

# Boundary Exchange (and tracers of Boundary Exchange)

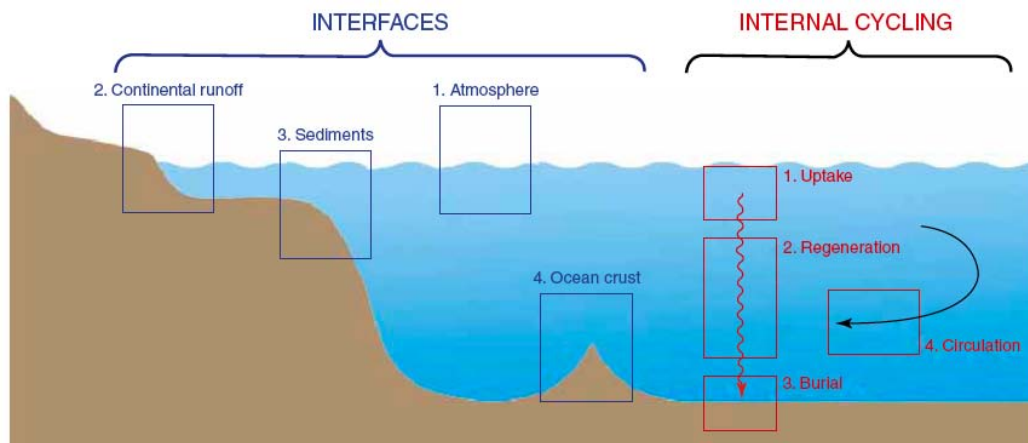
**U.S. GEOTRACES**

2011 Pacific Planning Workshop

Bob Anderson, Chris Hayes

Lamont-Doherty Earth Observatory

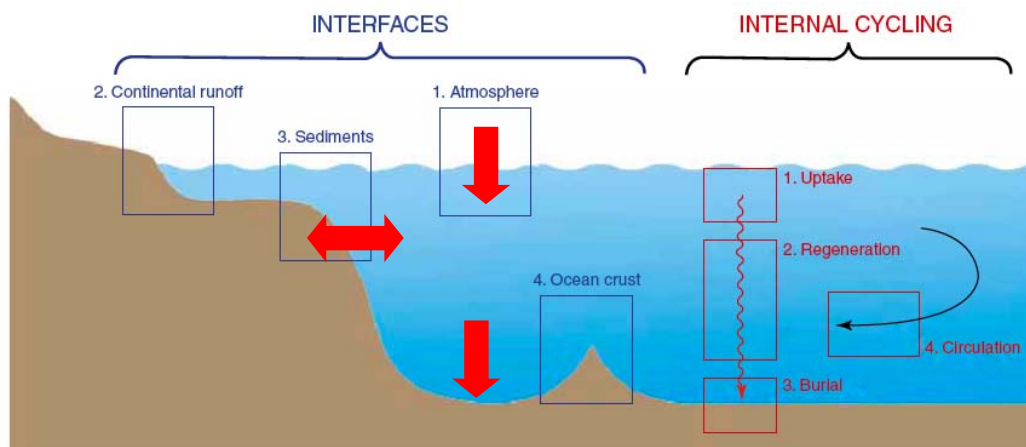
## GEOTRACES Strategy and Overarching Goals



Need to understand supply and removal at four interfaces  
and four types of internal cycling.

**GEOTRACES**

# GEOTRACES Strategy and Overarching Goals



Here - Focus on supply and removal at continental margins,  
and  
New strategy to estimate atmospheric deposition.



## TOPICS

- 1) Boundary removal and some surprises
- 2) Boundary sources - how important are they?
- 3) New strategy to estimate aerosol deposition

## Scavenging

Insoluble elements are extracted from seawater primarily by uptake onto/into particles that are removed by sedimentation.

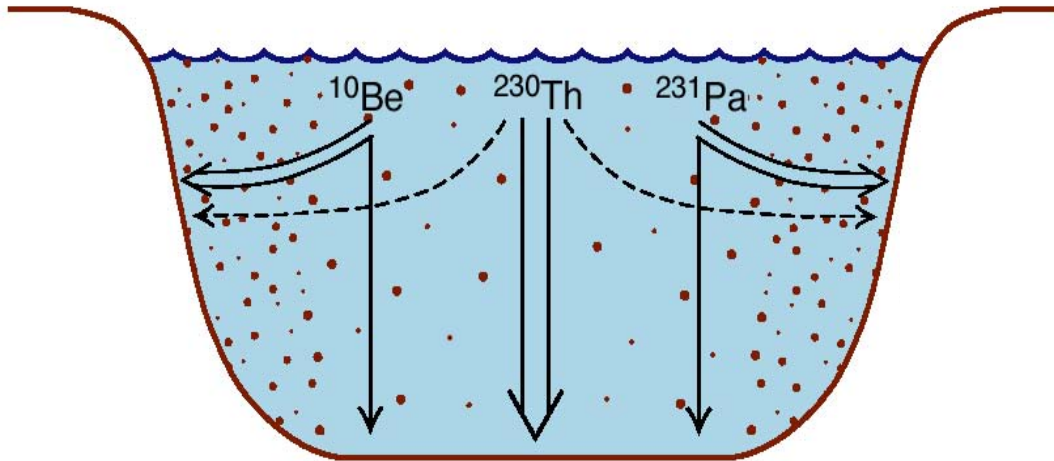
Goldberg (1954) termed this process “Scavenging”.

## Boundary Scavenging

Insoluble elements are removed from seawater at greater rates near ocean margins than in central gyres due to the greater abundance and flux of sinking particles near the continents.

Bacon and Spencer termed this process “Boundary Scavenging”.

# Boundary Scavenging



Principles:

If  $\tau_{\text{scav}} < \tau_{\text{mix}}$ , then tracer removal rate equals production.

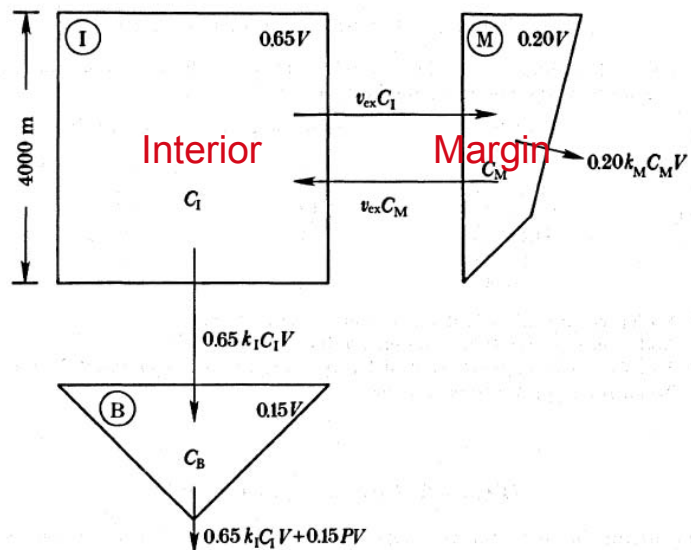
If  $\tau_{\text{scav}} > \tau_{\text{mix}}$ , then tracer removal increases with particle flux.

# Boundary Scavenging

Bacon 1988:

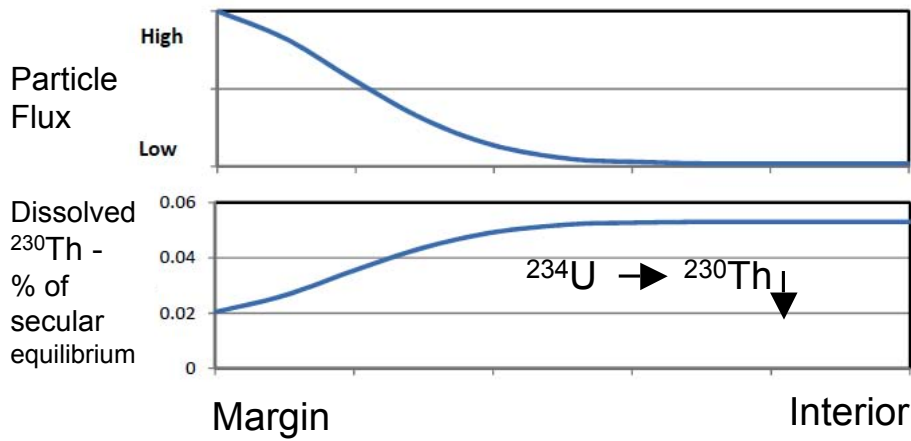
Three-box model to quantify fraction of a TEI deposited in Interior and Margin sediments as a function of rate constants for:

- Scavenging in each box and
- Lateral mixing.



For reasonable values of  $K_{\text{scav}}$  &  $K_{\text{mix}}$ , up to 80% of a TEI can be deposited in margin sediments representing 20% of ocean area.

# Conceptual illustration

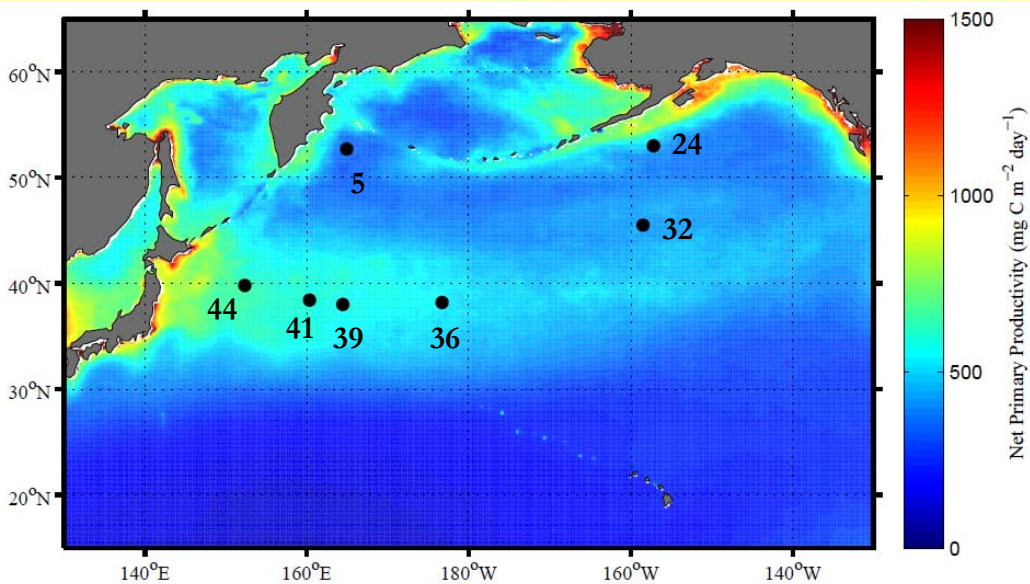


à la Bacon  
1988, *Phil. Trans. R. Soc. London*

Dissolved  $^{230}\text{Th}$  is an ideal tracer for boundary scavenging because its residence time in the deep sea (10-50 years) is less than the time scale for lateral mixing across ocean basins.

Substantial depletion in margin waters is expected.

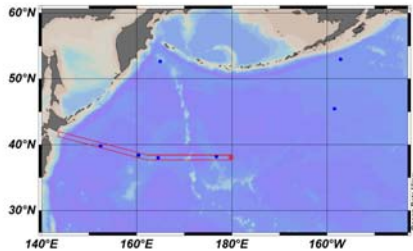
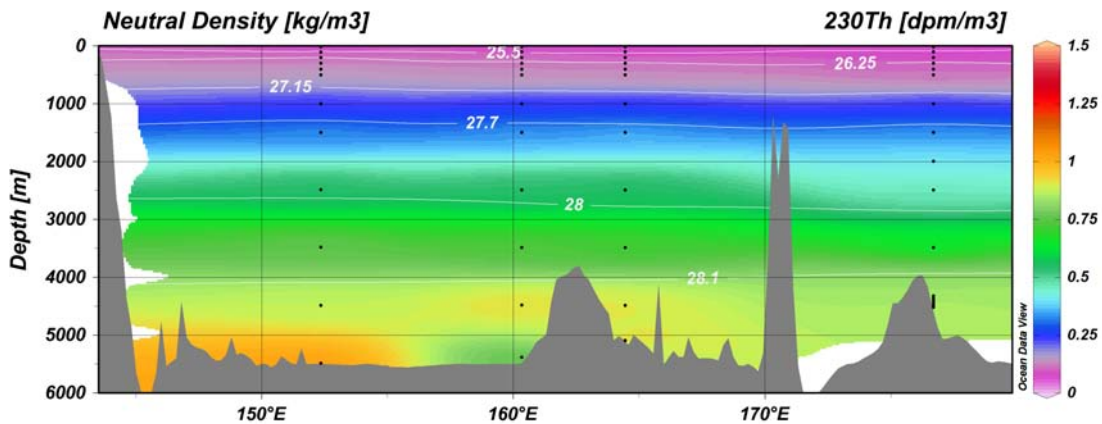
# N Pacific Satellite-based Net Primary Productivity (SeaWifs 1997-2009)



Labeled with SO-202  
Station numbers

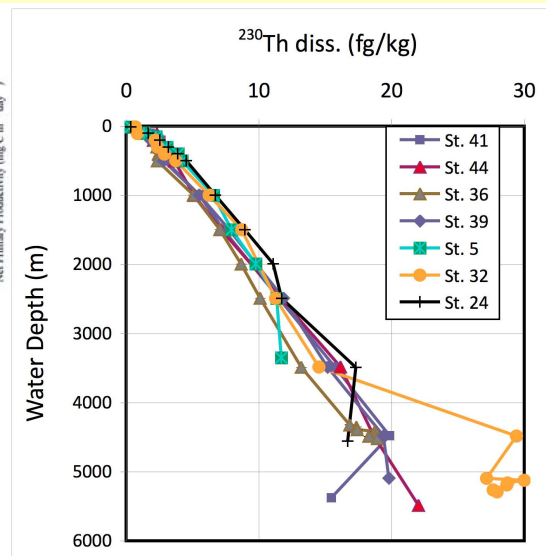
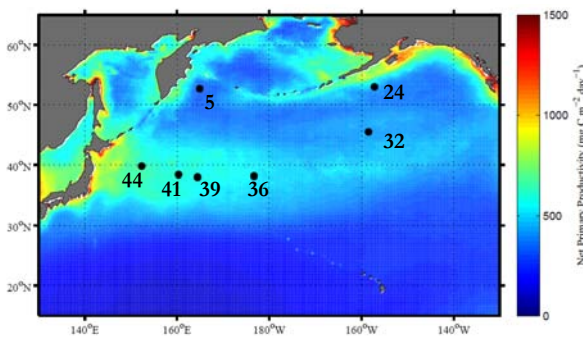
NPP algorithm of Behrenfeld & Falkowski 1997  
Data from <http://www.science.oregonstate.edu/ocean.productivity>

# Surprise #1: Expected depletion of dissolved $^{230}\text{Th}$ near the margin is missing



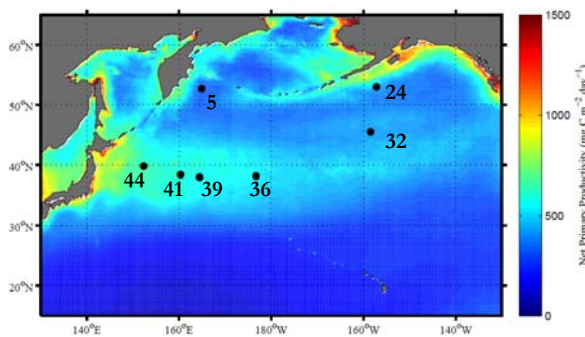
Unpublished data from Chris Hayes (LDEO).  
INOPEX SO-202 cruise in 2009.

# Dissolved $^{230}\text{Th}$ increases linearly with depth as expected for reversible scavenging

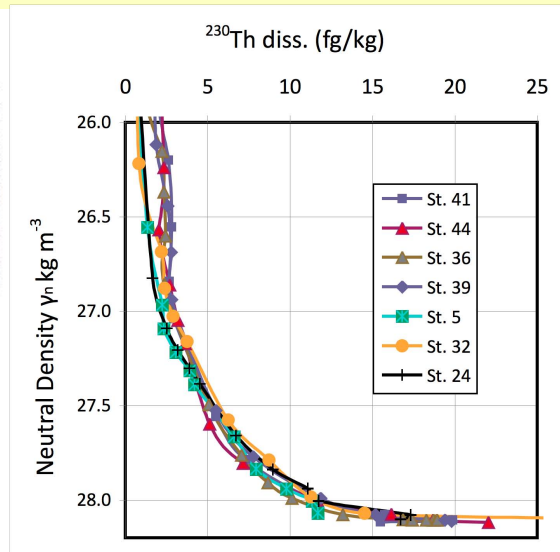


Unpublished data from Chris Hayes (LDEO).  
INOPEX SW-22, July 2011.xls

# Surprise #1: Expected depletion of dissolved $^{230}\text{Th}$ near the margin is missing



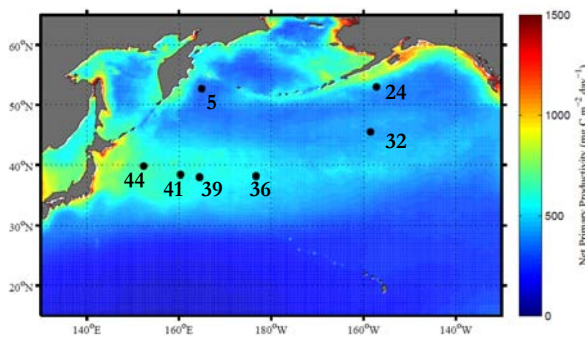
Lack of lateral gradients is even more striking when dissolved  $^{230}\text{Th}$  is plotted on constant density surfaces.



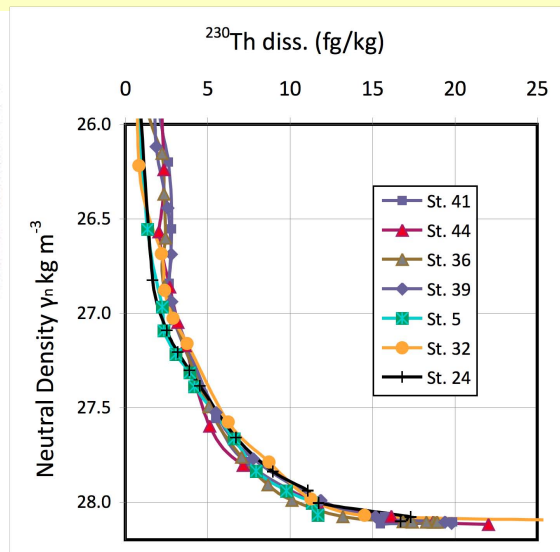
Unpublished data from Chris Hayes (LDEO). INOPEX SO-202 cruise in 2009.

INOPEX\_SW\_22,July2011.xls

# Surprise #1: Expected depletion of dissolved $^{230}\text{Th}$ near the margin is missing



No evidence for boundary scavenging within these 7 stations in the Subarctic N Pacific.

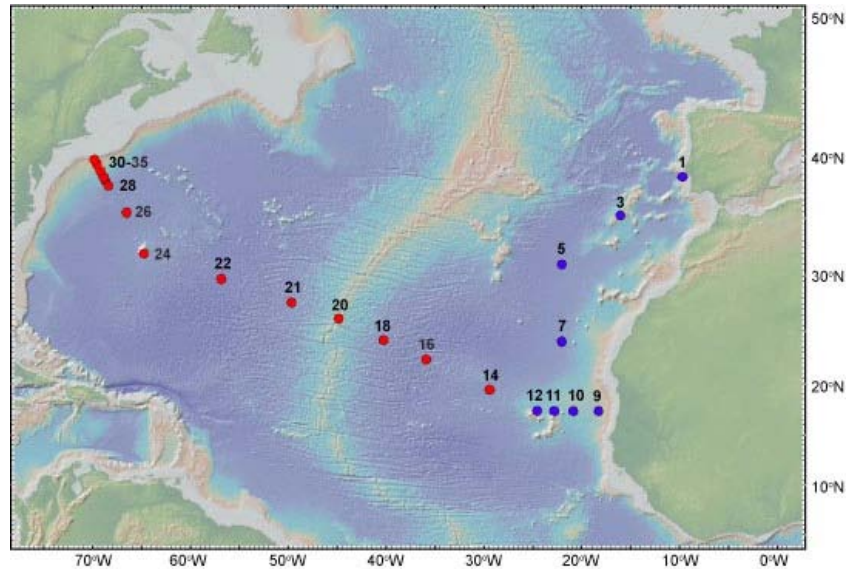


Unpublished data from Chris Hayes (LDEO). INOPEX SO-202 cruise in 2009.

INOPEX\_SW\_22,July2011.xls

# US GEOTRACES North Atlantic Section

Compare  $^{230}\text{Th}$  at Stations 9, 10 and 12.



Map from Katharina Pahnke

## Stations span a range of productivity and particle flux

Climatological Annual Primary Production from SeaWiFS and VGPM

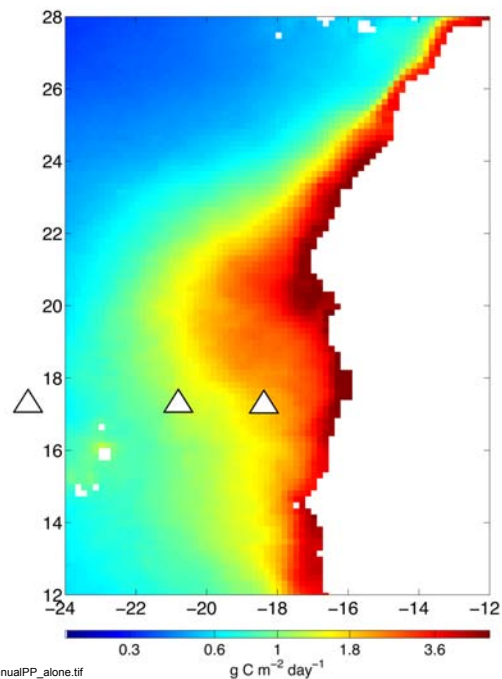


Image prepared by Mary-Elena Carr

CanaryAnnualPP\_alone.tif

$\text{g C m}^{-2} \text{ day}^{-1}$



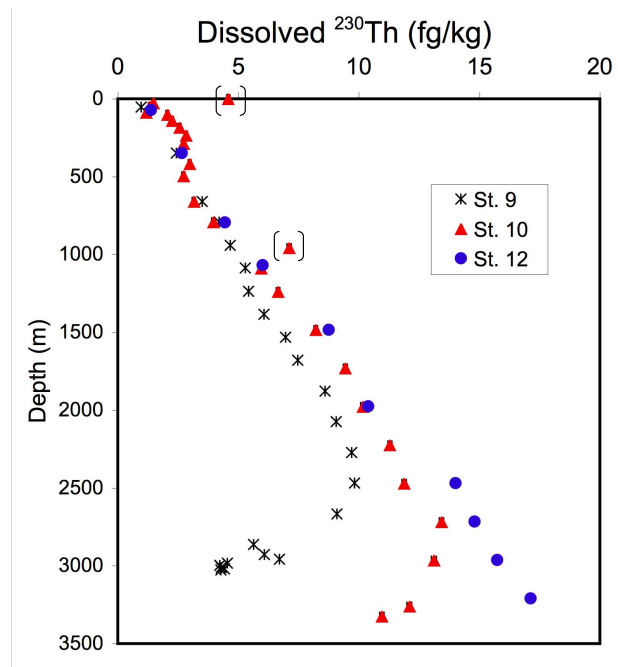
## Surprise #2: Large $^{230}\text{Th}$ gradients are near the bottom

Lateral gradients in the upper 2 km are small.

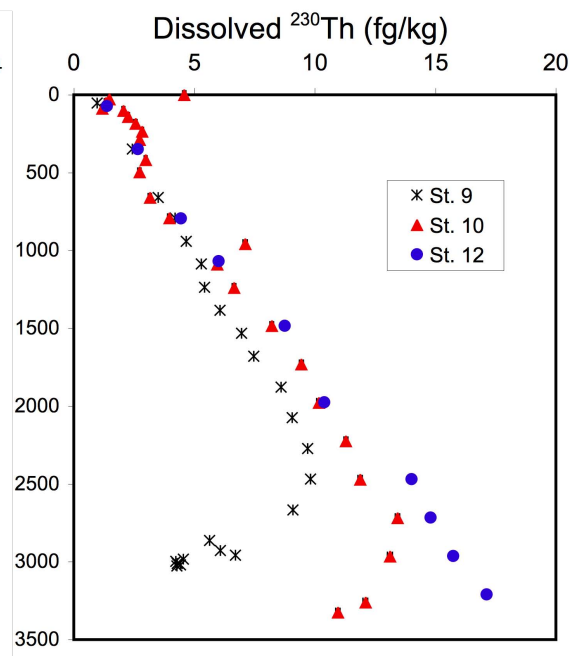
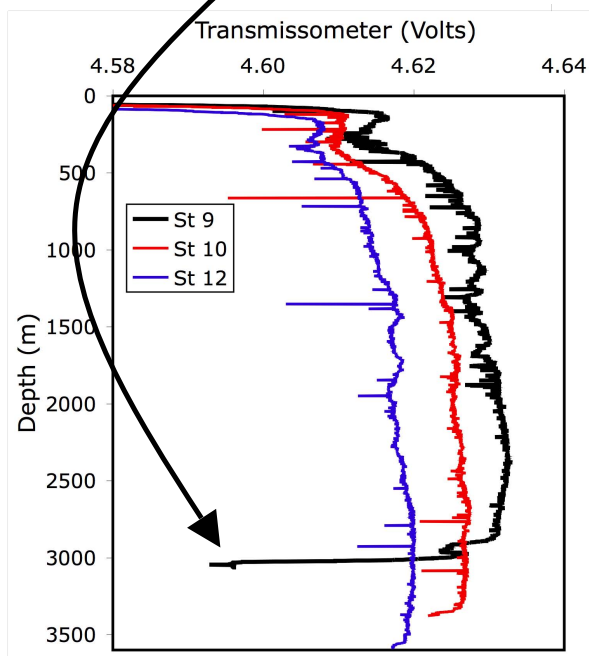
Vertical & lateral gradients in bottom km indicate **intense removal near bottom**, with intensity increasing toward the margin.

Unpublished results from Chris Hayes (LDEO) and Laura Robinson (WHOI)

KN199-4\_Lamont\_5Aug11.xls

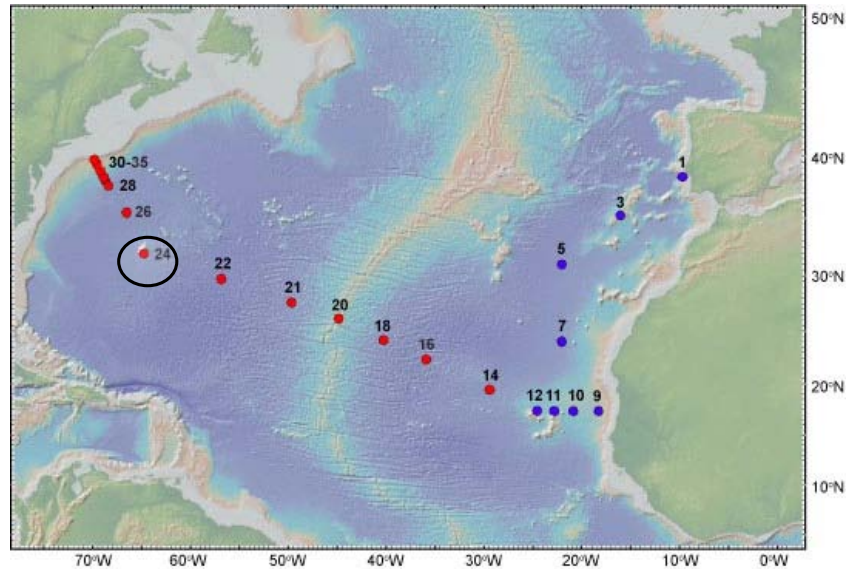


## Bottom scavenging by resuspended particles?



KN199-4\_Lamont\_5Aug11.xls

# GEOTRACES Intercalibration #1 at BATS



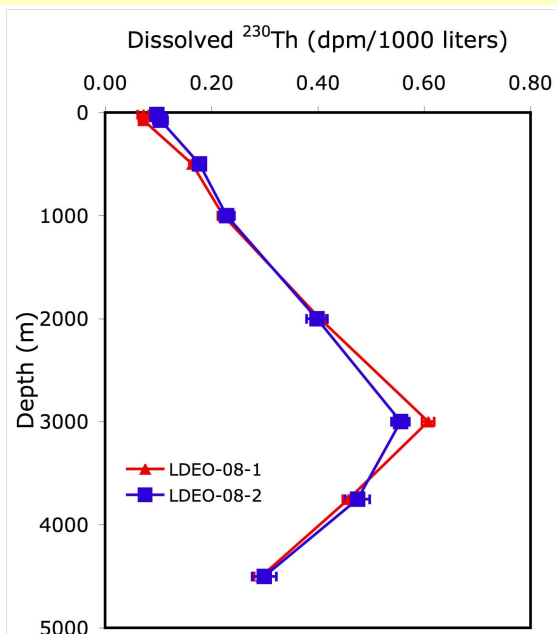
Map from Katharina Pahnke

## BATS: Dissolved $^{230}\text{Th}$ decreases in bottom km

Decrease toward bottom is seen in many Atlantic  $^{230}\text{Th}$  profiles.

Historically attributed to presence of recently ventilated **NADW** with **low  $^{230}\text{Th}$  concentrations**.

LDEO data from Anderson et al., submitted



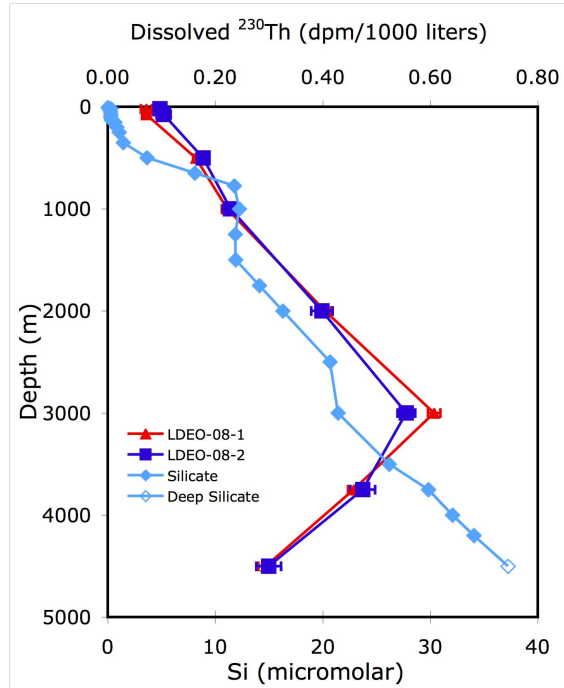
# BATS: Dissolved $^{230}\text{Th}$ decreases in bottom km

Dissolved Si increases to the bottom.

Si-rich deep water is from the Southern Ocean, not NADW.

**Decreasing  $^{230}\text{Th}$  toward the bottom cannot be explained by recent ventilation with NADW.**

BATS\_Ingrowth\_Baseline\_TimeSeries\_7March10.xls

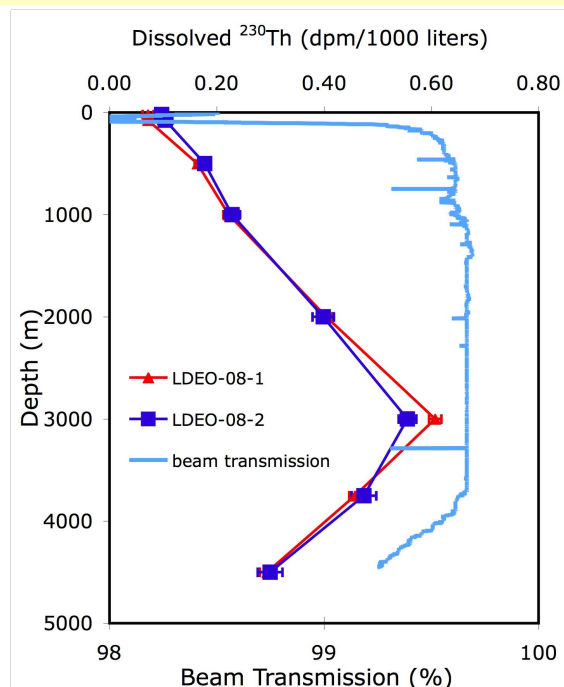


# Surprise #3: Removal of dissolved $^{230}\text{Th}$ in bottom km by resuspended particles

Transmissometer profile shows a thick layer of resuspended particles near the bottom.

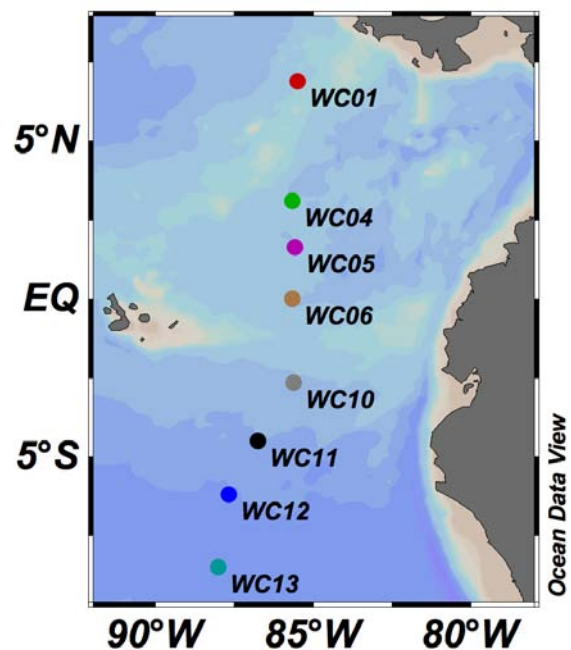
Bottom scavenging of  $^{230}\text{Th}$  by resuspended particles is inferred, but needs further testing.

BATS\_Ingrowth\_Baseline\_TimeSeries\_7March10.xls



## Meridional section of dissolved $^{230}\text{Th}$ collected Fall 2010

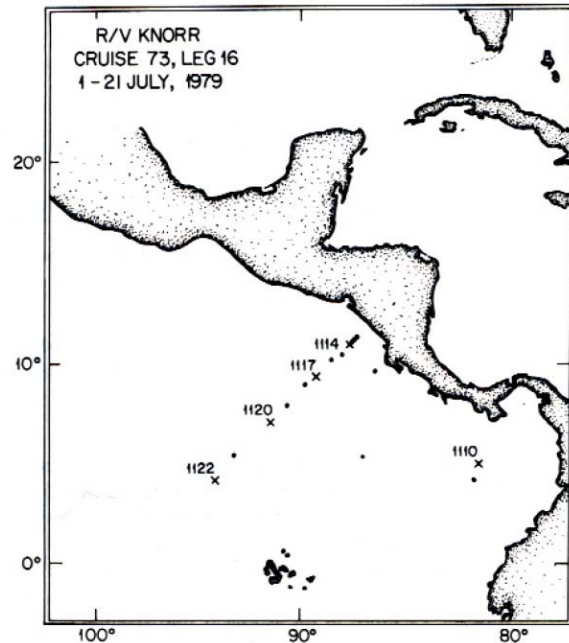
Ajay Singh and Franco  
Marcantonio, TAMU



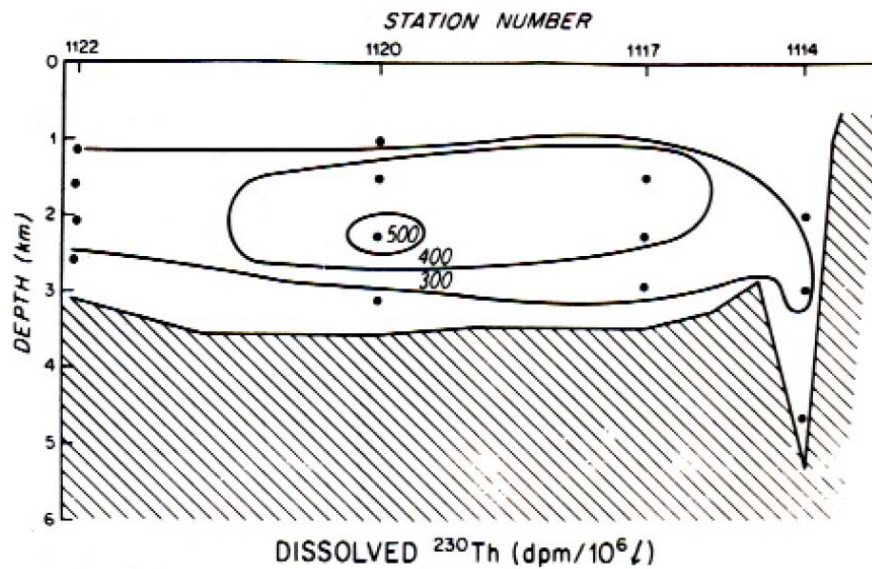
Near-bottom depletion indicates bottom  
scavenging in the Panama Basin

**Figure containing unpublished data from Singh  
and Marcantonio removed**

# Ancient History: Dissolved $^{230}\text{Th}$ section in the Guatemala Basin



Dissolved  $^{230}\text{Th}$  in the Guatemala Basin indicates bottom scavenging



Concentrations and distribution are similar to Panama Basin

Anderson et al., 1983

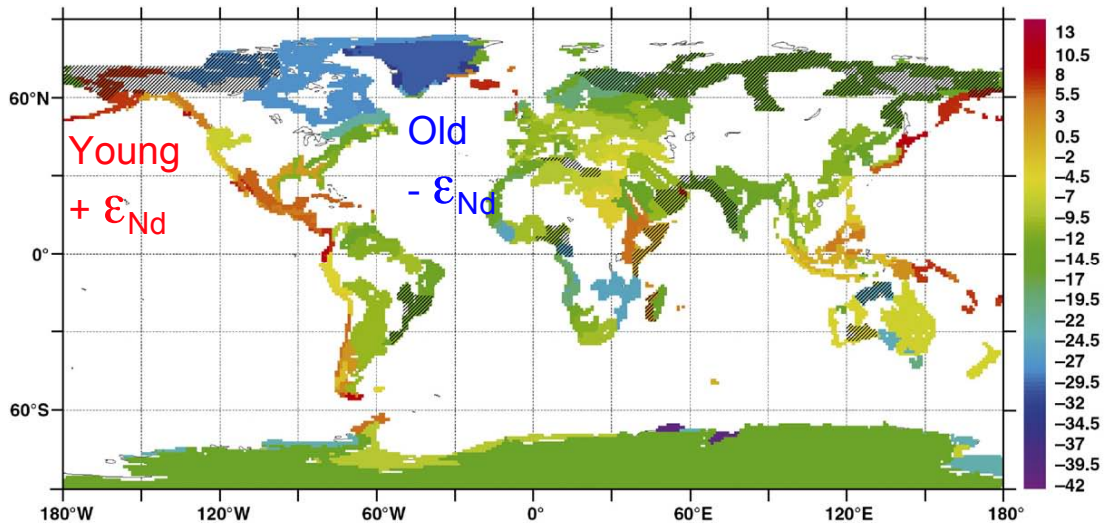
## Boundary Scavenging: New Hypotheses & Recommendations

- 1) Benthic process may play a greater role than high particle flux from biological productivity in removing particle-reactive TEIs.
- 2) Benthic removal processes are not in any TEI models that we are aware of.
- 3) Recommendation: Increase near-bottom sampling, including transmissometer, particulate TEIs, and other complementary variables.

## Boundary Exchange: Unanticipated sources revealed by Nd

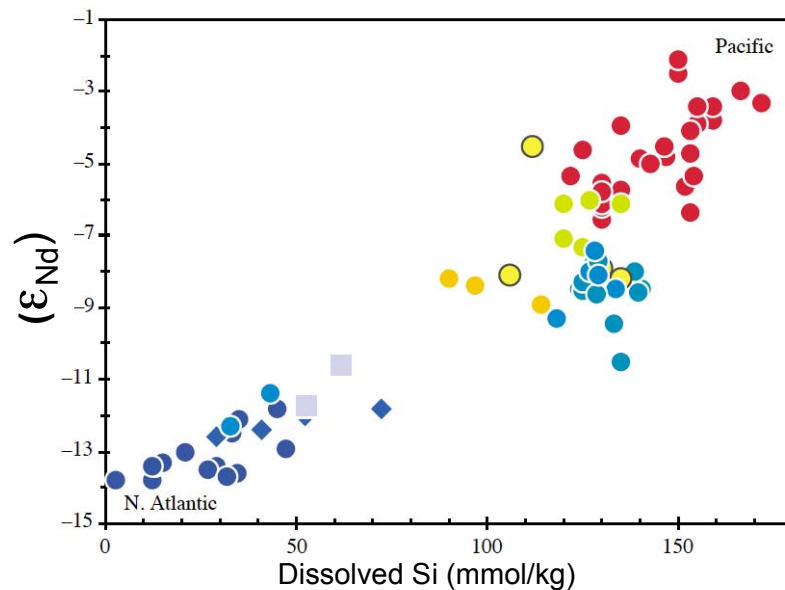
- 1) Nd is a REE (Lanthanide).
- 2)  $^{143}\text{Nd}/^{144}\text{Nd}$  is inversely proportional to the age of source rocks (ratio expressed as  $\epsilon_{\text{Nd}}$ ).
- 3) Simultaneous modeling of [Nd] and  $\epsilon_{\text{Nd}}$  constrains supply and removal.

# $\epsilon_{Nd}$ of margin sediments and coastal sources



Extrapolated from regional lithology.  
Jeandel et al., 2007

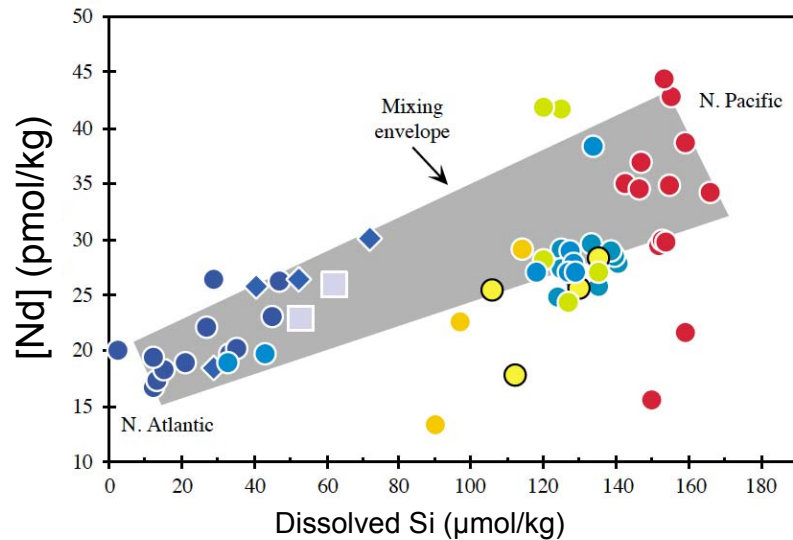
# $\epsilon_{Nd}$ suggests conservative behavior of Nd in deep ocean



Goldstein and Hemming 2003

## But [Nd] suggests non-conservative behavior of Nd in deep ocean

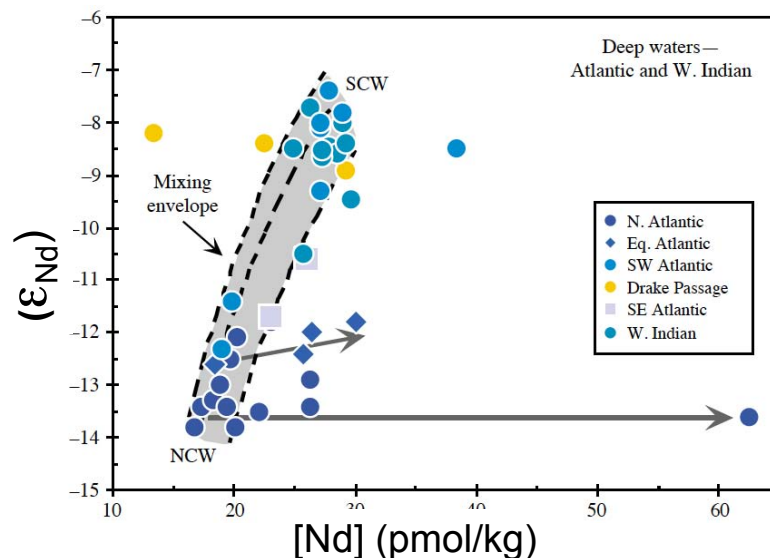
Points below mixing line suggest **removal** of Nd in many regions



Goldstein and Hemming 2003

## But [Nd] suggests non-conservative behavior of Nd in deep ocean

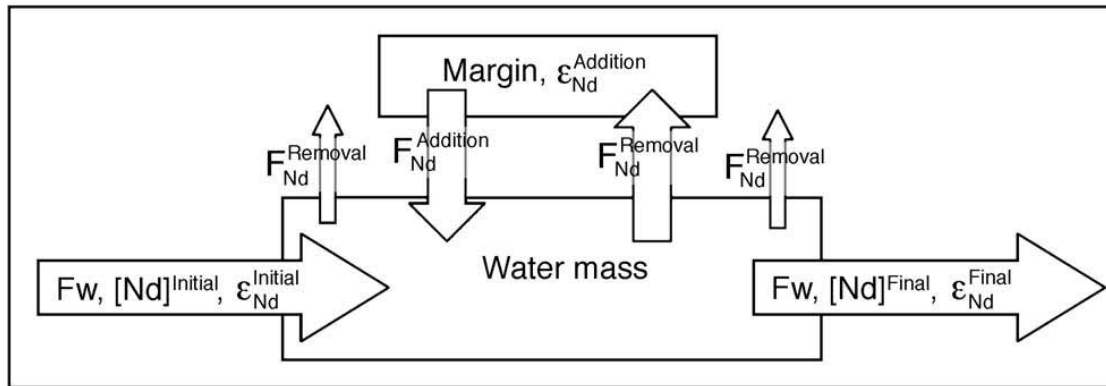
Some deep Atlantic data point to addition of Nd



Goldstein and Hemming 2003



## Exchange with margin sediments traced by simultaneous modeling of [Nd] & $\epsilon_{Nd}$



Lacan and Jeandel, 2005

## From modeling Nd

- 1) Consensus<sup>1</sup> - at a minimum, a sedimentary source of Nd must exist in the deep N Pacific.
- 2) Latest model<sup>2</sup> - best fit to global data suggests global sedimentary source of Nd  $\sim 20X$  > combined river + dust supply.
- 3) If Nd supply is by congruent dissolution of sediments<sup>3</sup>
  - a) Source of Ca & Mg is several % of river supply,
  - b) Source of Si  $\sim$  river supply,
  - c) Source of Fe  $\sim 20X$  river supply.

<sup>1</sup>modeling in France, Japan & U.S.

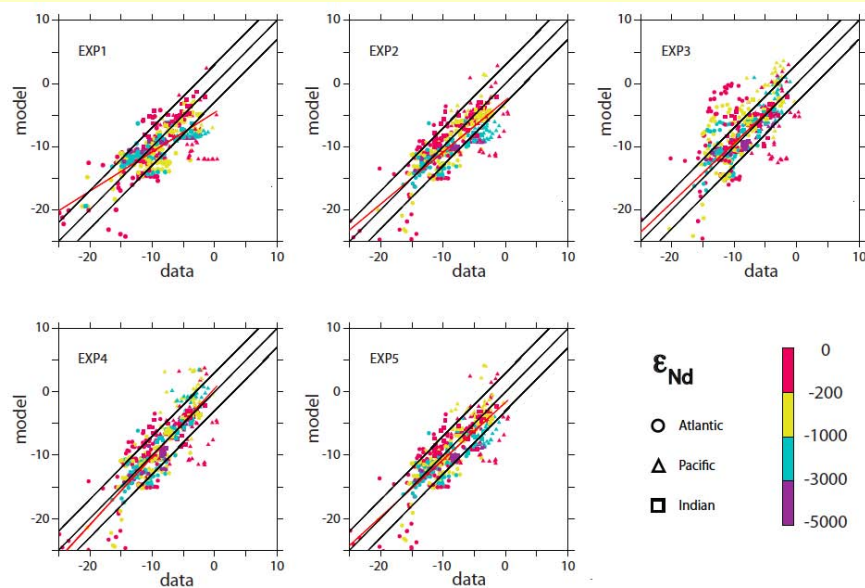
<sup>2</sup>Arsouse et al., 2009

<sup>3</sup>Jeandel et al., EOS, 2011

# Caveats

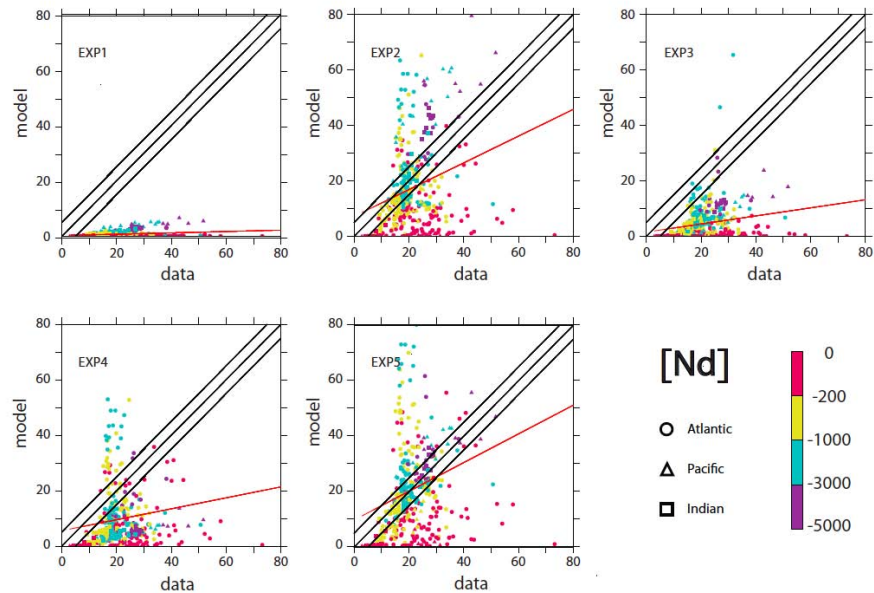
- 1) Although models fit global  $\epsilon_{Nd}$  well... (next slide)
- 2) ...fit to [Nd] remains poor.
- 3) Better constraints are needed for:
  - a) Partition coefficients for each type of particle,
  - b) Particle concentration,
  - c) Particle sinking & regeneration rates,
  - d) Spatial gradients of [Nd] and  $\epsilon_{Nd}$

## Model-data comparison for global $\epsilon_{Nd}$



5 model experiments with different conditions.  
Arsouze et al., 2009

# Model-data comparison for global [Nd]



5 model experiments with different conditions.  
Arsouze et al., 2009

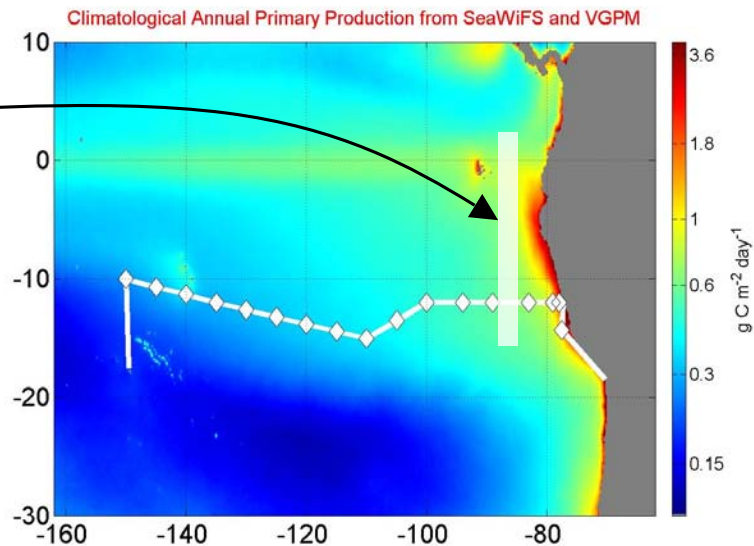
## Caveats

- 1) Although models fit global  $\epsilon_{Nd}$  well...
- 2) ...fit to [Nd] remains poor.
- 3) Better constraints are needed for:
  - a) Partition coefficients for each type of particle,
  - b) Particle concentration (including near-bottom),
  - c) Particle sinking & regeneration rates,
  - d) Spatial gradients of [Nd] and  $\epsilon_{Nd}$

# Eastern tropical Pacific is a good location to study boundary exchange

Nd results from German meridional section shown at Goldschmidt 2011.

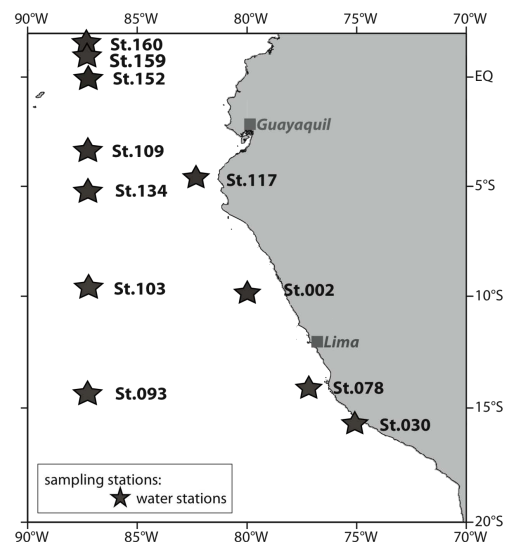
Surface water  $\epsilon_{Nd}$  is more positive than in any surrounding regions - implies a local source.



# Eastern tropical Pacific is a good location to study boundary exchange

20l of seawater were filtered (0.45 $\mu$ m) and acidified to pH2 (following GEOTRACES protocols)

Dissolved Nd isotope compositions and Nd concentrations were measured at the IFM-GEOMAR in Kiel (Germany) on a *Nu plasma* MC-ICPMS as well as on a *Thermo Scientific* TRITON TIMS



# Eastern tropical Pacific is a good location to study boundary exchange

Open symbols: North & Central Pacific.

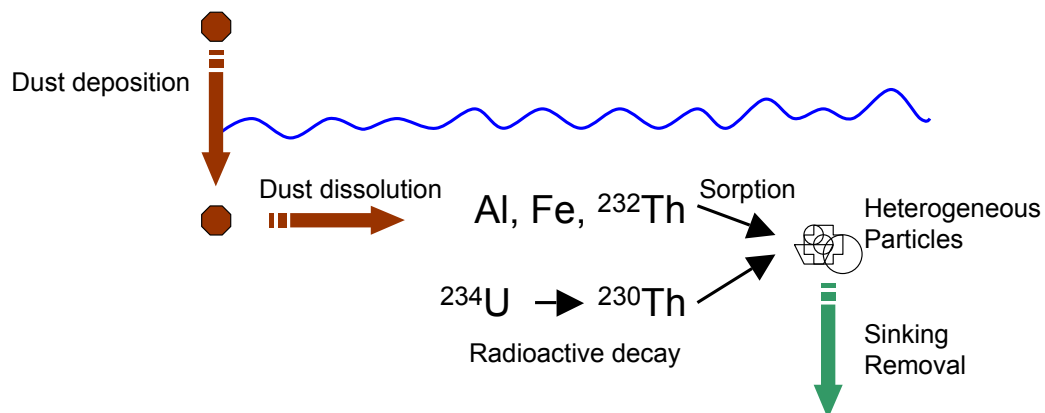
Filled symbols = EEP deep water.

Trend of observations requires both Nd removal (bottom scavenging?) and Nd supply (boundary exchange?).

**Figure containing unpublished data from Grasse and Frank removed**

P Grasse et al., *IFM-GEOMAR*

# New strategy to estimate TEI supply from aerosol deposition



# New strategy to estimate TEI supply from aerosol deposition

Combine information from Th isotopes

Radiogenic  $^{230}\text{Th}$



Source is uniform throughout the ocean

$^{230}\text{Th}/^{234}\text{U}$  gives Th **removal rate**

Lithogenic  $^{232}\text{Th}$

Source is as for other lithogenic elements (e.g., Al, Fe)

Removal rate equals that of  $^{230}\text{Th}$

**Assume steady state: Supply = removal**

$$\text{Metal supply rate} = (\text{Me}/^{232}\text{Th})_{\text{source}} \cdot ^{232}\text{Th}(\text{supply})$$

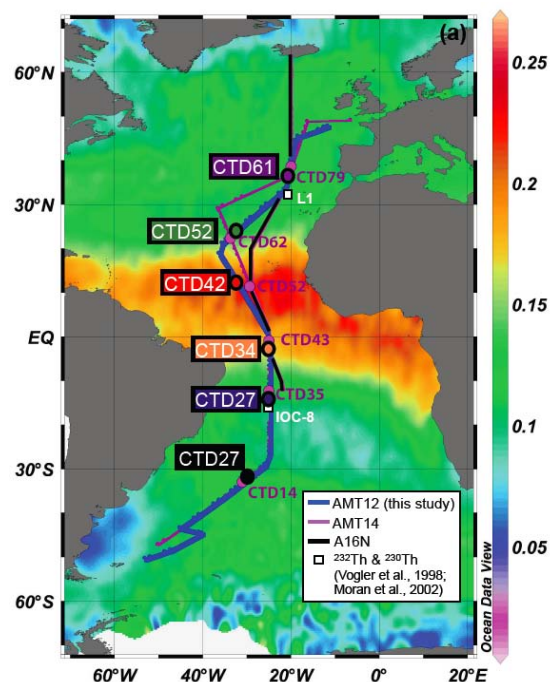
# New strategy to estimate TEI supply from aerosol deposition

First application -

AMT

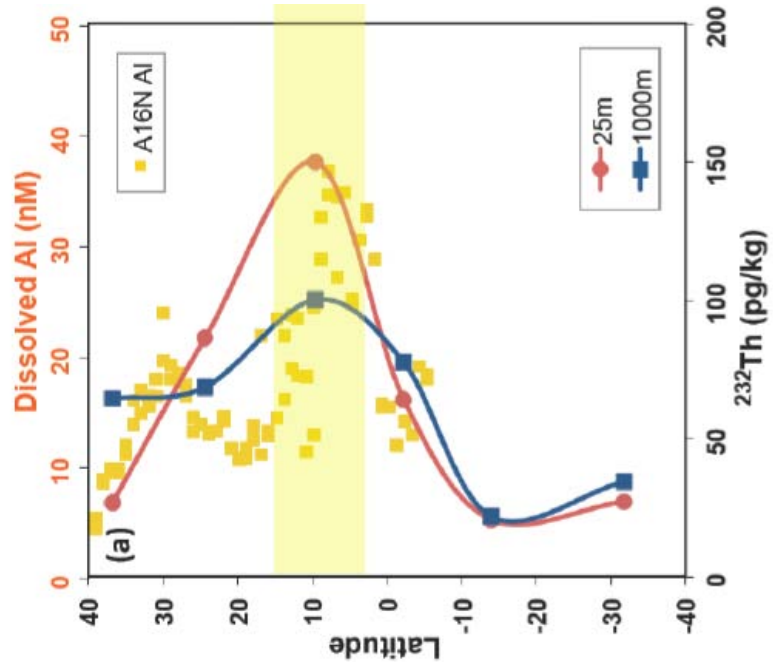
Hsieh et al., EPSL

submitted



# $^{232}\text{Th}$ distribution in surface water tracks AI (from dust)

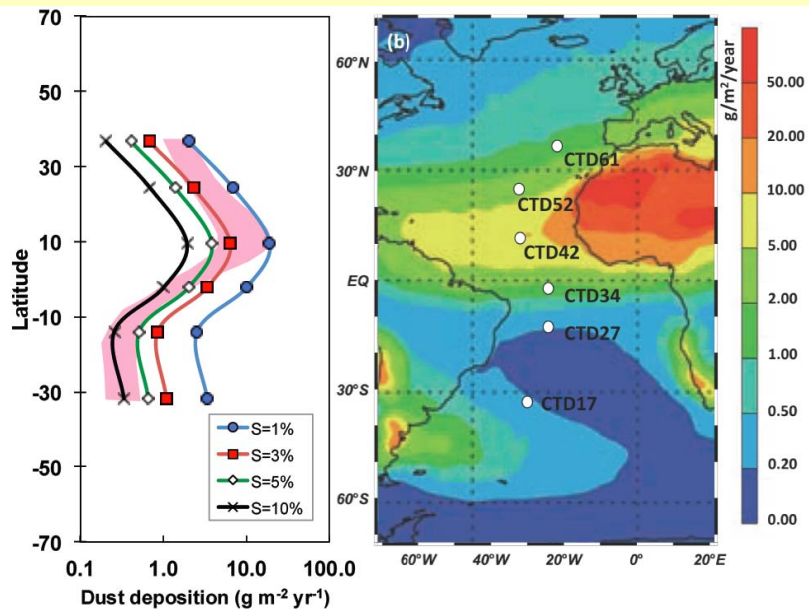
First application - AMT  
 Hseih et al., EPSL submitted



# $^{232}\text{Th}$ -derived estimate of dust flux

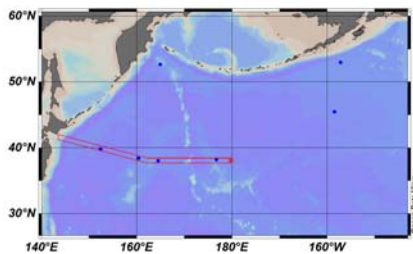
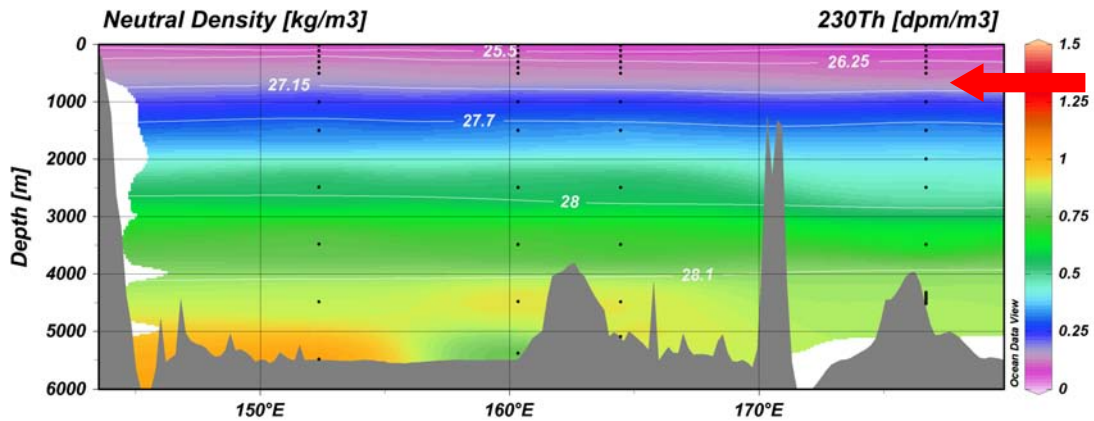
Total dust flux depends on % of Th that dissolves.

Pattern matches dust plume



Hseih et al., EPSL submitted

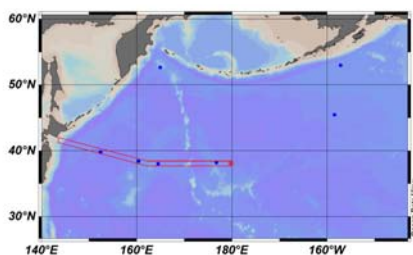
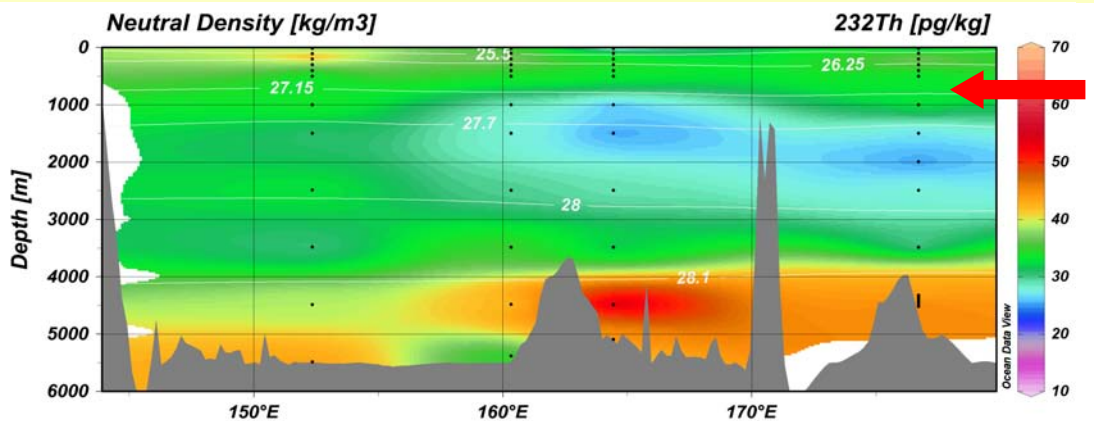
# $^{230}\text{Th}$ in the NW Pacific



Low surface concentrations

Unpublished data from Chris Hayes (LDEO).  
INOPEX SO-202 cruise in 2009.

# $^{232}\text{Th}$ in the NW Pacific

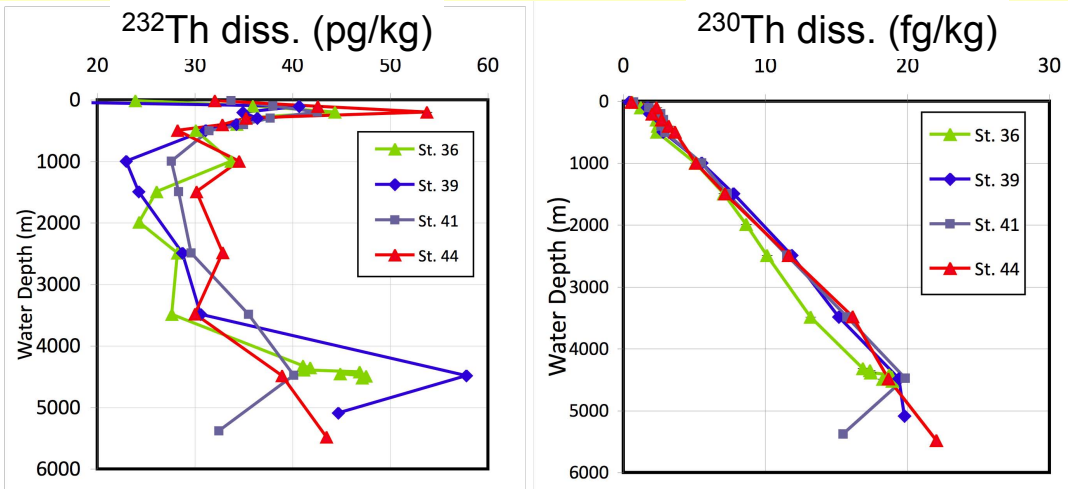


Higher concentrations at **surface** (dust) and near margin.

*Hayes, unpublished INOPEX data*



# NW Pacific Th profiles @ ~ 40°N



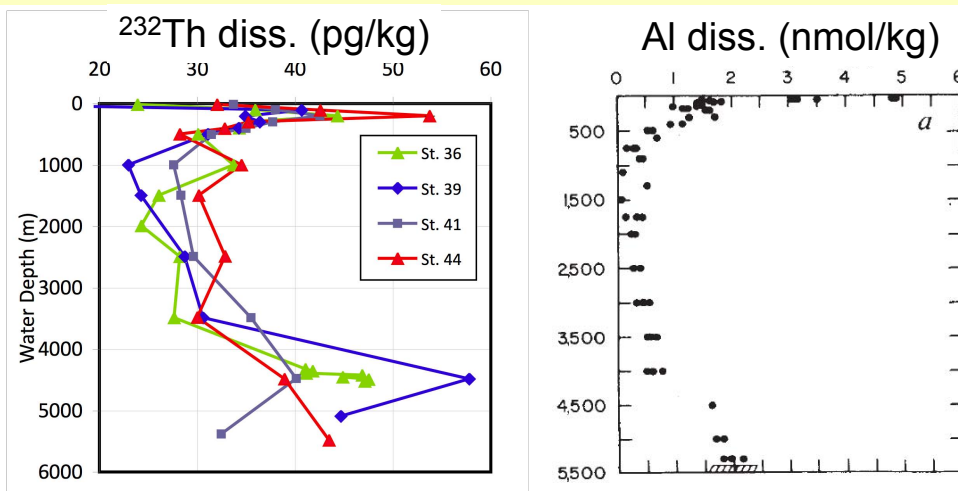
$^{230}\text{Th}$ : Radiogenic source, physical transport & scavenging

$^{232}\text{Th}$ : Lithogenic source, physical transport & scavenging

Hayes, unpublished

INOPEX\_SW\_22July2011.xls

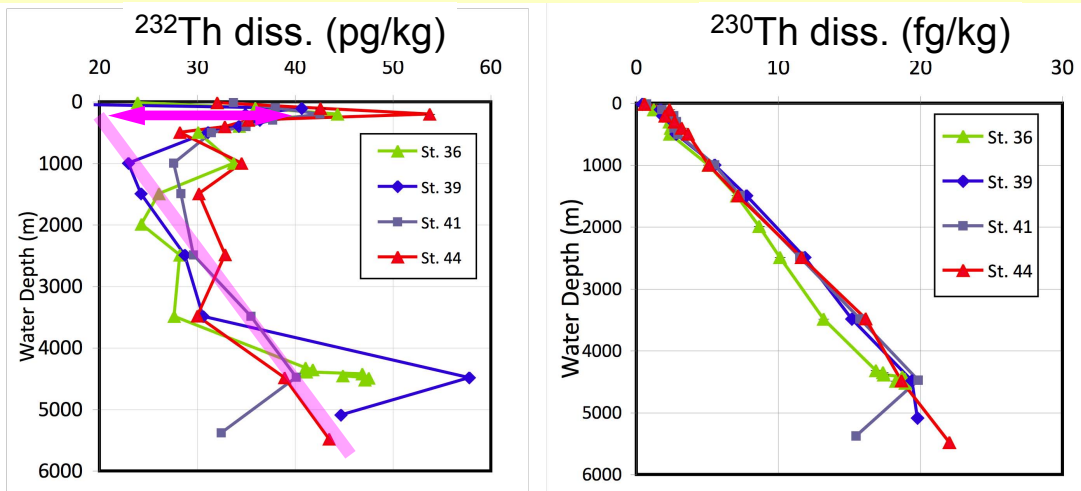
# NW Pacific $^{232}\text{Th}$ profiles @ ~ 40°N



Dissolved  $^{232}\text{Th}$  profiles are similar to that of Pacific Al.

Al from Orians and Bruland, 1985.

# NW Pacific surface enrichment of $^{232}\text{Th}$ supplied by dust

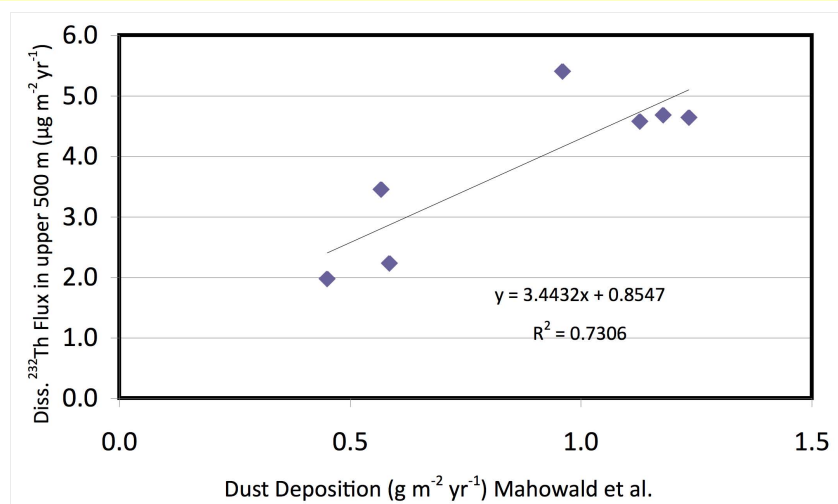


$^{230}\text{Th}$ : Radiogenic source, physical transport & scavenging

$^{232}\text{Th}$ : Lithogenic source, physical transport & scavenging

*Hayes, unpublished*

# NW Pacific: Dissolved $^{232}\text{Th}$ as a tracer of dust supply



Dissolved  $^{232}\text{Th}$  flux correlates with spatial pattern of dust flux from model of Mahowald et al.

*Hayes, unpublished*

## Estimated Fe supply: Assumptions and caveats

Surface excess  $^{232}\text{Th}$  ~ 20 pg/kg (Avg ~10 over 500 m)

0-500m residence time  $^{230}\text{Th}$  ~ 3-4 years\*

Assume Crustal Fe/Th ~5000 (weight ratio)

Assume Fe and Th dissolve equally (test experimentally)

**Estimate soluble Fe supply (dust?) ~ 10 mg Fe m<sup>-2</sup> yr<sup>-1</sup>**

Duce Map: **Total** Fe flux (dust) ~100 mg Fe m<sup>-2</sup> yr<sup>-1</sup>

Caveats:

\*Need to model physical transport (lateral & vertical)

Th is 3X more soluble than Fe

(Pete Morton, pers comm)

## Summary & Recommendations: Boundary sources and sinks

Benthic processes may contribute more to TEI removal than conventional boundary scavenging.

Increase emphasis on near-bottom distributions of dissolved and particulate TEIs.

Boundary exchange with margin sediments may be a significant source of TEIs.

Measure [Nd] and  $\epsilon_{\text{Nd}}$ , and consider other TEI systems that will constrain benthic sources (e.g.,  $^{232}\text{Th}$  -  $^{230}\text{Th}$ ).

Novel applications of  $^{232}\text{Th}$  -  $^{230}\text{Th}$  will aid in quantifying supply of TEIs by dust.

Need experiments to constrain solubilities of TEIs relative to that of  $^{232}\text{Th}$ .