%]
MNADW [%]
IW [%]
AABW [%]
IIW [%]
Depth [m]
0
1000
2000
3000
4000
5000
10°S
5°S
EQ
Ocean Data View / DIVA
EQ
5°S
10°S
15°S
90°E
95°E
100°E
105°E
14
13
11
8
9
50 m
100 m
250 m
500 m
750 m
1000 m
1250 m
1500 m
2000 m
2500 m
3000 m
3500 m
4000 m
4500 m
5000 m
5500 m
6000 m
6500 m
Ocean Data View

Excess Nd and their isotope composition
















Thanks