Scavenging Systematics and Surprises in GEOTRACES Data

Synthesis workshop - Biogeochemical Cycling of Trace Elements within the Ocean
1 – 4 August 2016
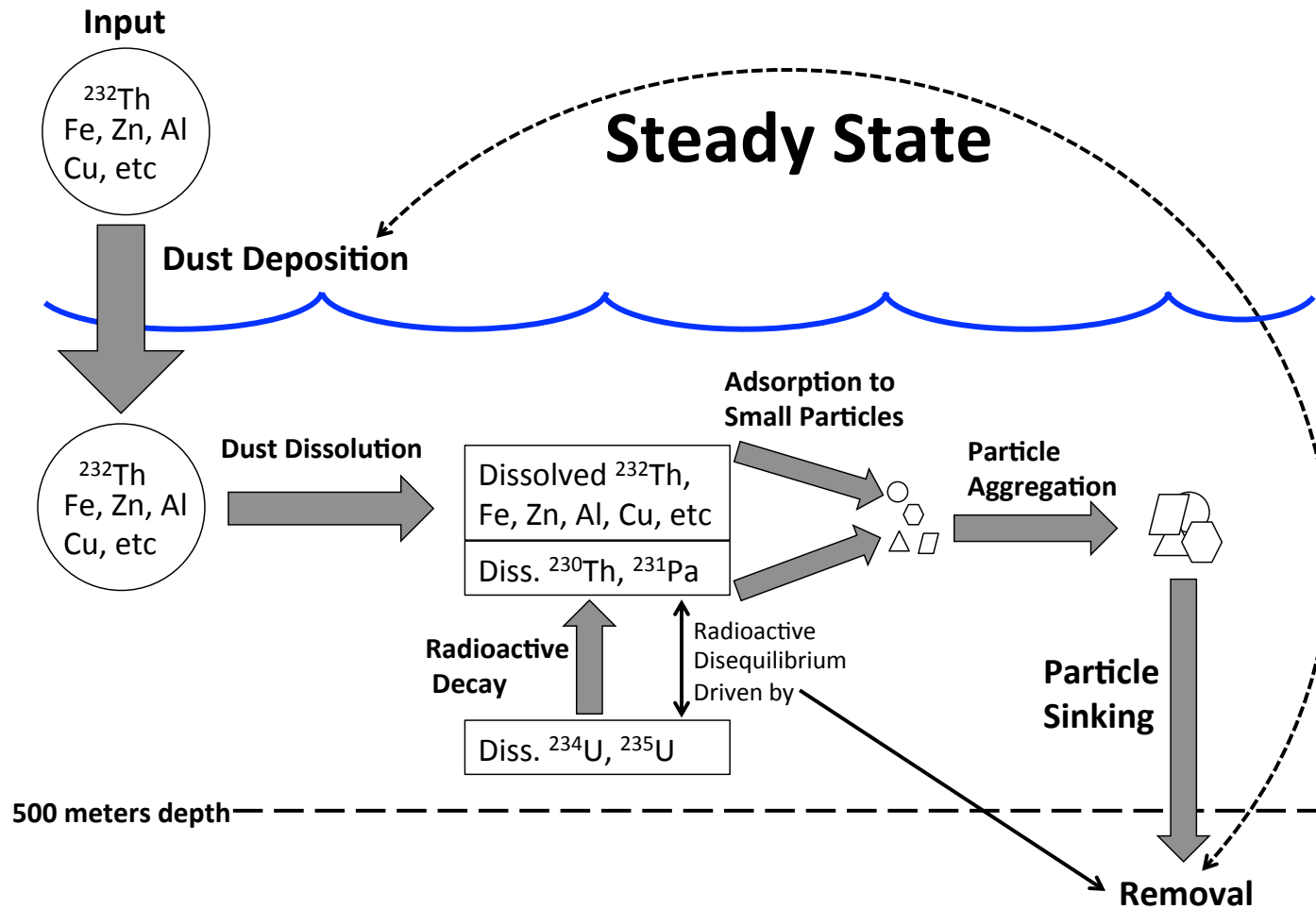
Bob Anderson

Lamont-Doherty Earth Observatory
COLUMBIA UNIVERSITY | EARTH INSTITUTE

With contributions from many generators of GEOTRACES data
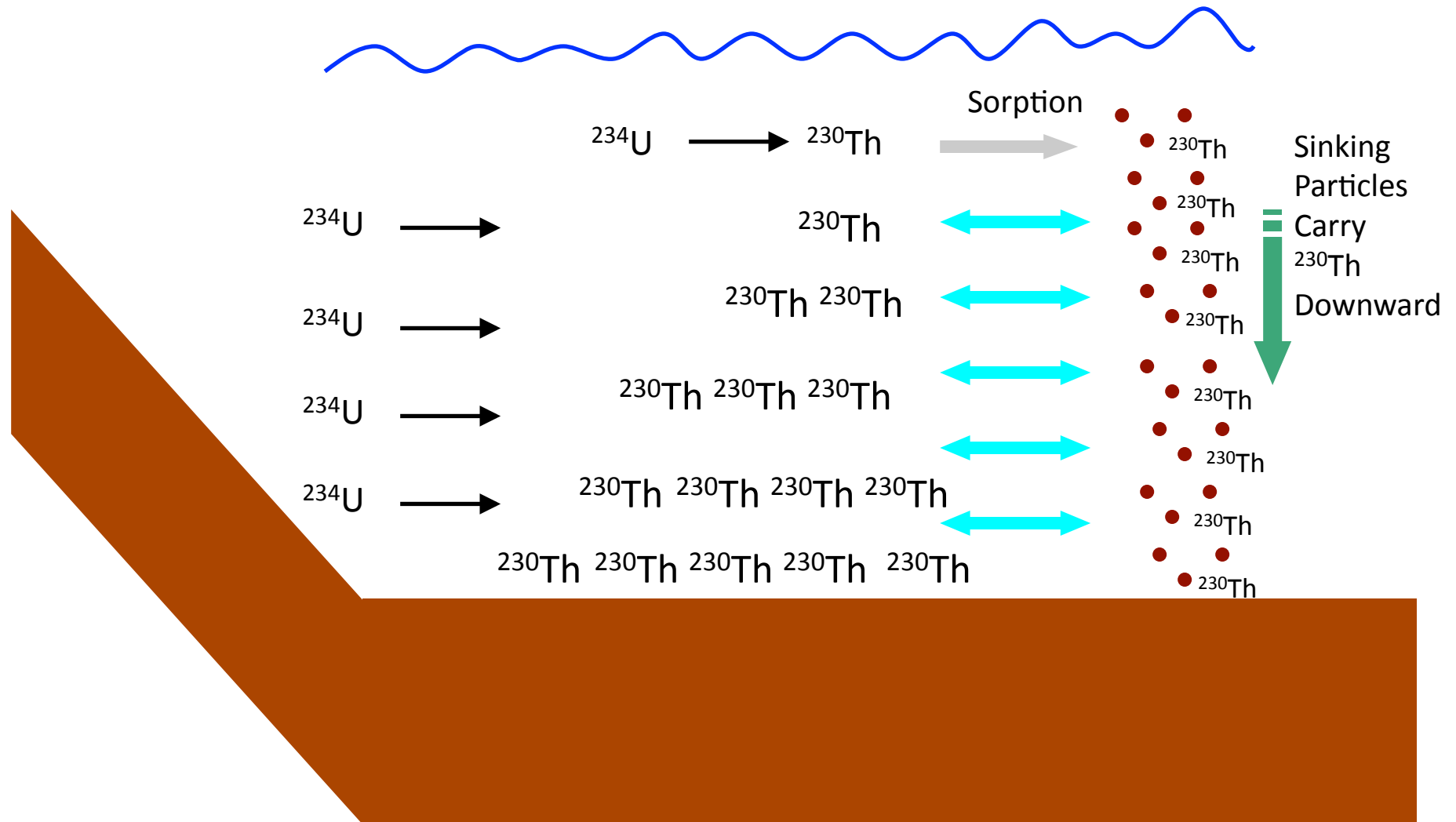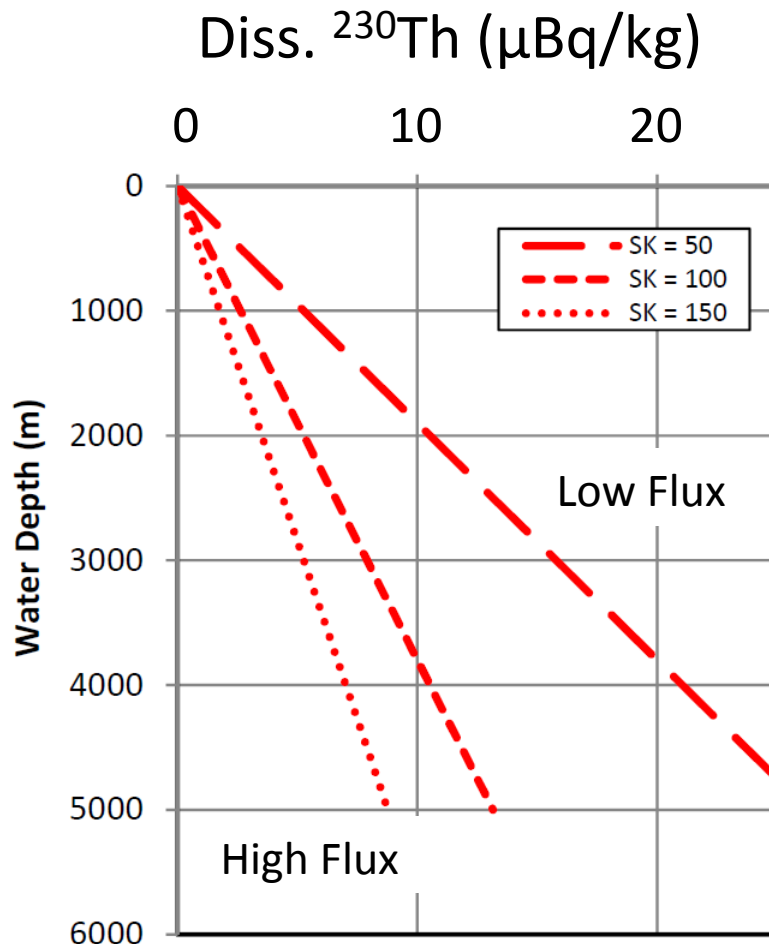
http://www.geotraces.org/

Dissolved ^{232}Th and ^{230}Th trace scavenging and removal processes

Reversible scavenging causes ^{230}Th concentration to increase with depth

Linear ^{230}Th concentration profiles in a simple 1-D ocean model

Diss. ^{230}Th (µBq/kg)

Water Depth (m)

Legend:
- SK = 50
- SK = 100
- SK = 150

Low Flux

High Flux

Bacon and Anderson, 1982
Based on Krishnaswami et al., 1976

$$\frac{dC_d}{dZ} = \frac{P}{SK}$$

$$\frac{dC_p}{dZ} = \frac{P}{S}$$

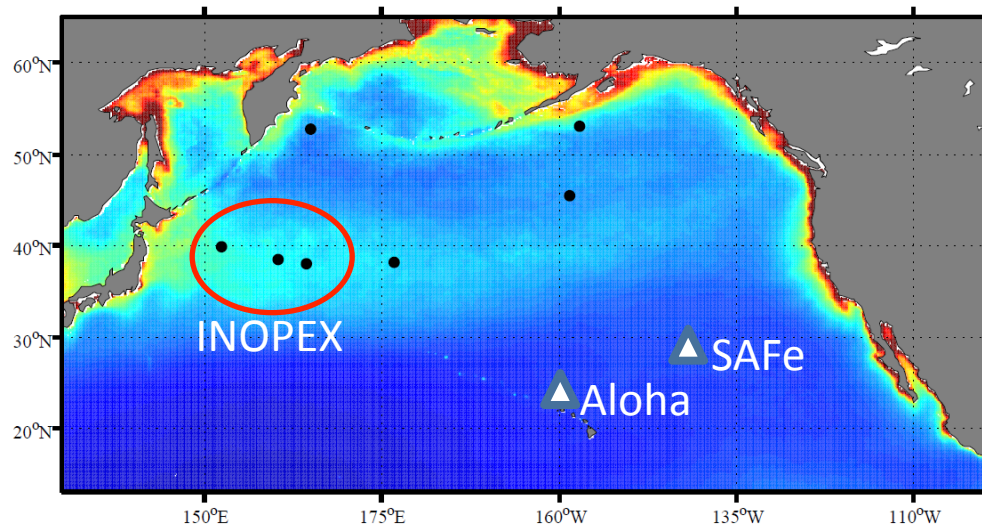$P = 0.5\ fg\ kg^{-1}\ yr^{-1}$
$S \sim 1000\ m\ yr^{-1}$
$K \sim 0.2$

P is production due to U decay
S is sinking rate of particles
K is solid-solution distribution coefficient

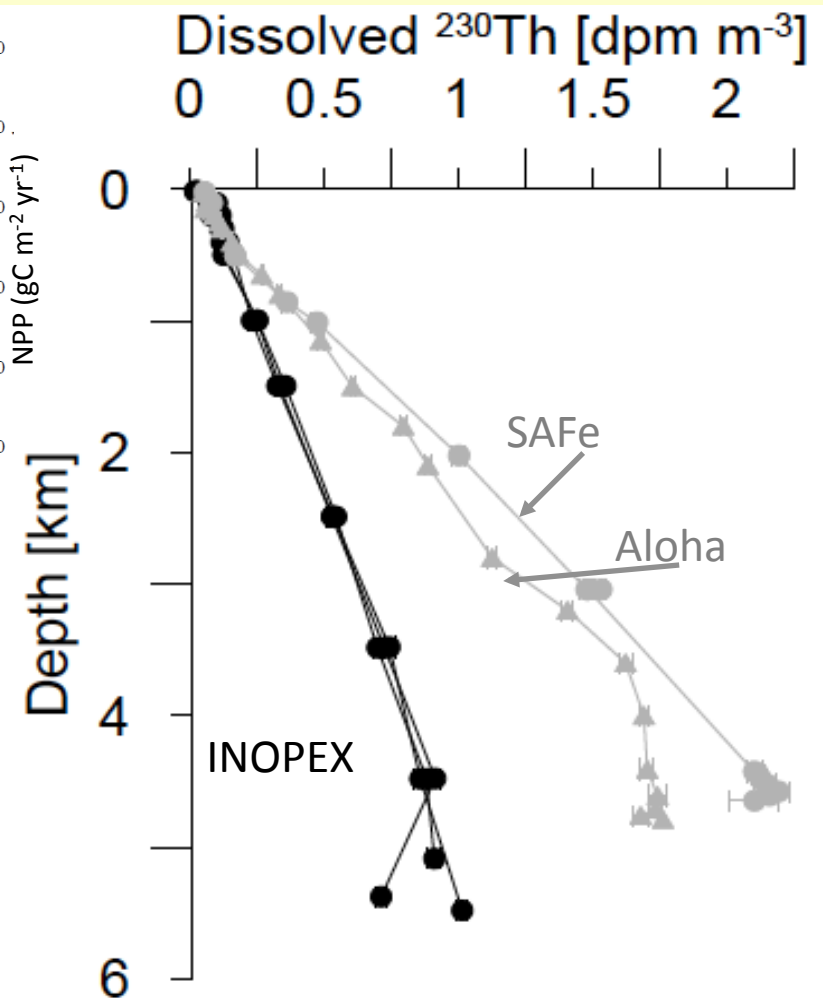K varies with abundance and reactivity of particles

Simple 1-D scavenging model fits ^{230}Th data at many Pacific stations

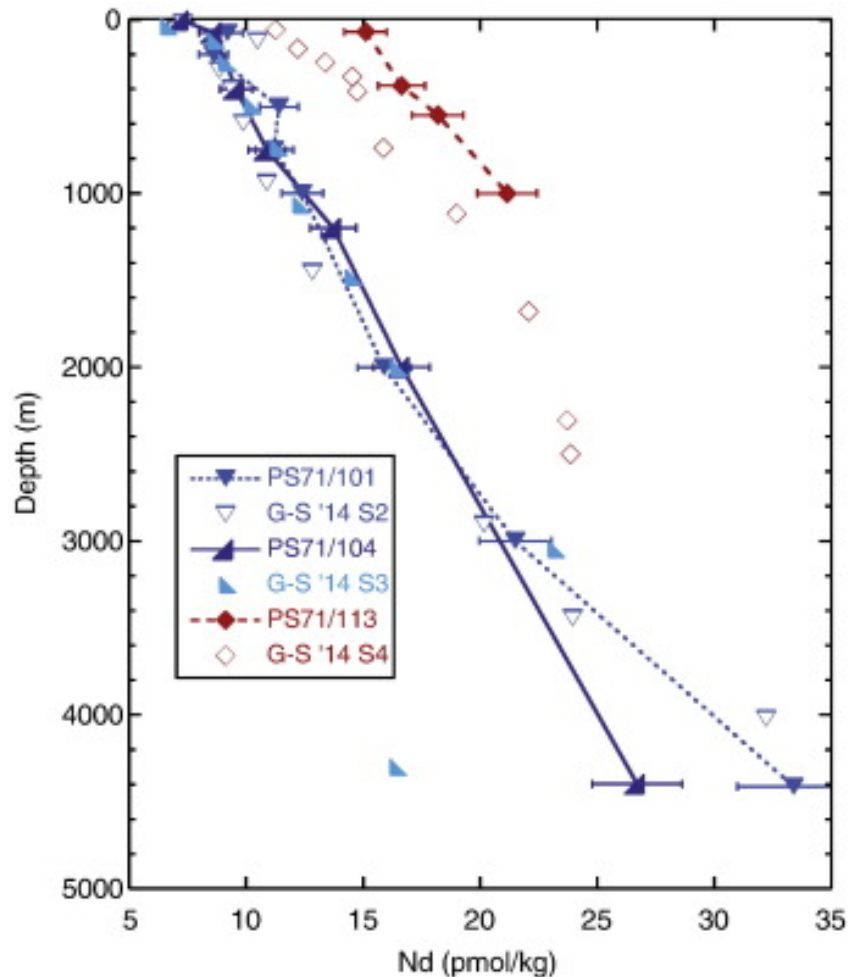Higher particle flux (K) in NW Pacific lowers ^{230}Th Concentration.

Hayes et al., EPSL 2013

Aloha data from Roy-Barman et al., 1996

What can we infer from concentration profiles of other trace elements?

What can we infer from concentration profiles of other trace elements?

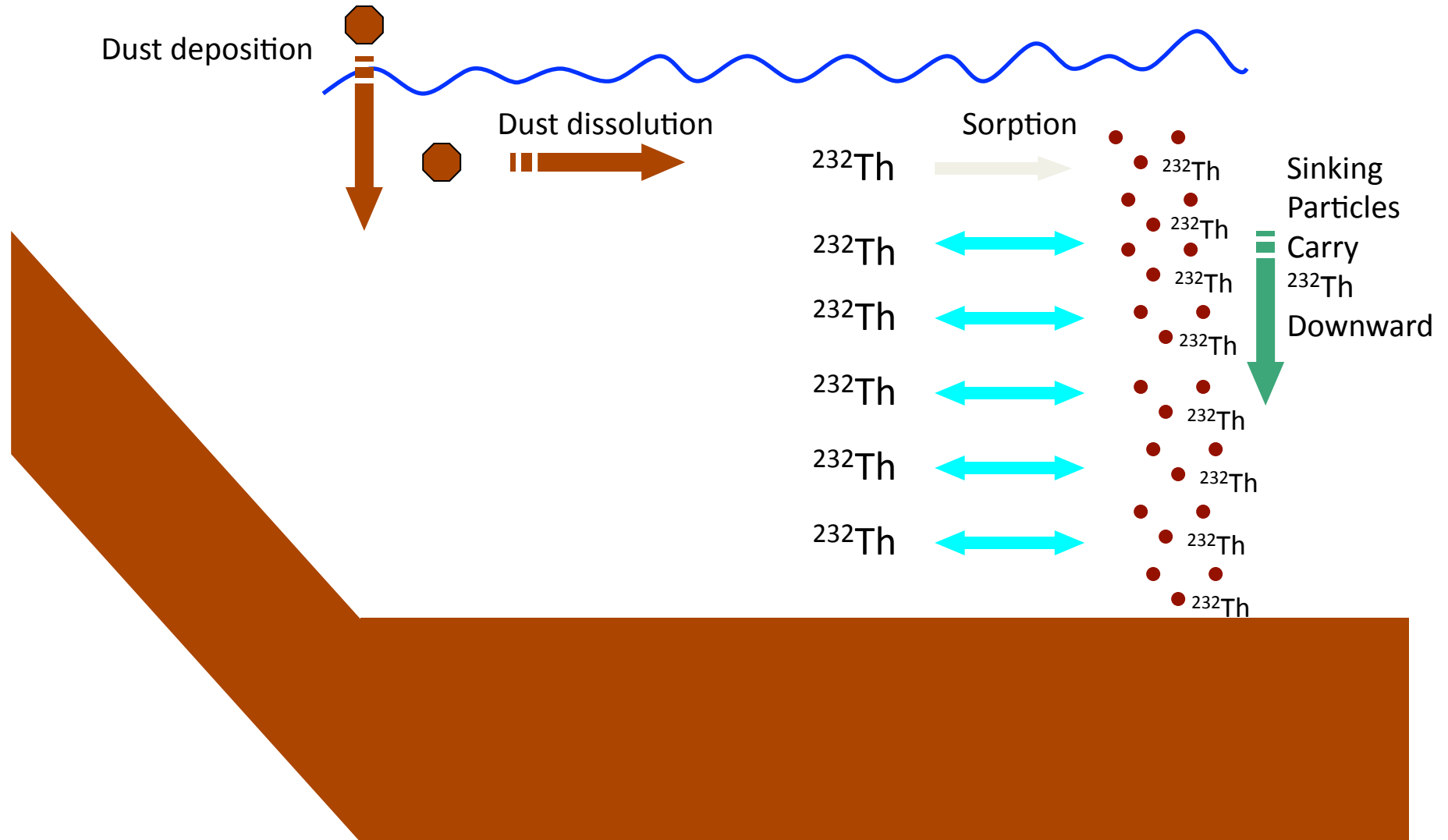Fig. S1, Hathorne et al., Mar. Chem. 2015

Linear concentration profiles of LREE

Variously described as indicating:

Irreversible scavenging – Hathorne et al., 2015

Reversible scavenging – Lambelet et al, 2016
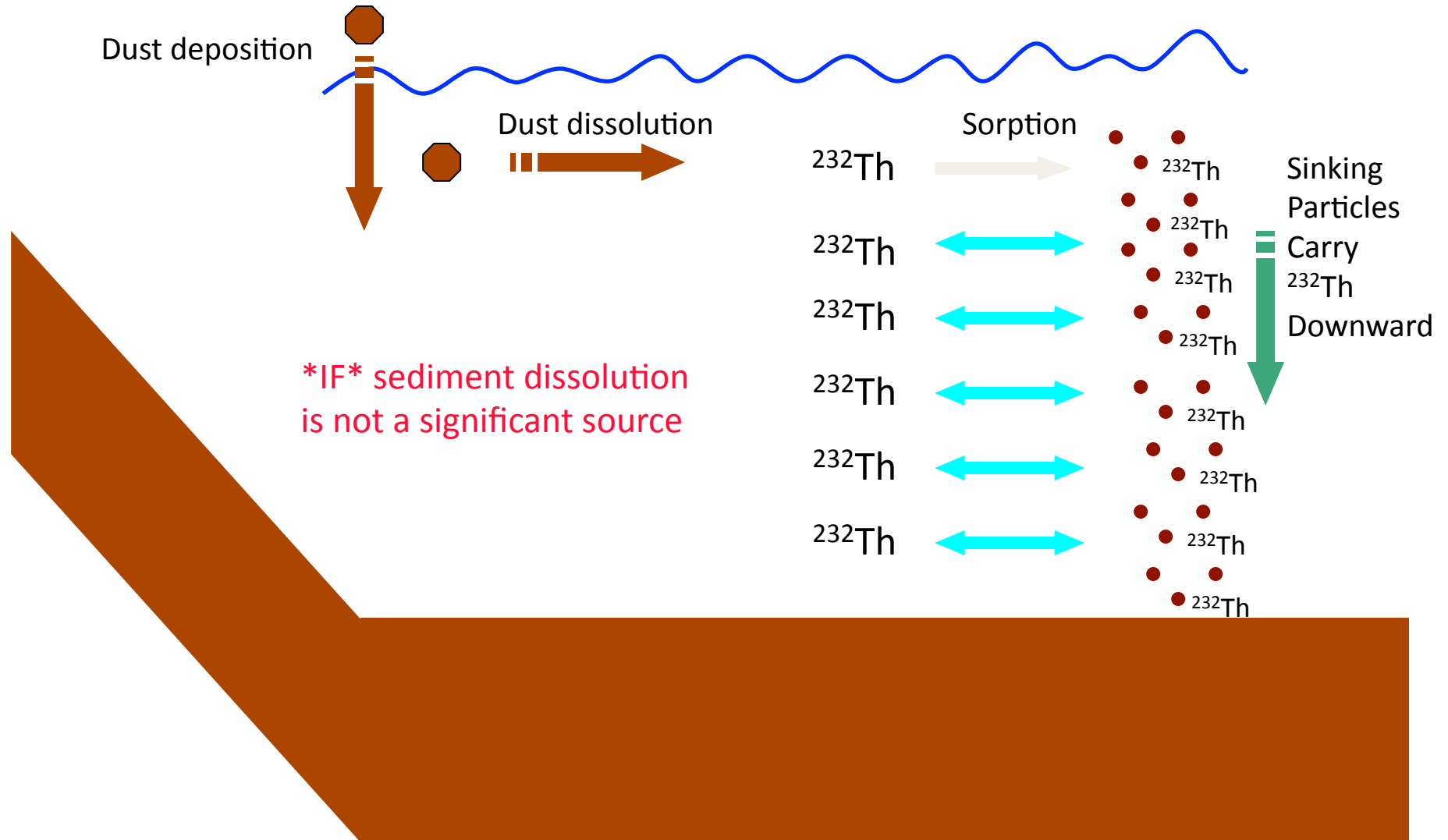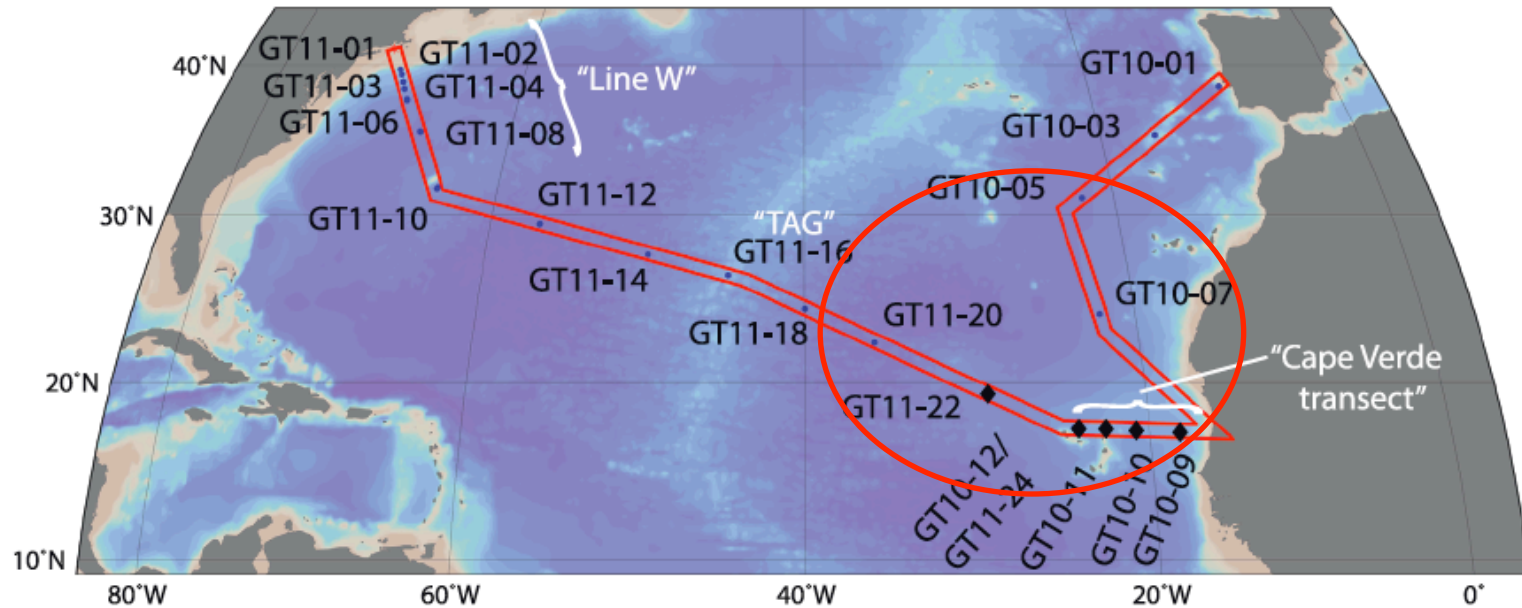
Reversible scavenging causes ^{232}Th concentration to be invariant with depth
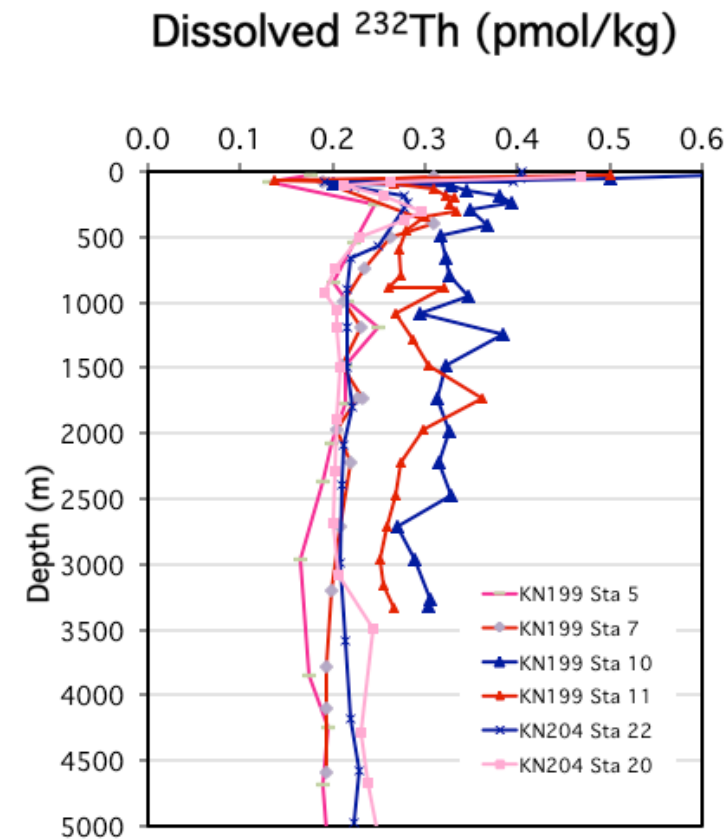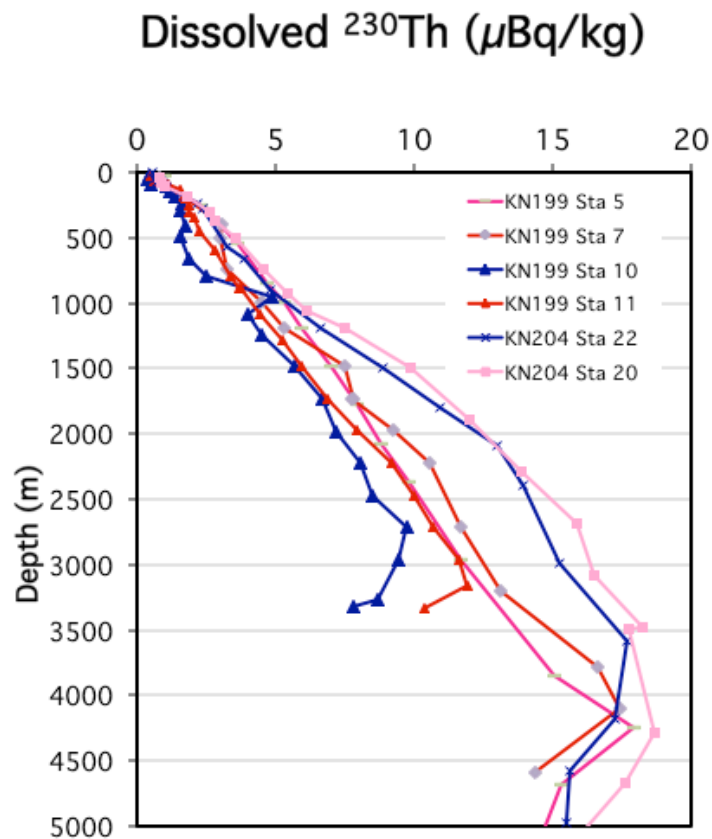
Reversible scavenging causes ^{232}Th concentration to be invariant with depth

US GEOTRACES Atlantic Results – GA03

Dissolved Th profiles illustrate reversible scavenging for different source distributions

Dissolved ^{230}Th (μBq/kg)

Dissolved ^{232}Th (pmol/kg)

^{230}Th: Radiogenic source throughout the water column, physical transport & scavenging

^{232}Th: Lithogenic source at sea surface, physical transport & scavenging

So - What can we infer from the linear concentration profiles of LREE?

Fig. S1, Hathorne et al., Mar. Chem. 2015
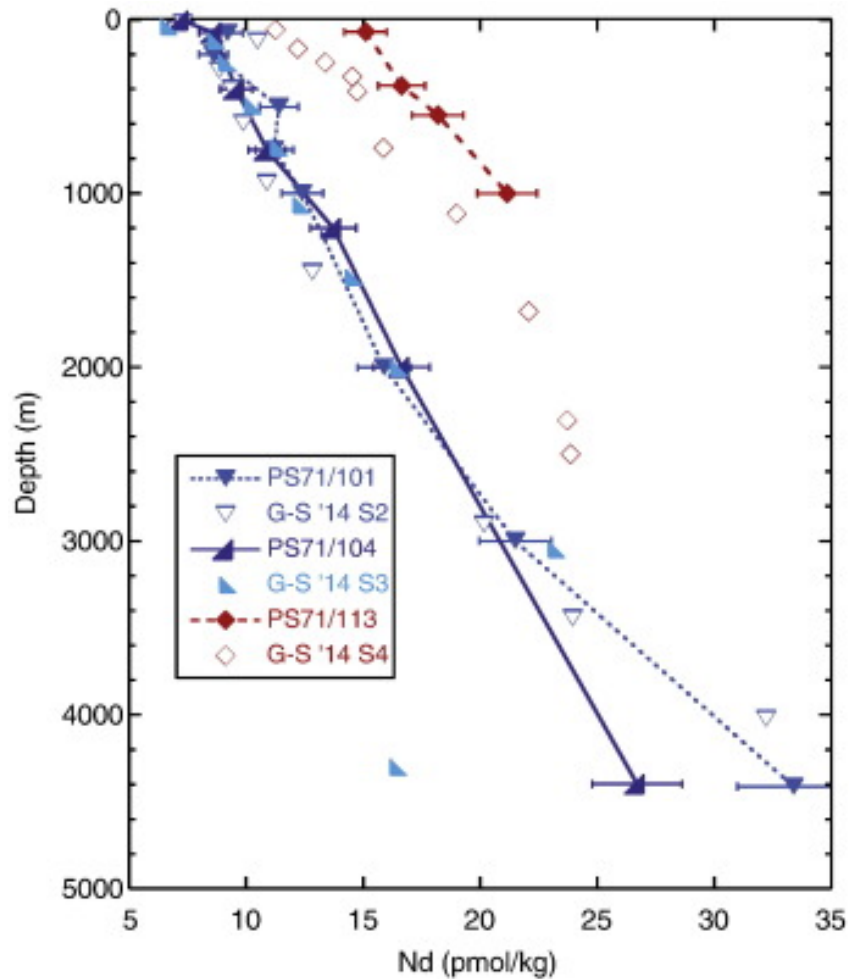
Simplified view of reversible scavenging if Nd source is exclusively at the sea surface

dissolved   *particulate*

$$d[Nd] = \frac{p[Nd]}{K \bullet Cp}$$

Equilibrium partition coefficient

Particle concentration

So - What can we infer from the linear concentration profiles of LREE?

Fig. S1, Hathorne et al., Mar. Chem. 2015
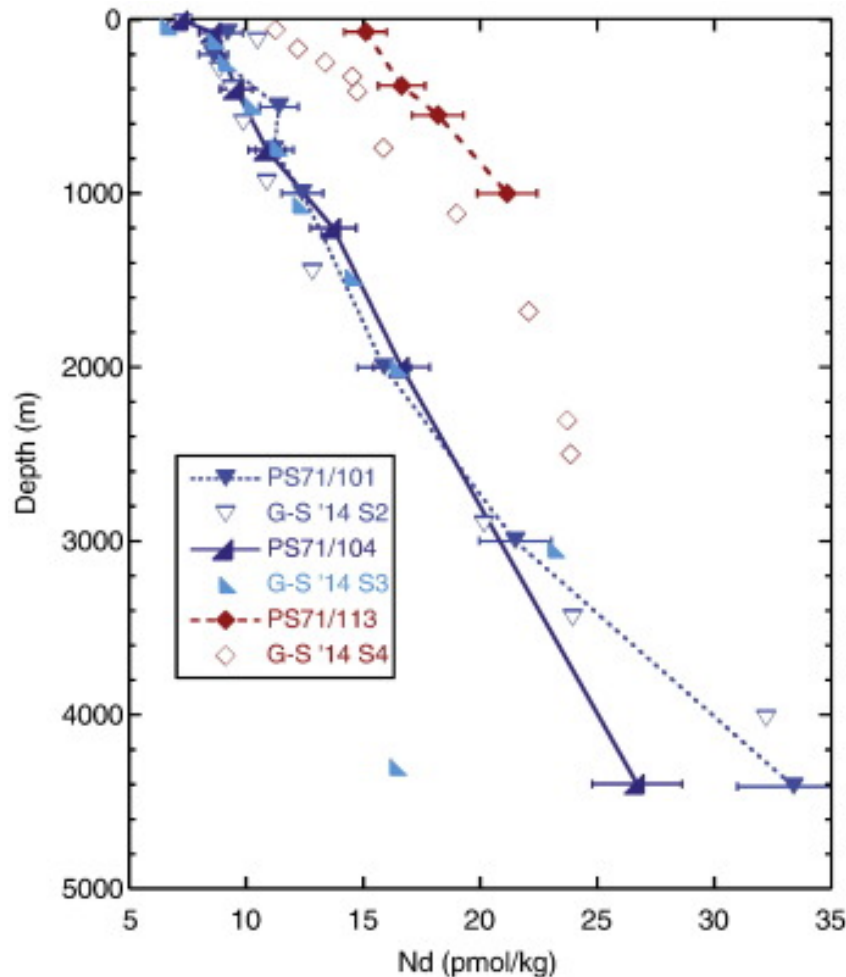
Increasing [Nd] with depth indicates one of the following:

1) A source of dissolved [Nd] at depth
2) Particle affinity for scavenging Nd decreases with depth, or
3) Particle concentration decreases with depth (regeneration)

$$d[Nd] = \frac{p[Nd]}{K \cdot Cp}$$

Equilibrium partition coefficient

Particle concentration

GEOTRACES principle to apply in "Synthesis" (TEIs = trace elements & isotopes)

Studying multiple TEIs simultaneously provides information that is inaccessible by examining a single element in isolation.
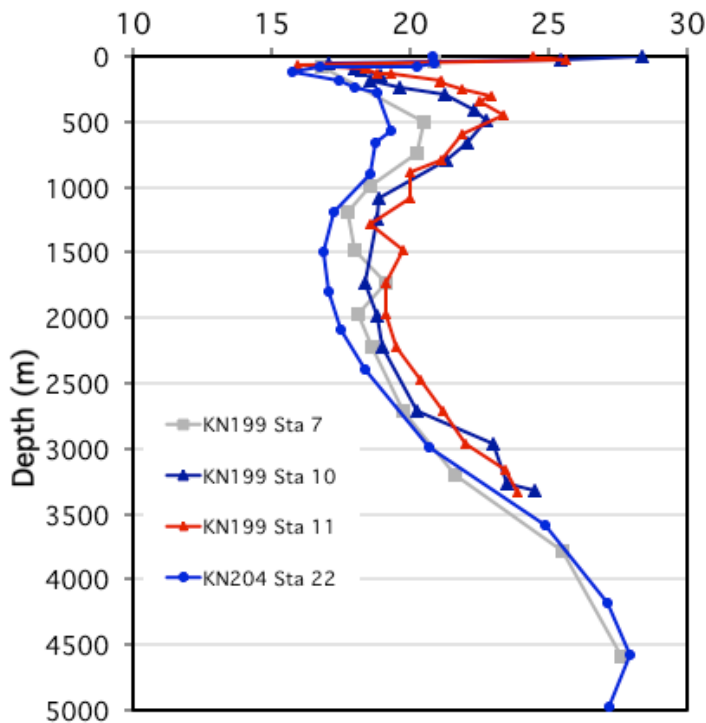
Each element can be understood as a special case in a continuum of geochemical properties, where the similarities and contrasts among the elements offer insights into each individual element.

In many cases, the better constrained, or more simply defined, behavior of one element illuminates the behavior of another.

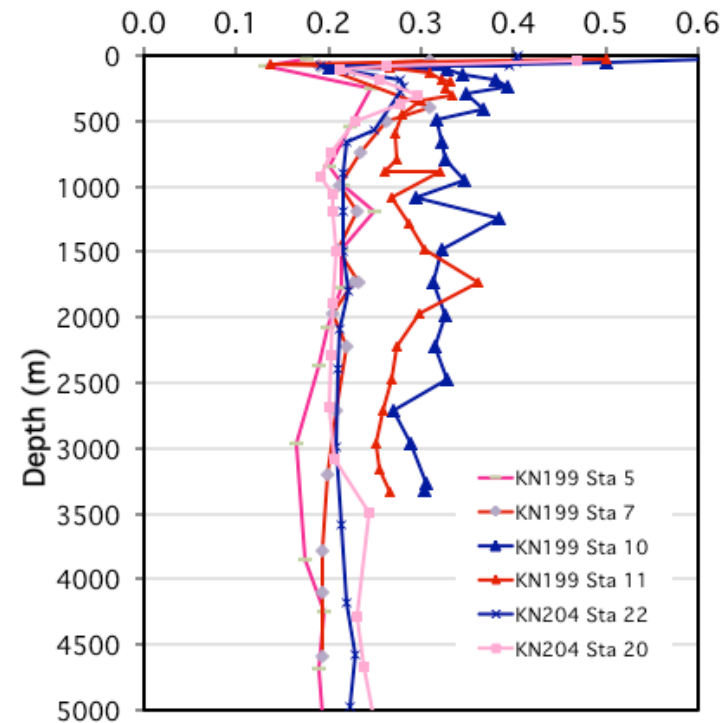*Modified from the GEOTRACES Science Plan, 2006*

Dissolved Nd profiles indicate multiple processes affect E Trop N Atlantic distributions
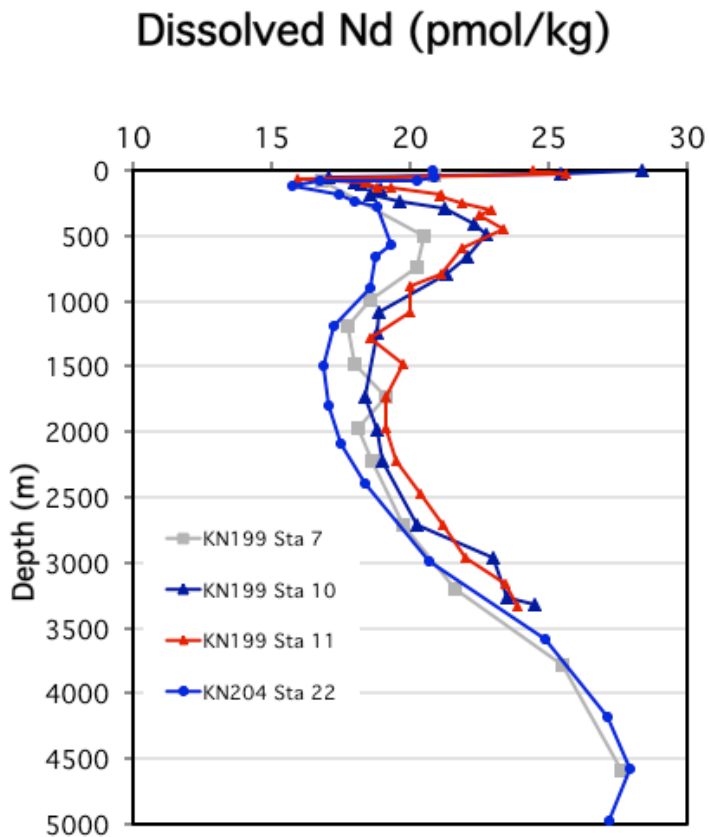

Dissolved Nd (pmol/kg)

- KN199 Sta 7
- KN199 Sta 10
- KN199 Sta 11
- KN204 Sta 22

Stichel et al., 2015

Dissolved ^{232}Th (pmol/kg)

- KN199 Sta 5
- KN199 Sta 7
- KN199 Sta 10
- KN199 Sta 11
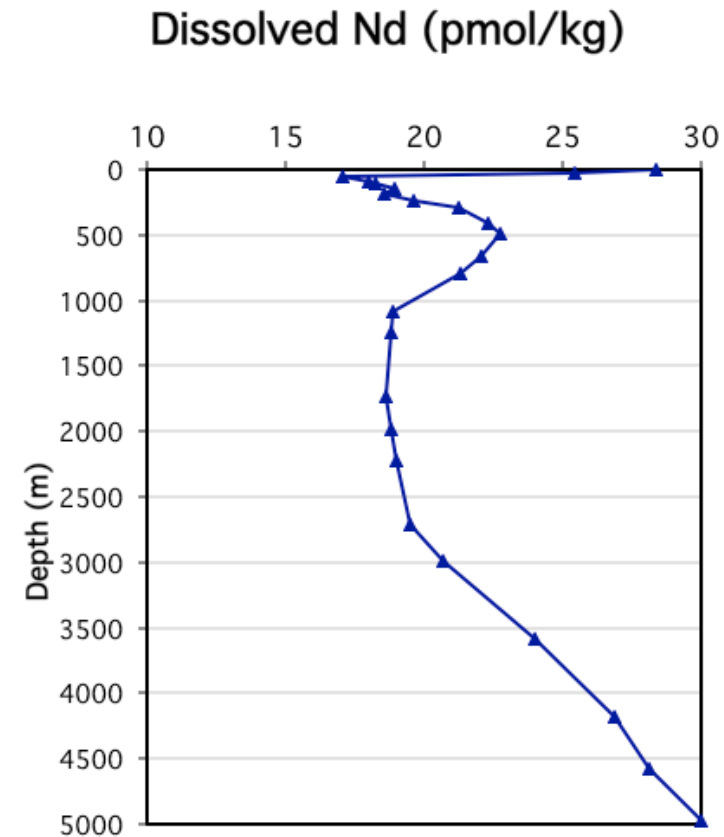- KN204 Sta 22
- KN204 Sta 20

Unpublished

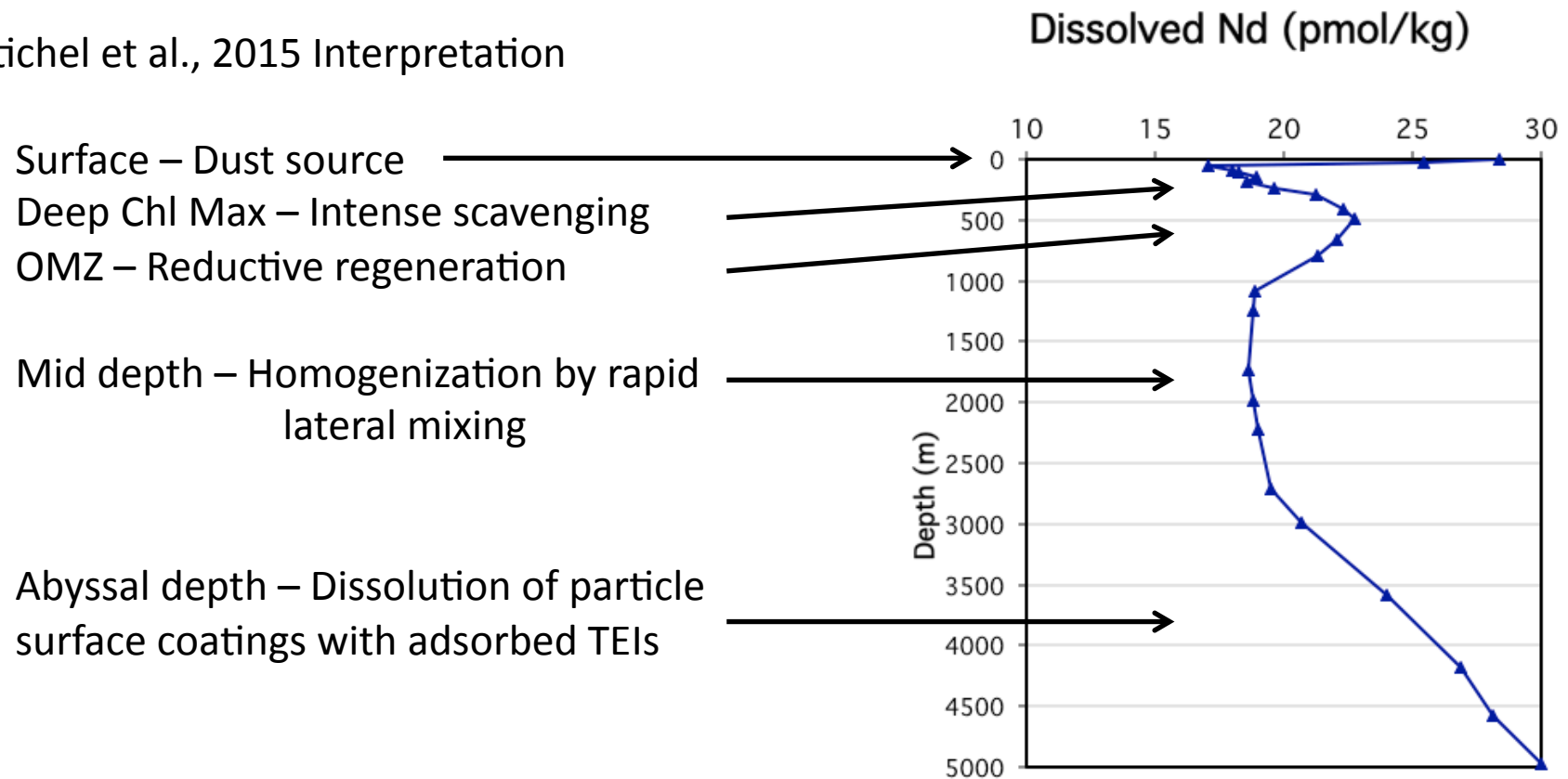# Idealized E Atlantic dissolved Nd profile for illustrations

Stichel et al., 2015

Idealized representative [Nd] profile

Idealized dissolved Nd profiles indicate multiple processes affect E Trop N Atlantic distributions

Stichel et al., 2015 Interpretation

Surface – Dust source
Deep Chl Max – Intense scavenging
OMZ – Reductive regeneration

Mid depth – Homogenization by rapid lateral mixing

Abyssal depth – Dissolution of particle surface coatings with adsorbed TEIs

Dissolved Nd (pmol/kg)

Idealized dissolved Nd profiles indicate multiple processes affect E Trop N Atlantic distributions
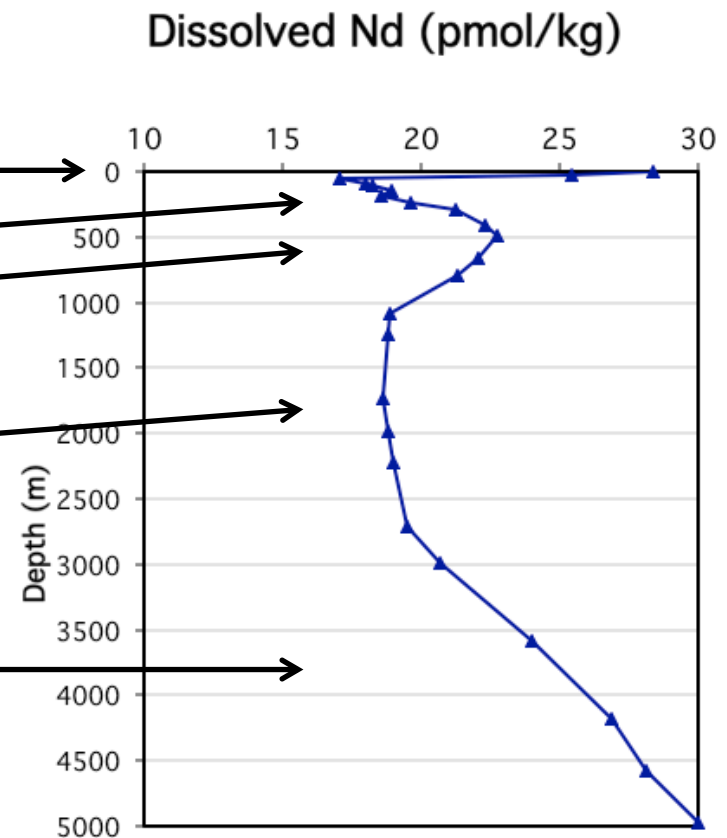
Alternative Interpretation

Surface – Dust source & rapid aggregation
Deep Chl Max – Aggregate bypass
OMZ – Aggregate fragmentation &
    desorption

Mid depth – Reversible scavenging

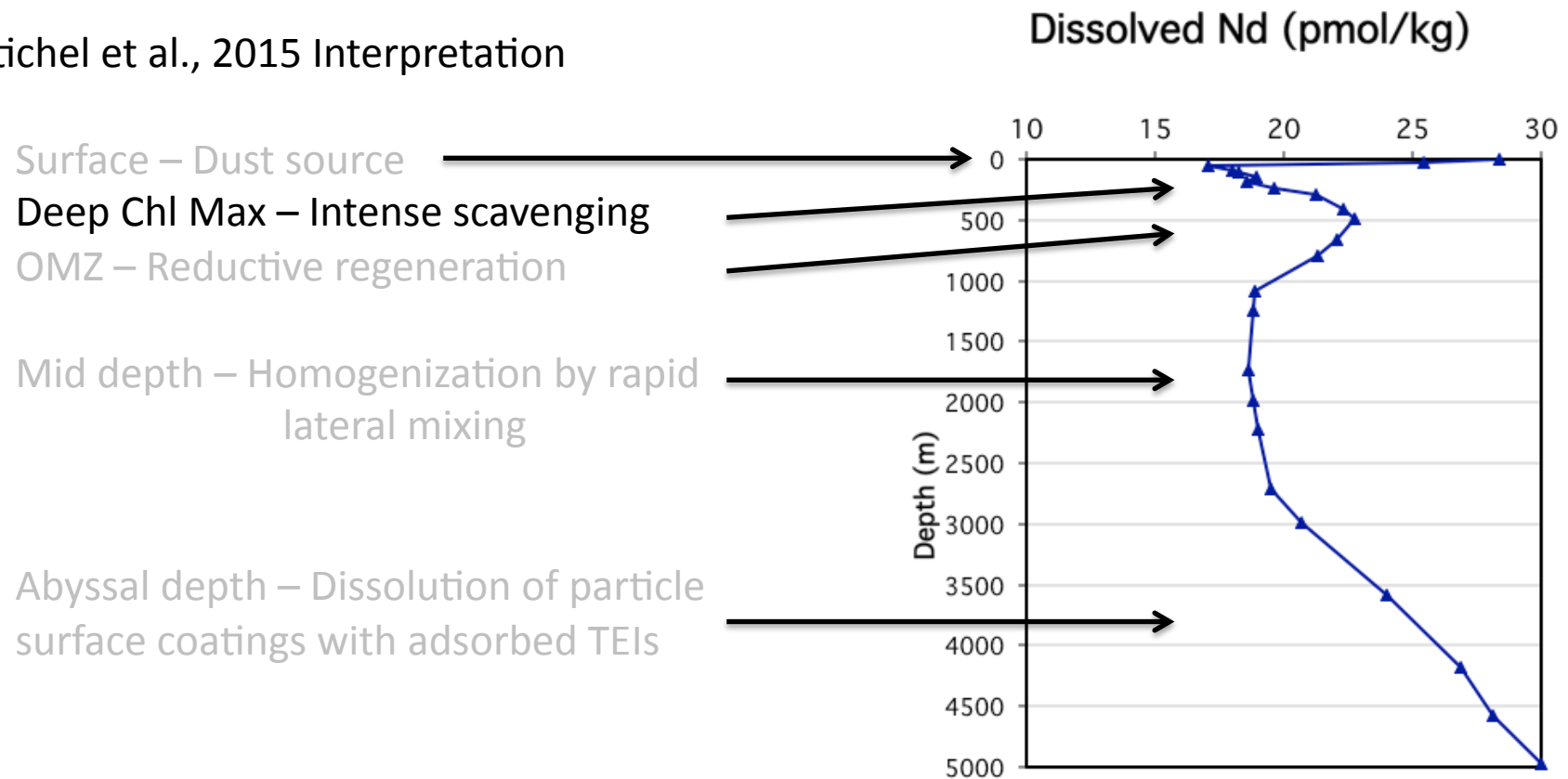Abyssal depth – Advection of
"preformed" [Nd]

Ohnemus and Lam, 2015
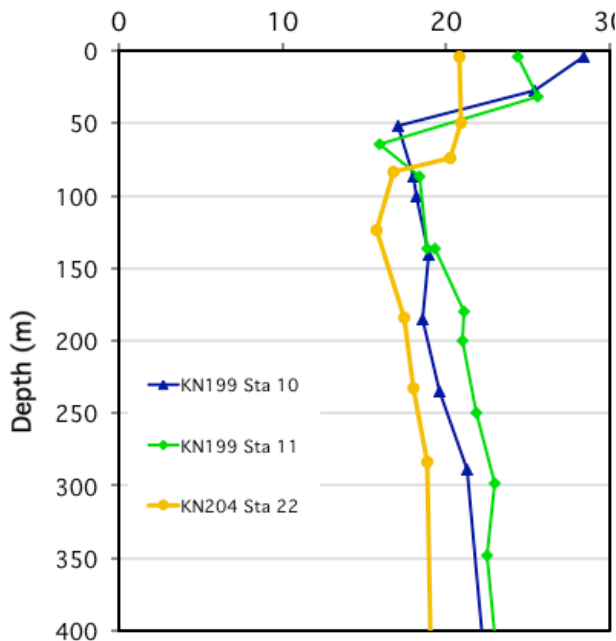Anderson, first principles
Zheng et al., 2016

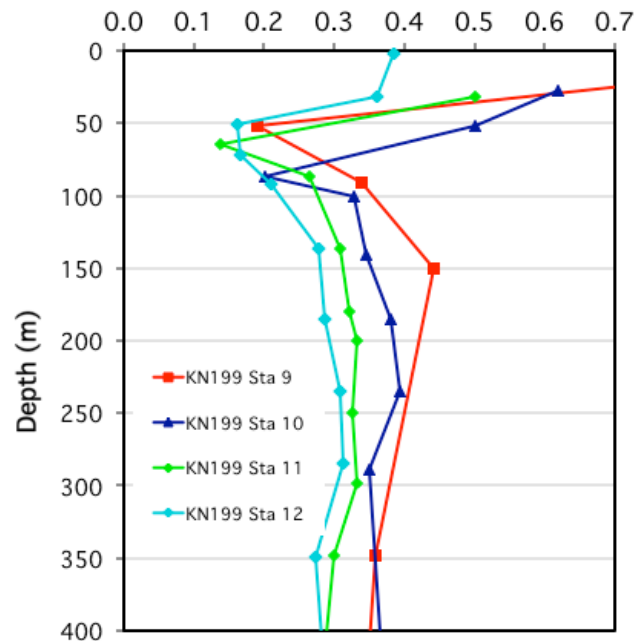# Deep Chlorophyll Maximum: DCM @ ~60 – 120 m

Stichel et al., 2015 Interpretation

Surface – Dust source

Deep Chl Max – Intense scavenging

OMZ – Reductive regeneration

Mid depth – Homogenization by rapid lateral mixing

Abyssal depth – Dissolution of particle surface coatings with adsorbed TEIs

Dissolved Nd (pmol/kg)

Depth (m)

Non-biologically active <u>dissolved</u> metals have minima at the DCM (60 – 130 m)

Stichel et al., 2015

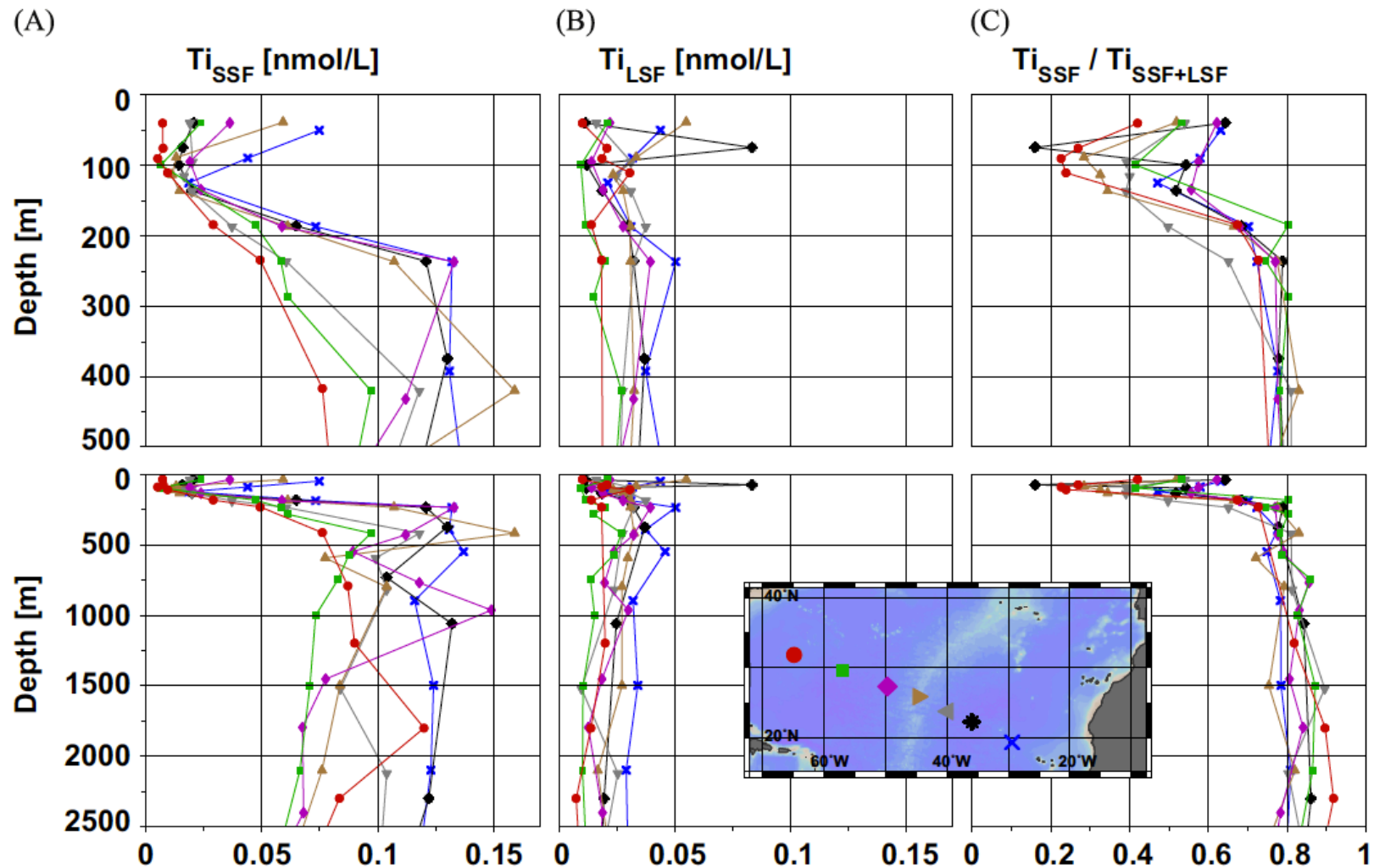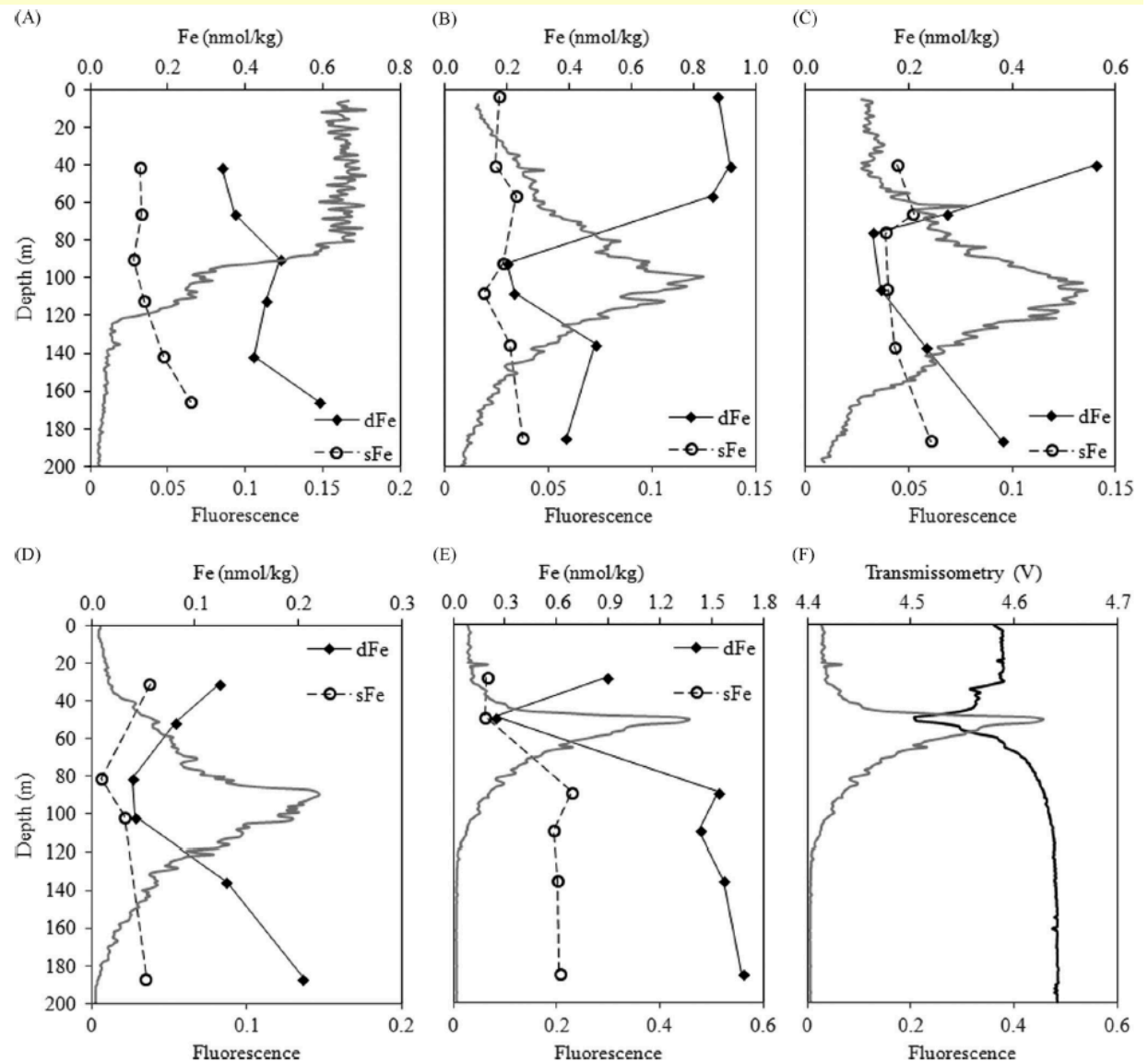Unpublished KN199
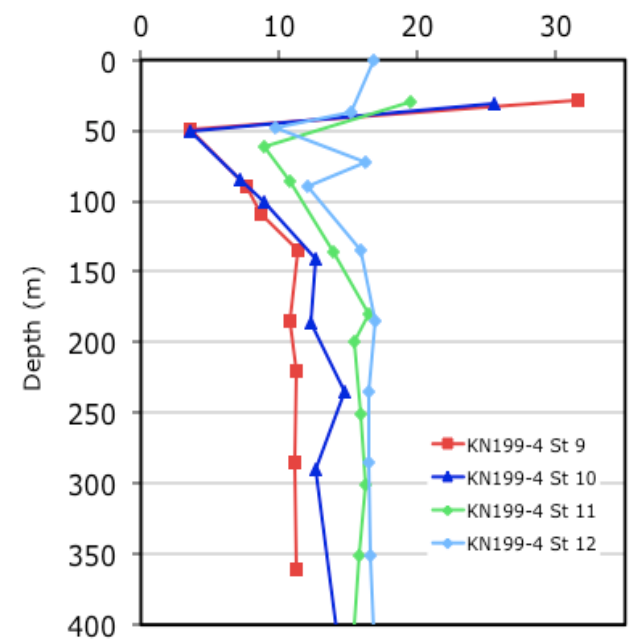
Measures et al., 2015

Non-biologically active particulate metals also have minima at the deep chlorophyll maximum

Ohnemus and Lam, 2015

Surface dFe is mainly colloidal but colloids disappear at the deep chlorophyll maximum

US GEOTRACES
GA03
Eastern Atlantic

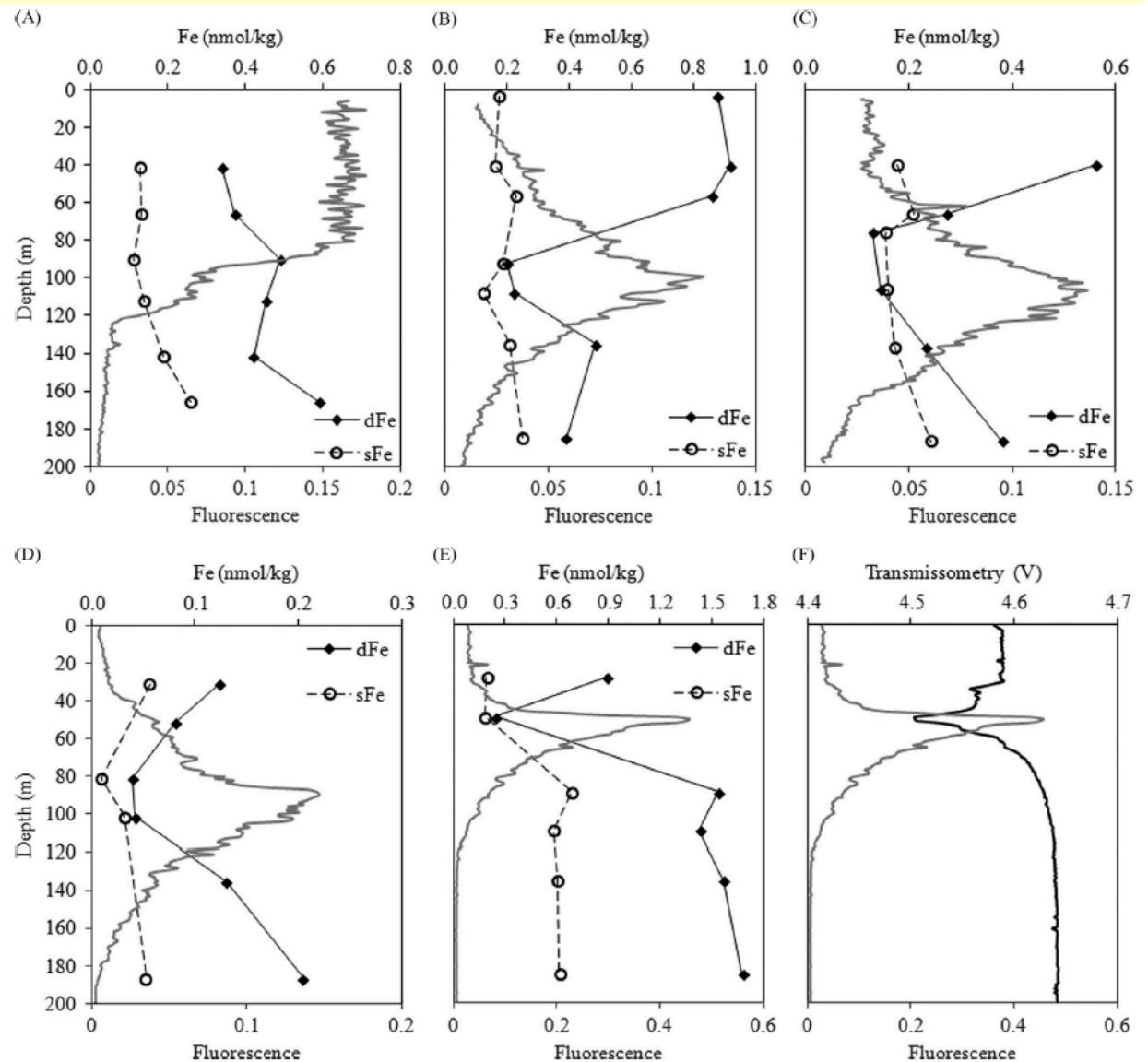Fitzsimmons et al., 2015

Surface dFe is mainly colloidal but colloids disappear at the deep chlorophyll maximum

Is colloidal Fe consumed biologically?

Rapidly removed by aggregation and sinking?

Fitzsimmons et al., 2015

[Al] and [Ti] minima at Chl max but <u>very</u> low colloid abundance
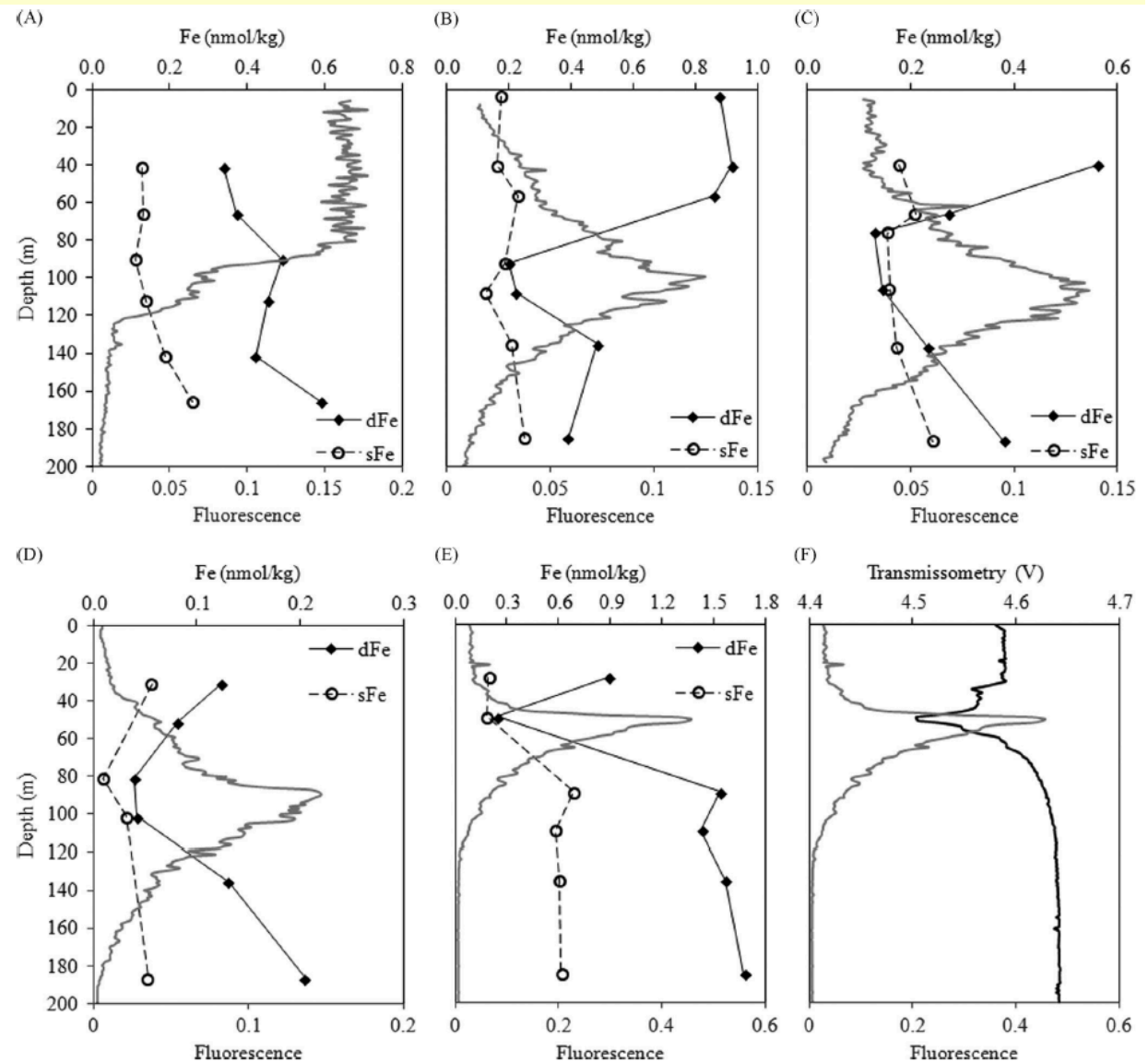
c[Al] = d[Al] – s[Al]
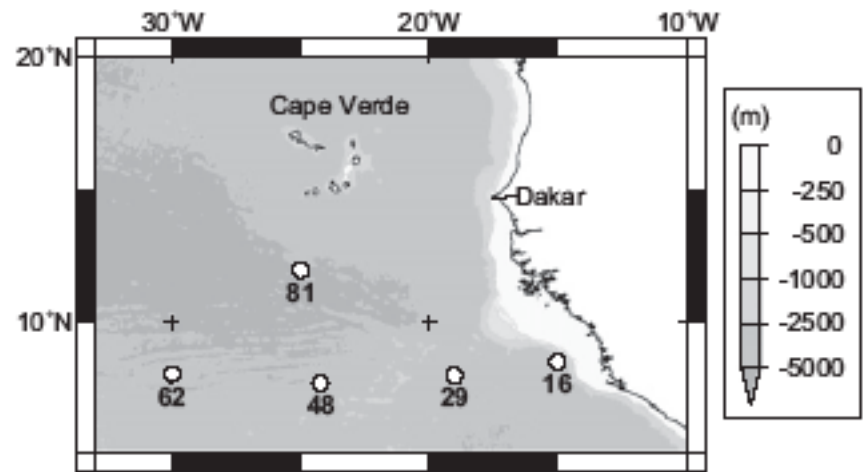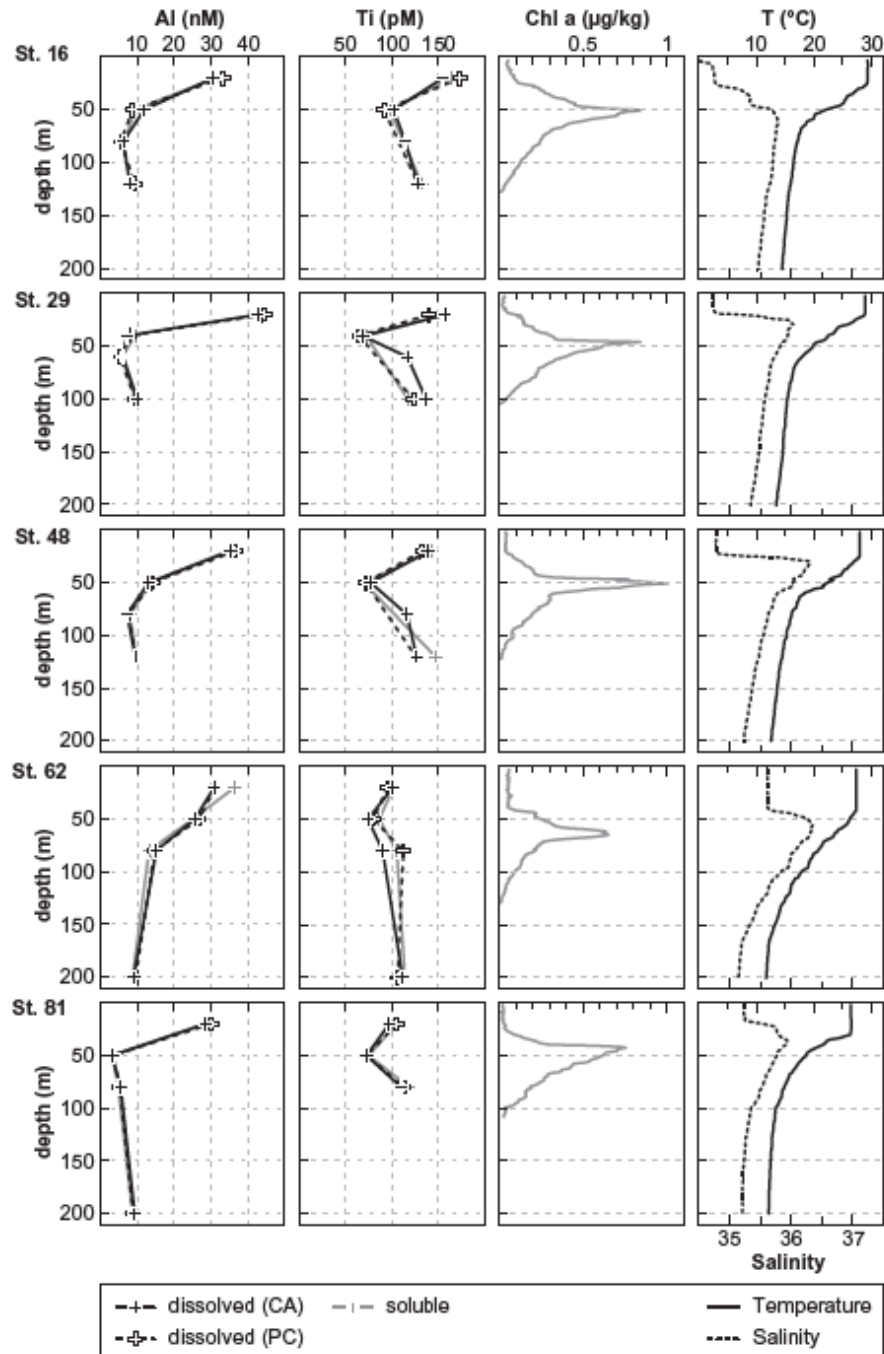
Dammshauser and Croot, 2012

Surface dFe is mainly colloidal but colloids disappear at the deep chlorophyll maximum
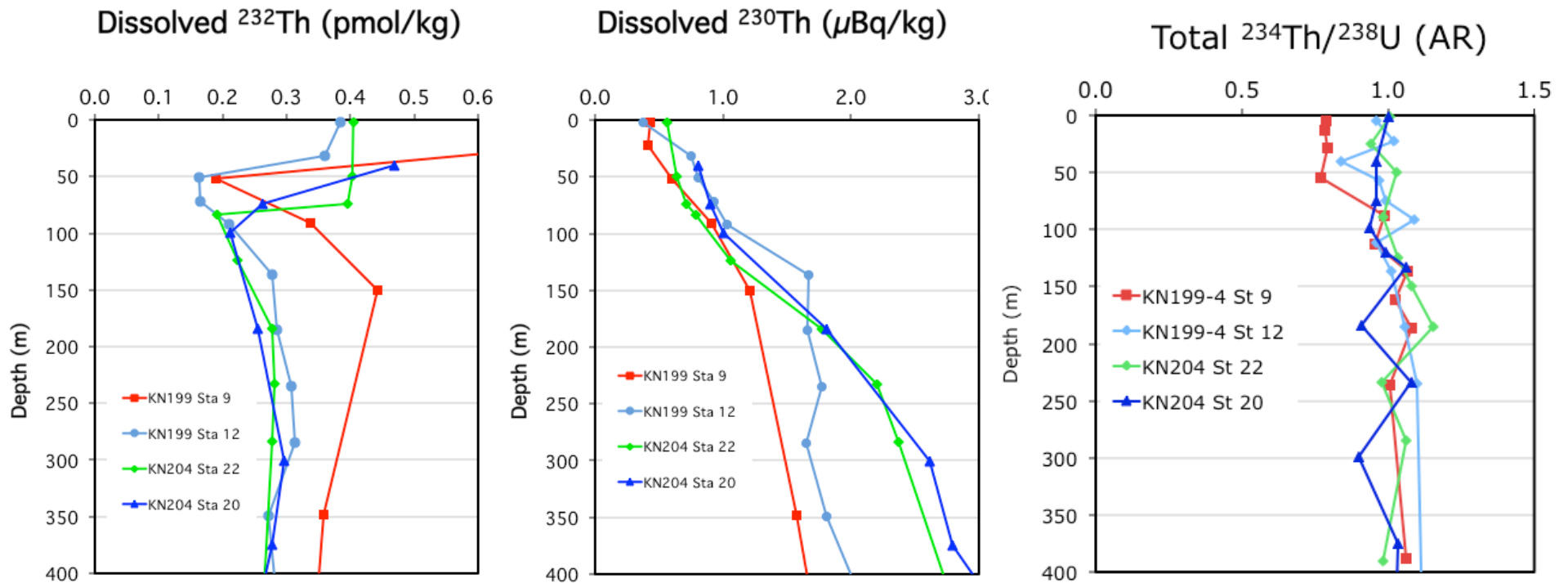
Is colloidal Fe consumed biologically?

Rapidly removed by aggregation and sinking?

If minima in Al and Ti reflect the same process that leads to minima in Fe, Th and Nd then colloid cycling is not the answer.

Fitzsimmons et al., 2015

Radiogenic ^{230}Th and ^{234}Th do not exhibit minimum concentrations at the DCM
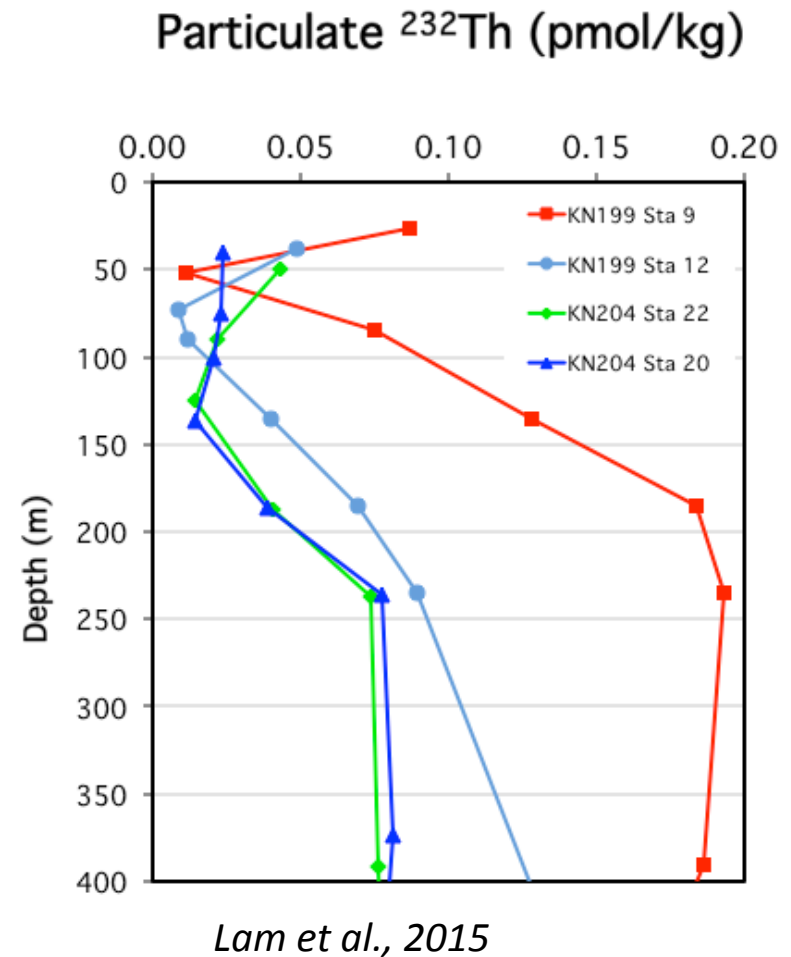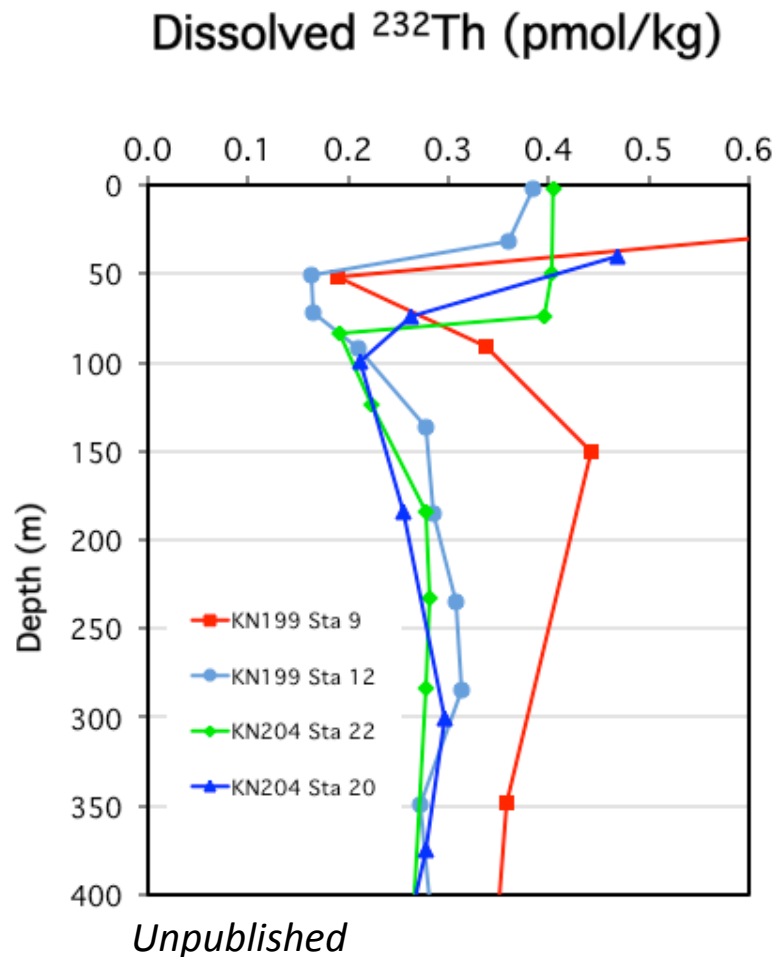

Unpublished   Hayes et al., 2015   Owens et al., 2015

A minimum dissolved ^{232}Th coincides with deep chl. maximum
Why do ^{230}Th and ^{234}Th not show a similar minima?

Dissolved ^{232}Th deficit in DCM is not simply transferred to particles

Dissolved ^{232}Th (pmol/kg)

Unpublished

Particulate ^{232}Th (pmol/kg)

Lam et al., 2015

Deep chlorophyll maximum summary

Upper ocean processes affect transport and transformation of micronutrients

Processes may affect bioavailability

Processes affect distributions of bio-active and non-bioactive metals alike

Hypotheses to explain TEI behavior in DCM do not fit all TEIs.

BUT! Examining multiple TEIs allows us to eliminate some hypotheses.
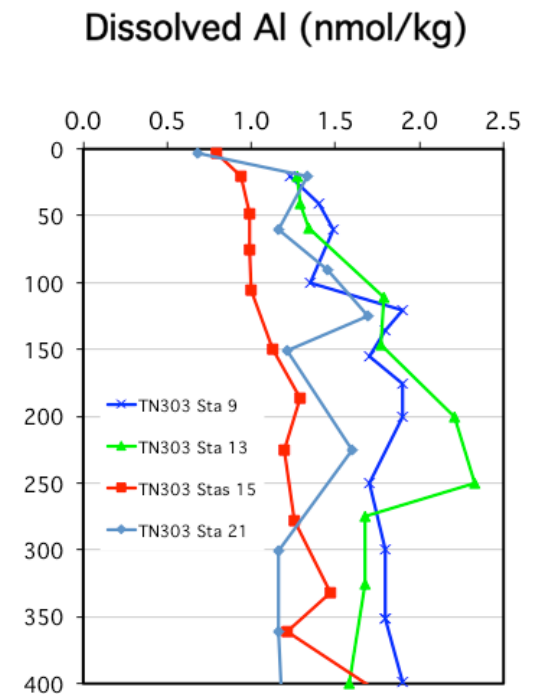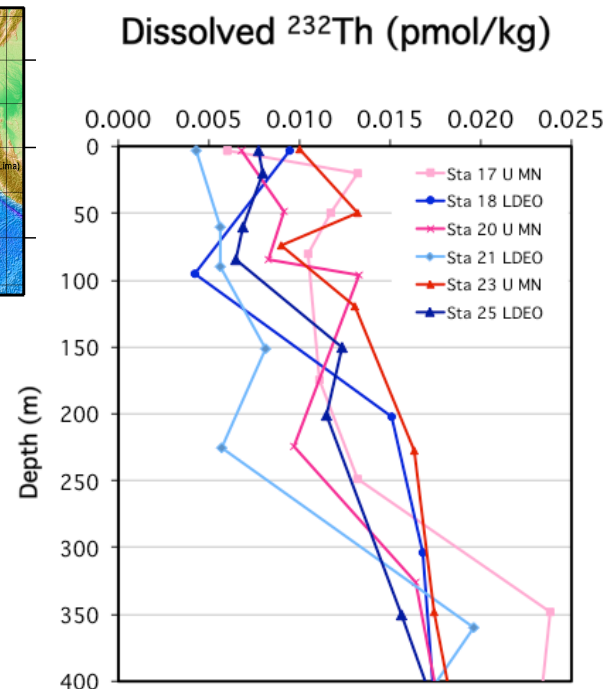
Deep chl. maximum – Additional clues

Similar TEI minima are not seen at the DCM in the eastern tropical South Pacific

GEOTRACES GP16 – Peru to Tahiti – DCM at 60 to 100 m (D. Ohnemus, pers comm)

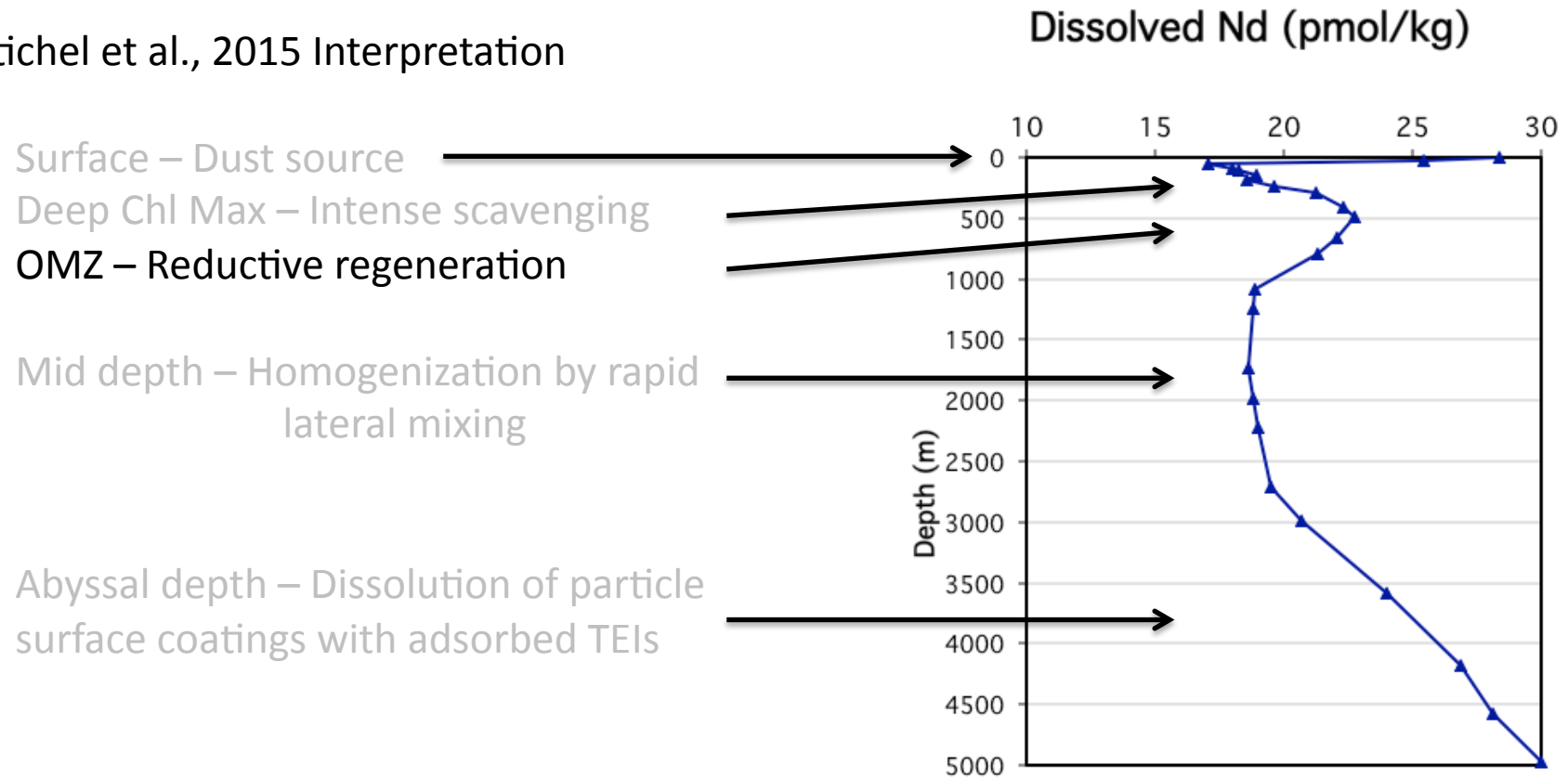**Use regional contrasts as well as multiple TEIs to test hypotheses.**
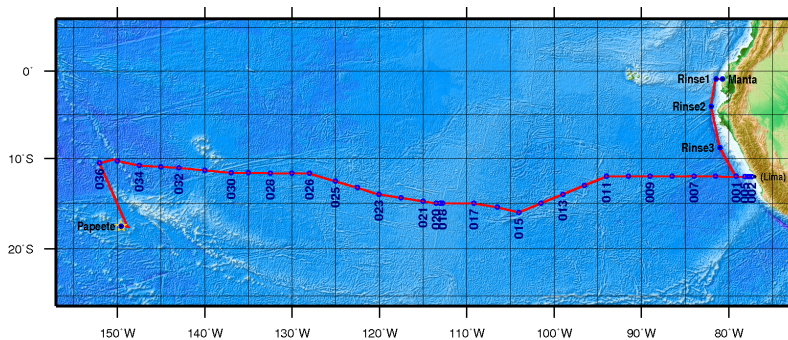
Unpublished Th
Al from Resing et al., 2015

Idealized dissolved Nd profile

Stichel et al., 2015 Interpretation

Surface – Dust source

Deep Chl Max – Intense scavenging

OMZ – Reductive regeneration

Mid depth – Homogenization by rapid
lateral mixing

Abyssal depth – Dissolution of particle
surface coatings with adsorbed TEIs

Reductive mobilization is evident in pattern of REE enrichment in S Atlantic OMZ

Xinyuan Zheng et al., 2016
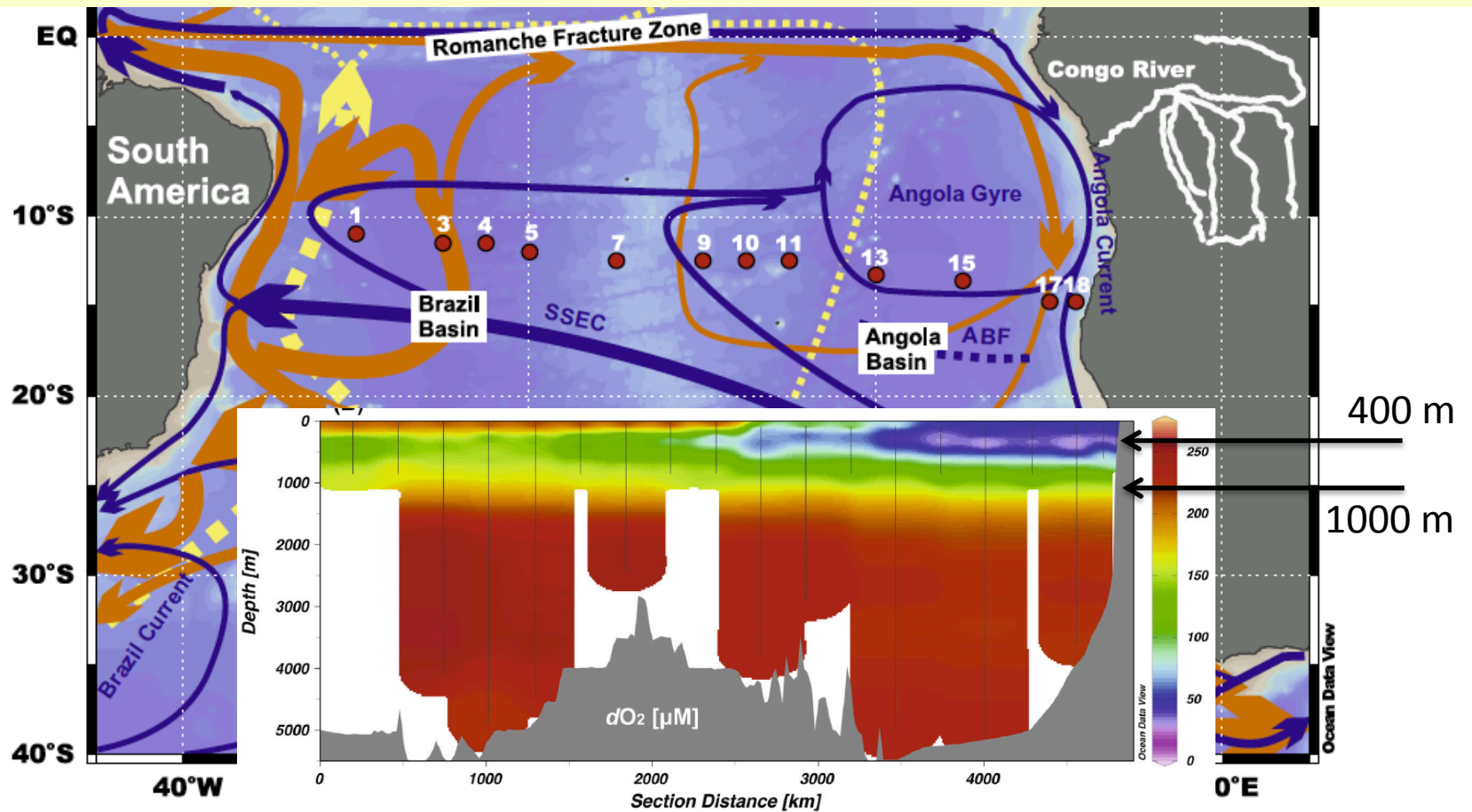
Reductive mobilization is evident in pattern of REE enrichment in S Atlantic OMZ
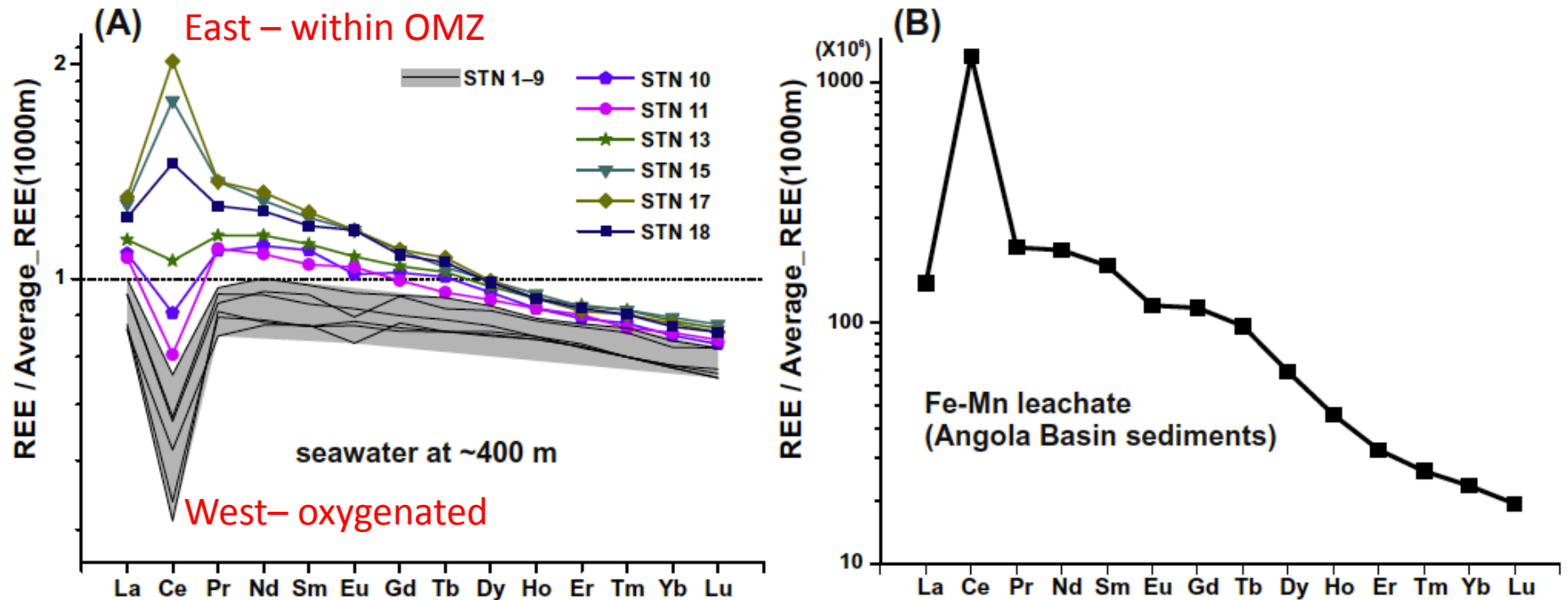
LREE enrichment & positive Ce anomaly at 400 m (OMZ) in the east, normalized to 1000 m.

Contrast to LREE depletion & negative Ce anomaly at 400 m (OMZ) in the west.

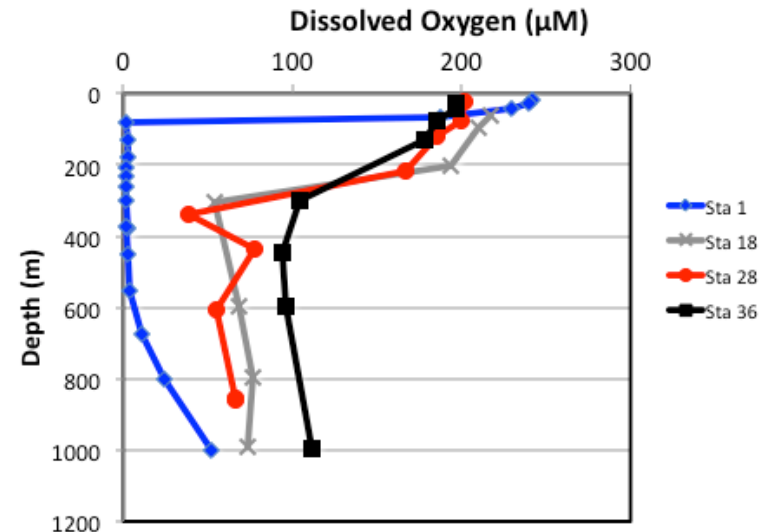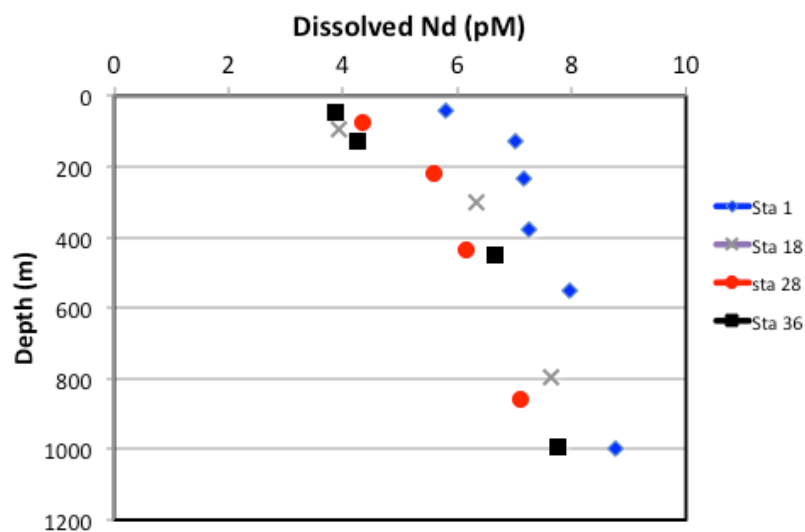Pattern similarity to reductive leach of sediments supports redox mobilization.

Mobilization in anoxic aggregate micro-environments?

Xinyuan Zheng et al., 2016

Reductive mobilization– Additional clues

Similar mobilization is not seen in the OMZ in the eastern tropical South Pacific

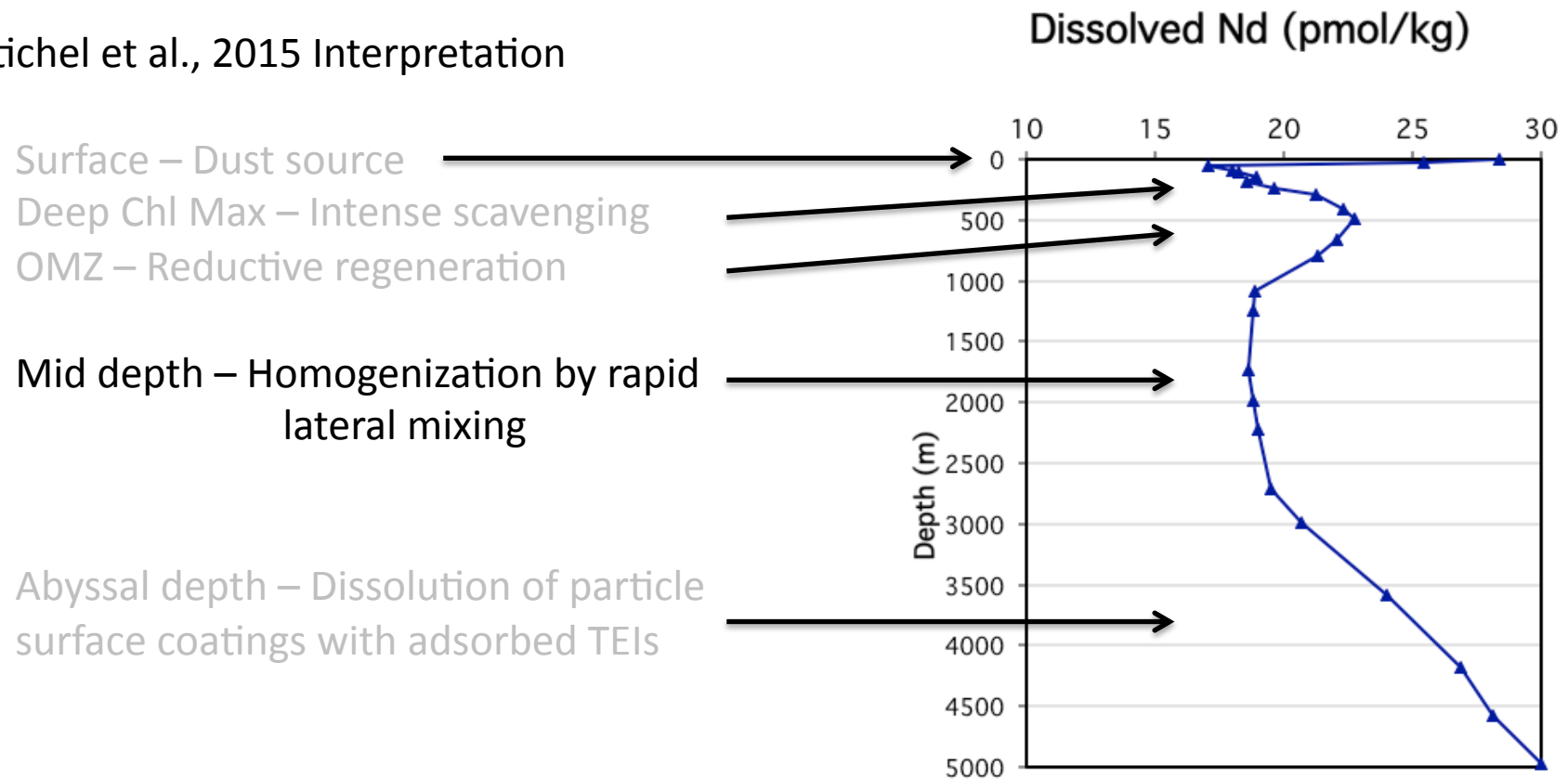*Hypotheses to explain OMZ behavior must account for regional contrasts.*

Yingzhe Wu, LDEO, unpublished data   GEOTRACES GP16 – Peru to Tahiti
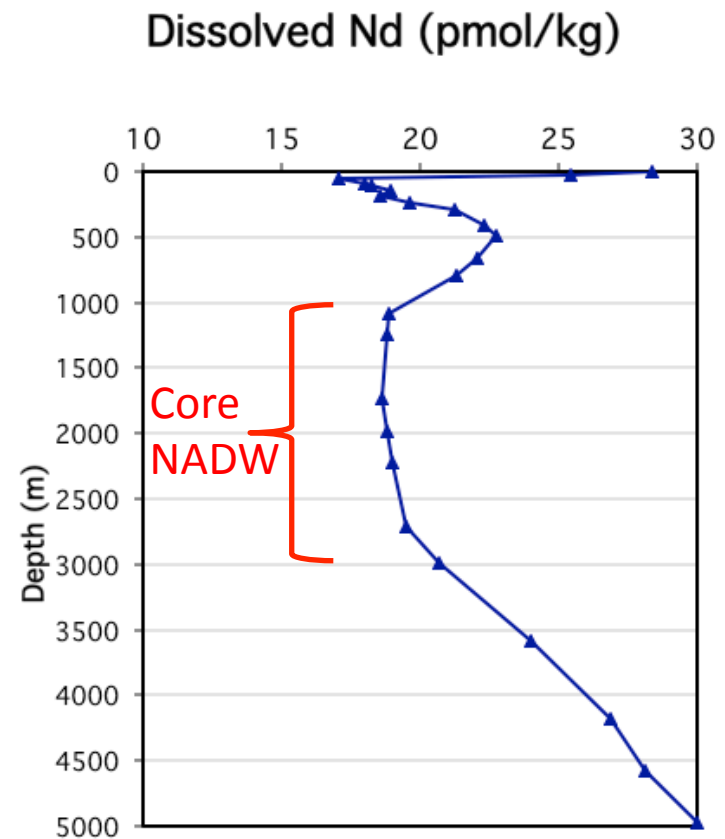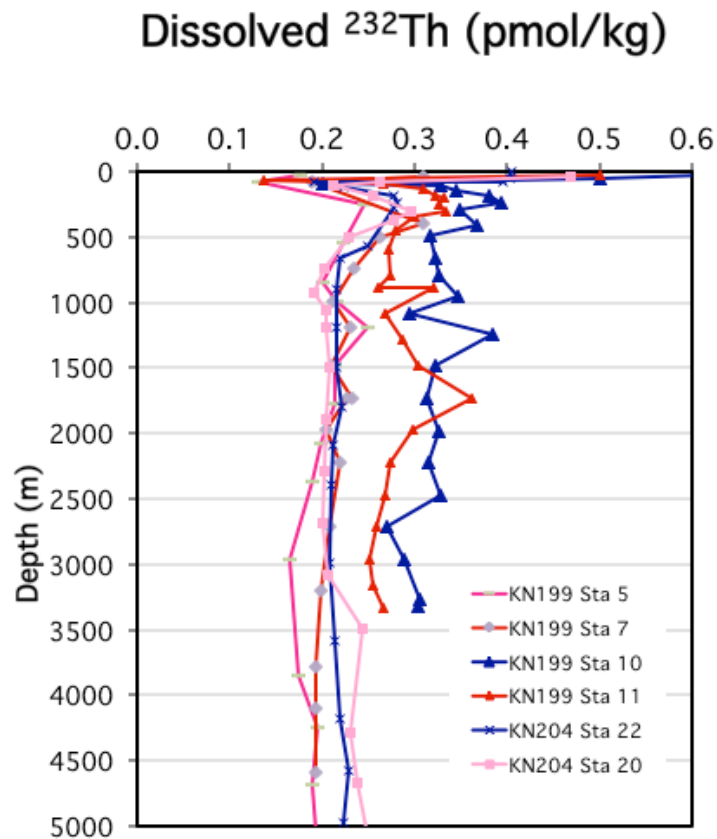
See also Grasse et al., EPSL 2012

Idealized dissolved Nd profiles indicate multiple processes affect E Trop N Atlantic distributions

Stichel et al., 2015 Interpretation

Dissolved Nd (pmol/kg)

Surface – Dust source
Deep Chl Max – Intense scavenging
OMZ – Reductive regeneration

Mid depth – Homogenization by rapid
lateral mixing

Abyssal depth – Dissolution of particle
surface coatings with adsorbed TEIs

Constant concentration with depth is consistent with reversible scavenging (^{232}Th)

Dissolved ^{232}Th (pmol/kg)

Dissolved Nd (pmol/kg)

KN199 Sta 5
KN199 Sta 7
KN199 Sta 10
KN199 Sta 11
KN204 Sta 22
KN204 Sta 20

Core NADW

There is no need to invoke rapid lateral mixing to explain the uniform [Nd] between 1 and 3 km in the eastern Atlantic

Idealized dissolved Nd profiles indicate multiple processes affect E Trop N Atlantic distributions

Stichel et al., 2015 Interpretation

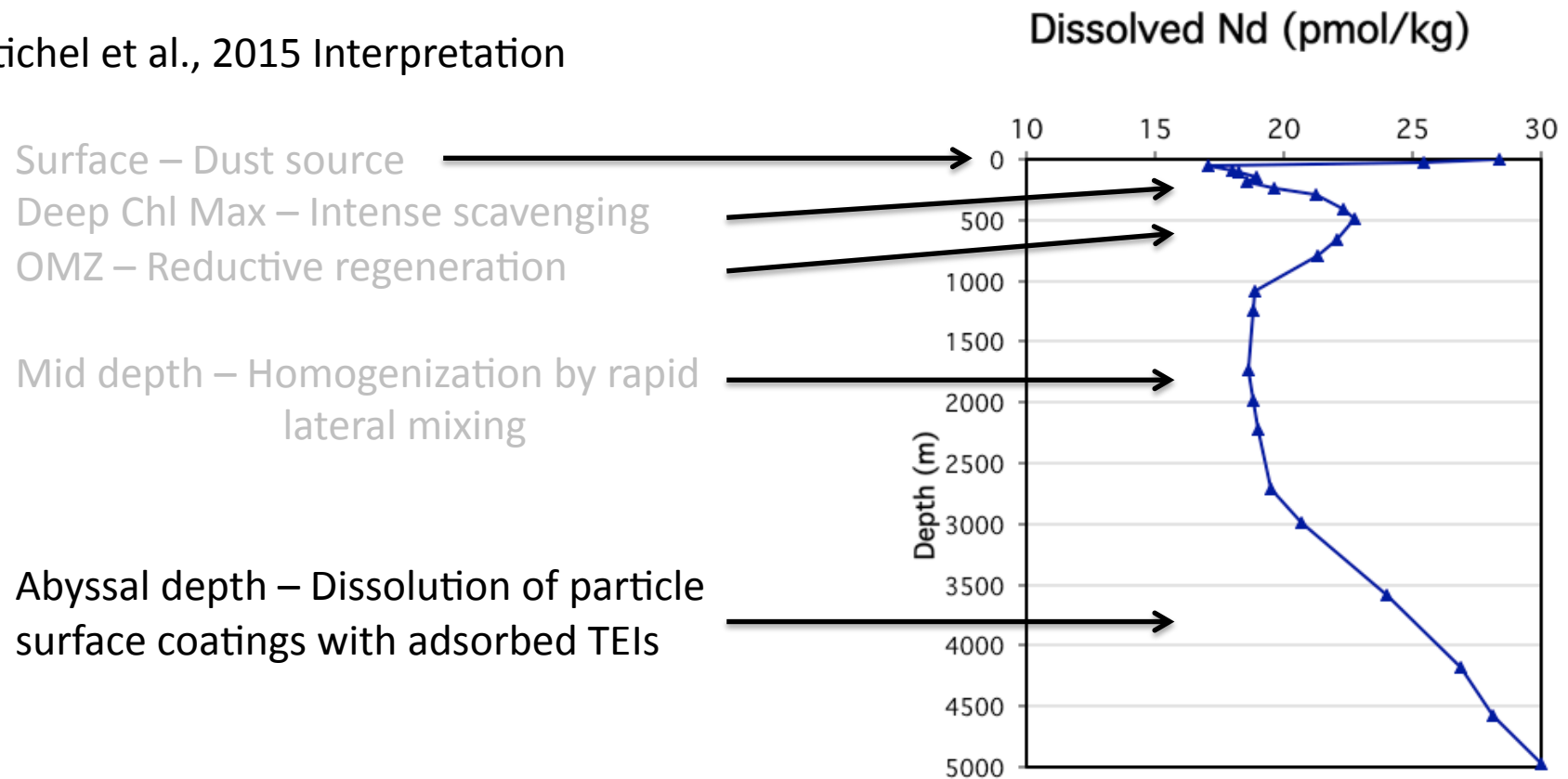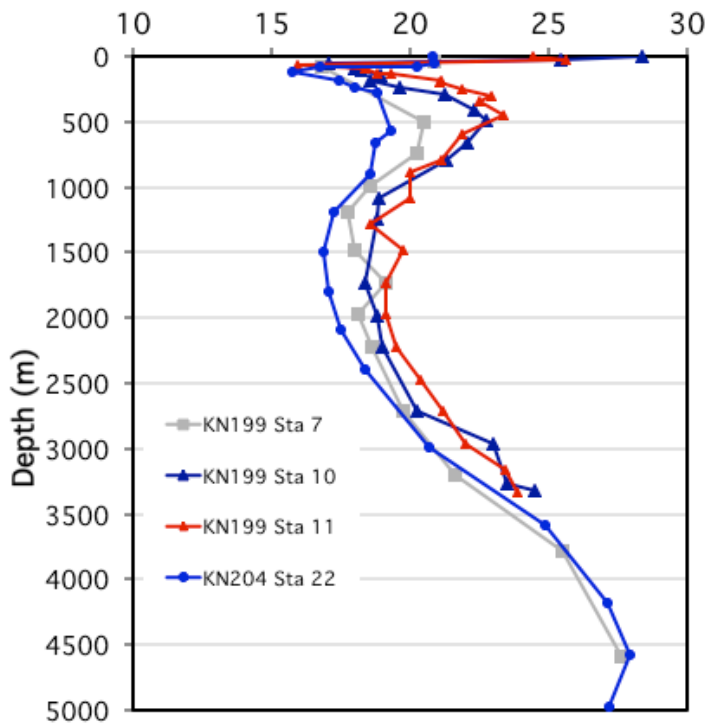Surface – Dust source
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surface coatings with adsorbed TEIs
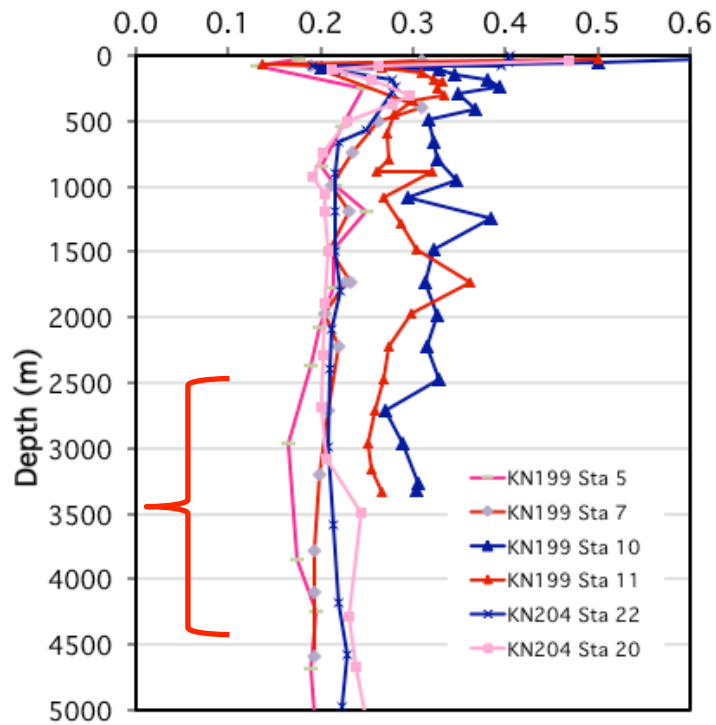
Dissolved Nd (pmol/kg)

Dissolved ^{232}Th profiles show no signs of mobilization by dissolution of particle coatings
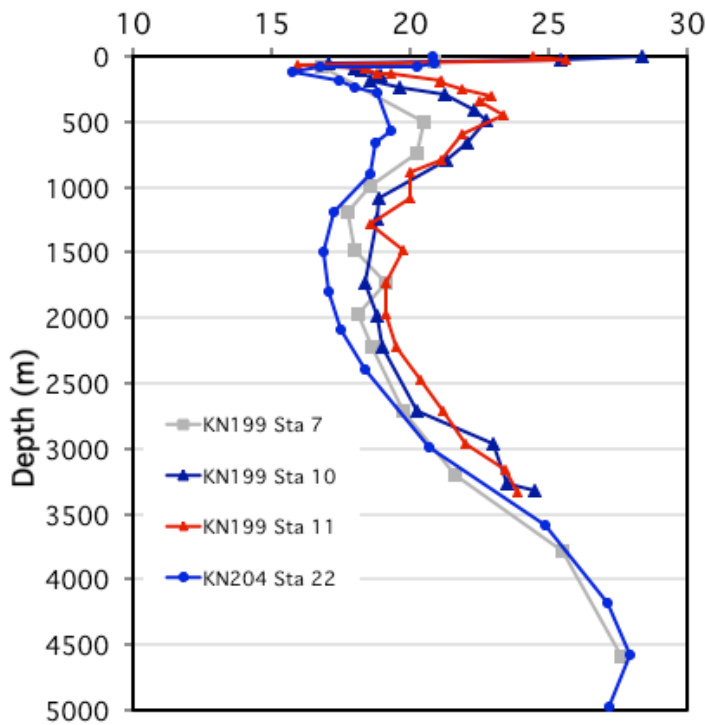

Dissolved Nd (pmol/kg)

Stichel et al., 2015
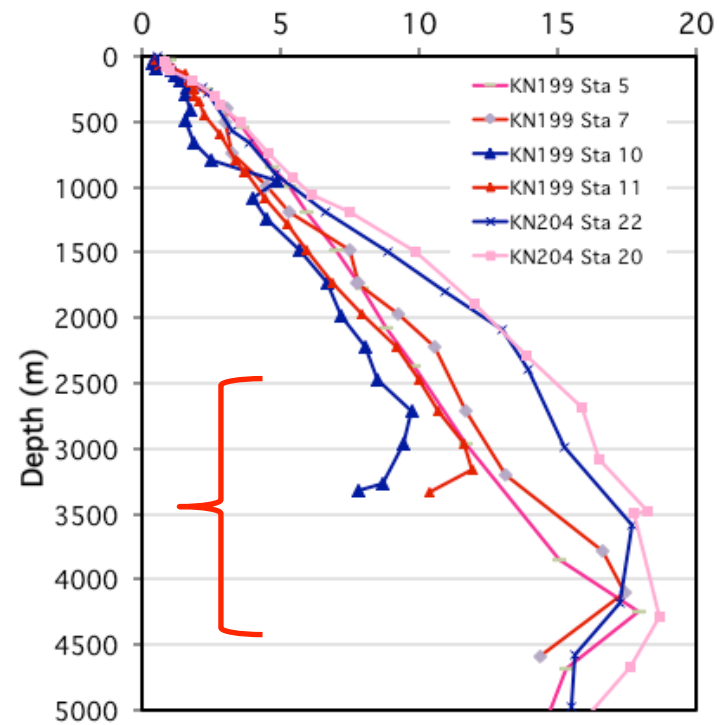
Dissolved ^{232}Th (pmol/kg)

Unpublished

Dissolved ^{230}Th profiles indicate enhanced removal below 2.5 km, not mobilization

Stichel et al., 2015

Hayes et al., 2015

How can we reconcile the contrasting indicators below 2.5 km?
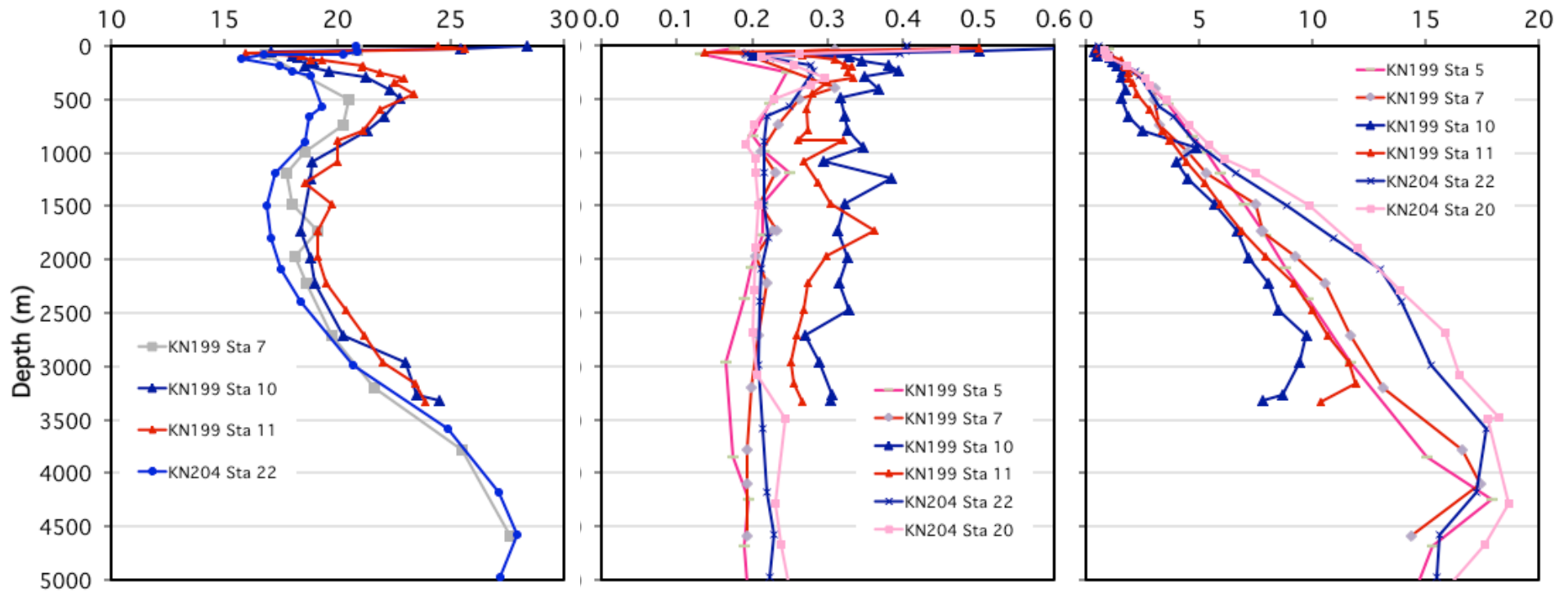
Mobilization below 2.5 km

Stichel et al., 2015

Reversible Scavenging

Unpublished

Bottom scavenging

Hayes et al., 2015

Physical transport of preformed trace elements

South Atlantic (CoFeMUG)

Preformed [Nd] accounts for >75% of the total [Nd]

End-member mixing of preformed tracers accounts for linear relationships, e.g., Nd – vs. – Si
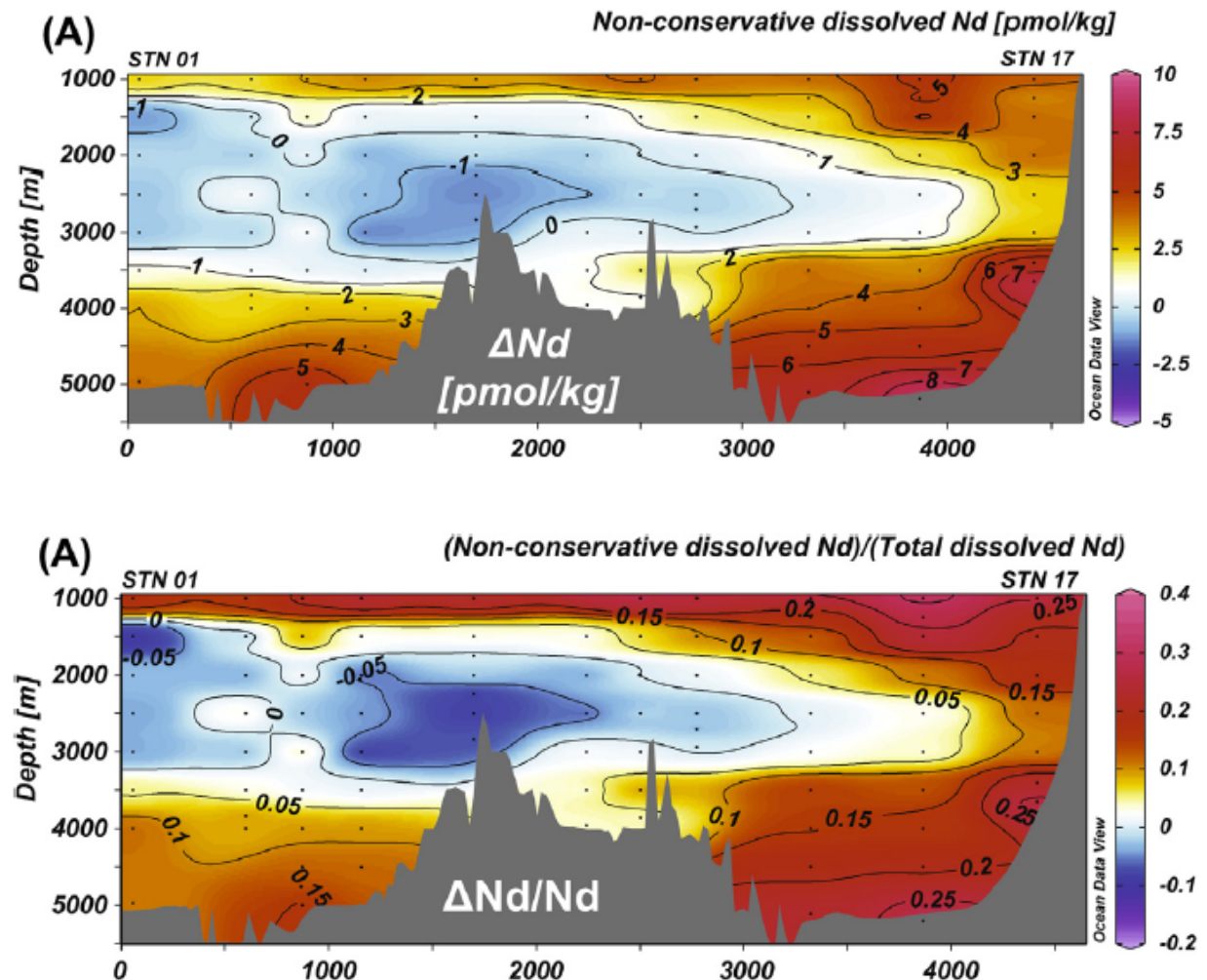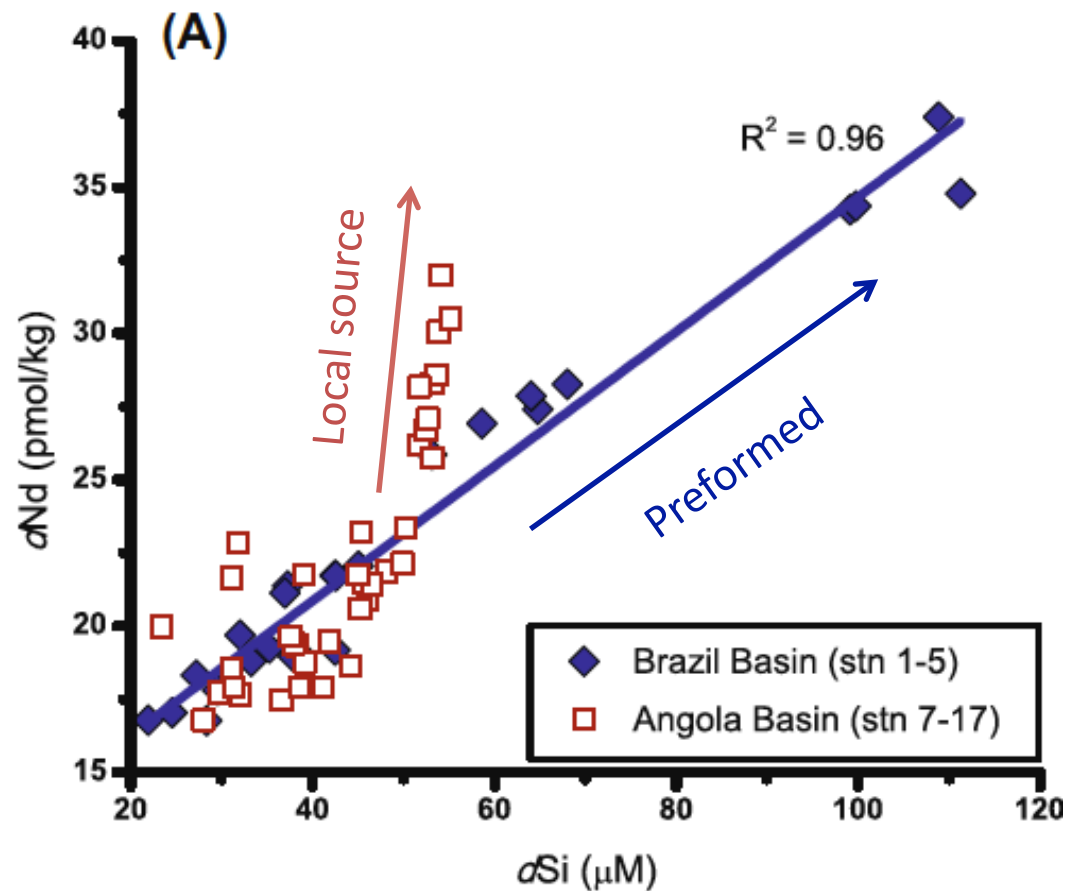

Xinyuan Zheng et al., 2016

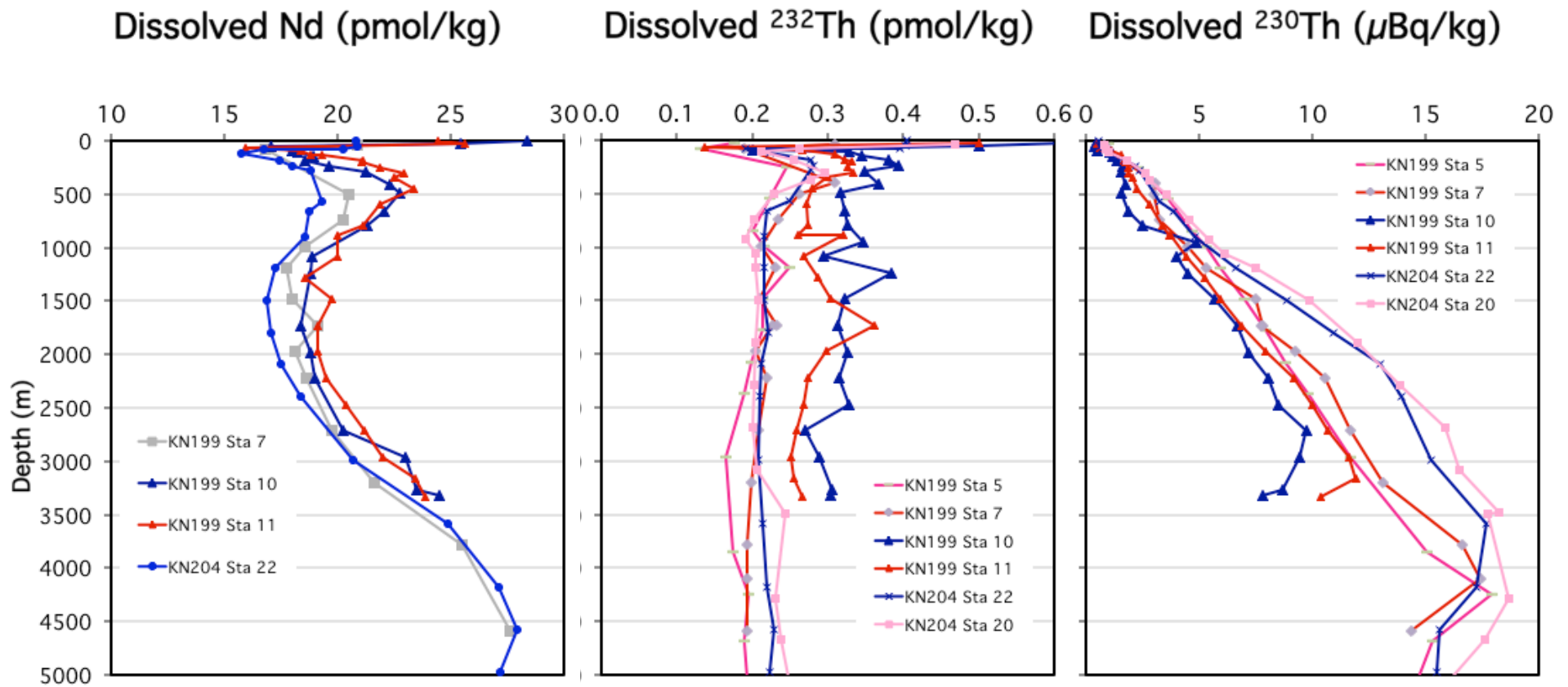# Physical transport of preformed trace elements

South Atlantic (CoFeMUG)

Preformed [Nd] accounts for
>75% of the total [Nd]

End-member mixing of
preformed tracers accounts
for linear relationships,
e.g., Nd – vs. – Si

Departures indicate local
supply or removal.

Xinyuan Zheng et al., 2016

How can we reconcile the contrasting indicators below 2.5 km?

Preformed "AABW" below 2.5 km   Reversible Scavenging   Bottom scavenging

By invoking influence of all processes simultaneously.

Summary

Multiple processes affect trace element distributions.

Diagnostic tracers help discriminate among processes (eliminate hypotheses).

Advection of preformed tracers affects all but those with the shortest residence times.

SYNTHESIS = Identifying key processes by comparing tracers with distinct attributes in contrasting chemical environments.