Inverse models of GEOTRACES datasets

New insights into trace metal scavenging

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GEOTRACES

Objectives

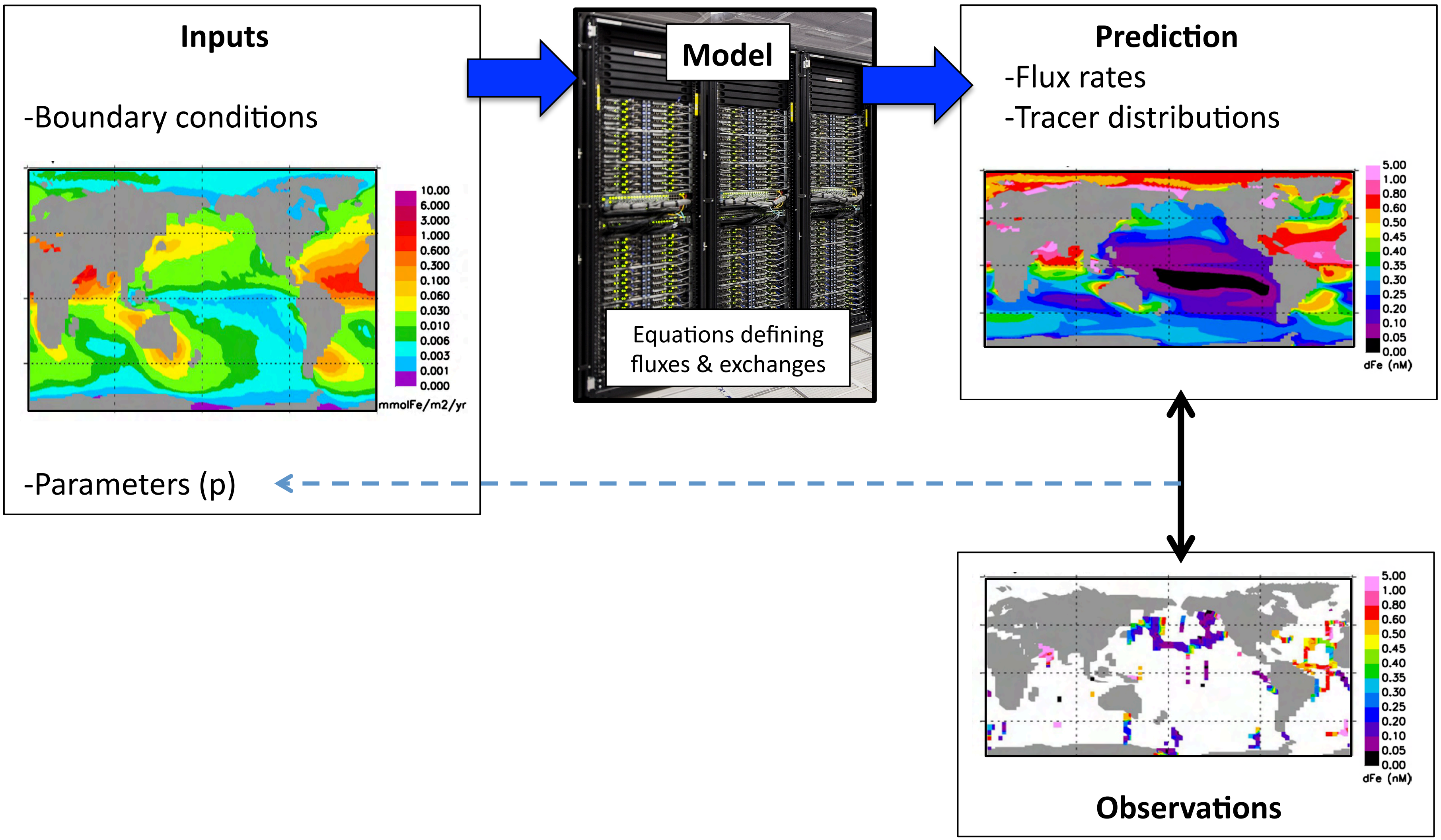
- Concept of a data-assimilating (inverse) model
  - Differences/similarities to other model approaches
  - Important considerations
- How can they be used to extract new information from data?
  - Rates
  - Processes
  - Chemical mechanisms

Objectives

- Concept of a data-assimilating (inverse) model
  - Differences/similarities to other model approaches
  - Important considerations

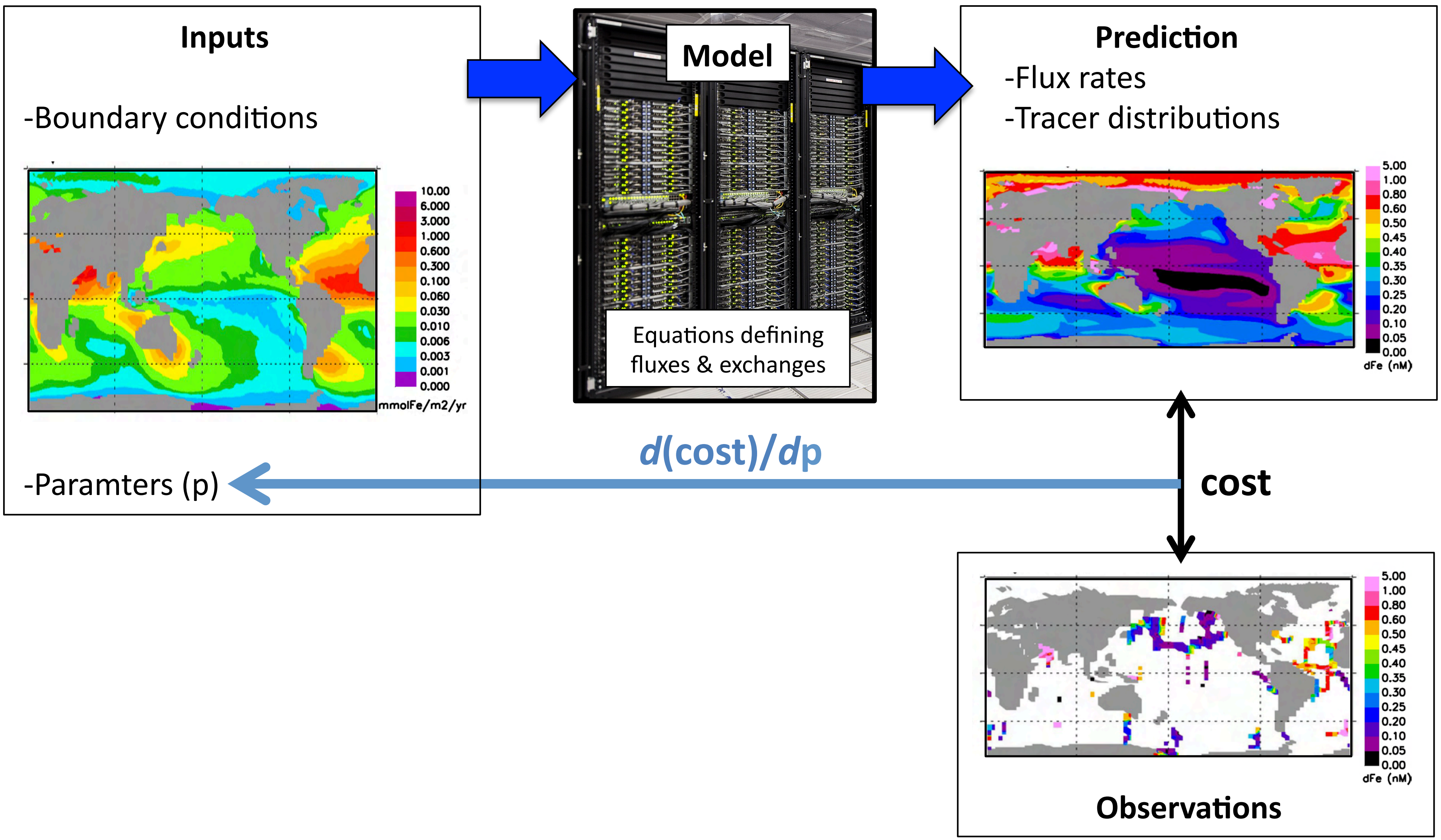
- How can they be used to extract new information from data (about trace element scavenging)?
  - Rates (lifetime of hydrothermal Fe)
  - Processes (global Zn distribution)
  - Chemical mechanisms (Cd scavenging in low O_2)

“Traditional” models



Figures: Moore & Braucher 2008

Data-assimilating models



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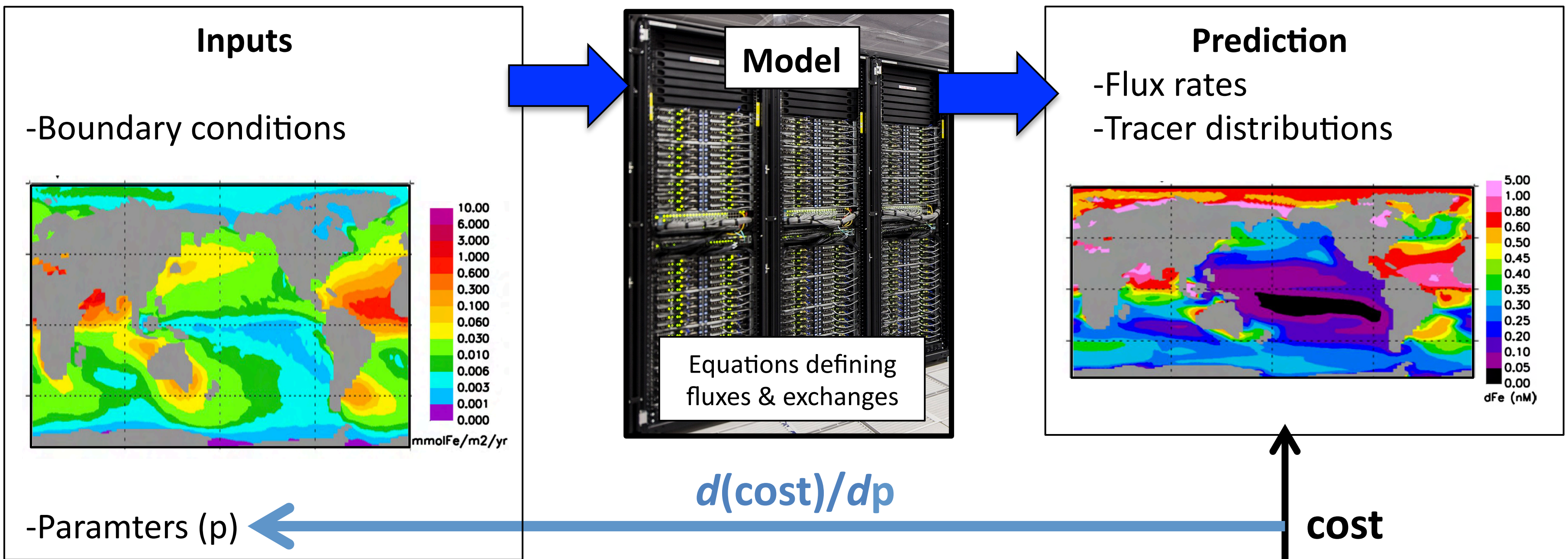
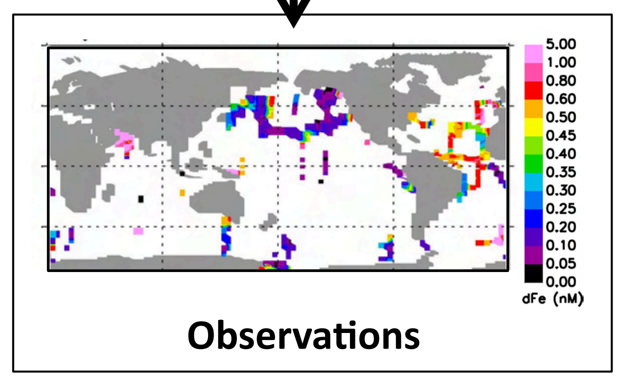
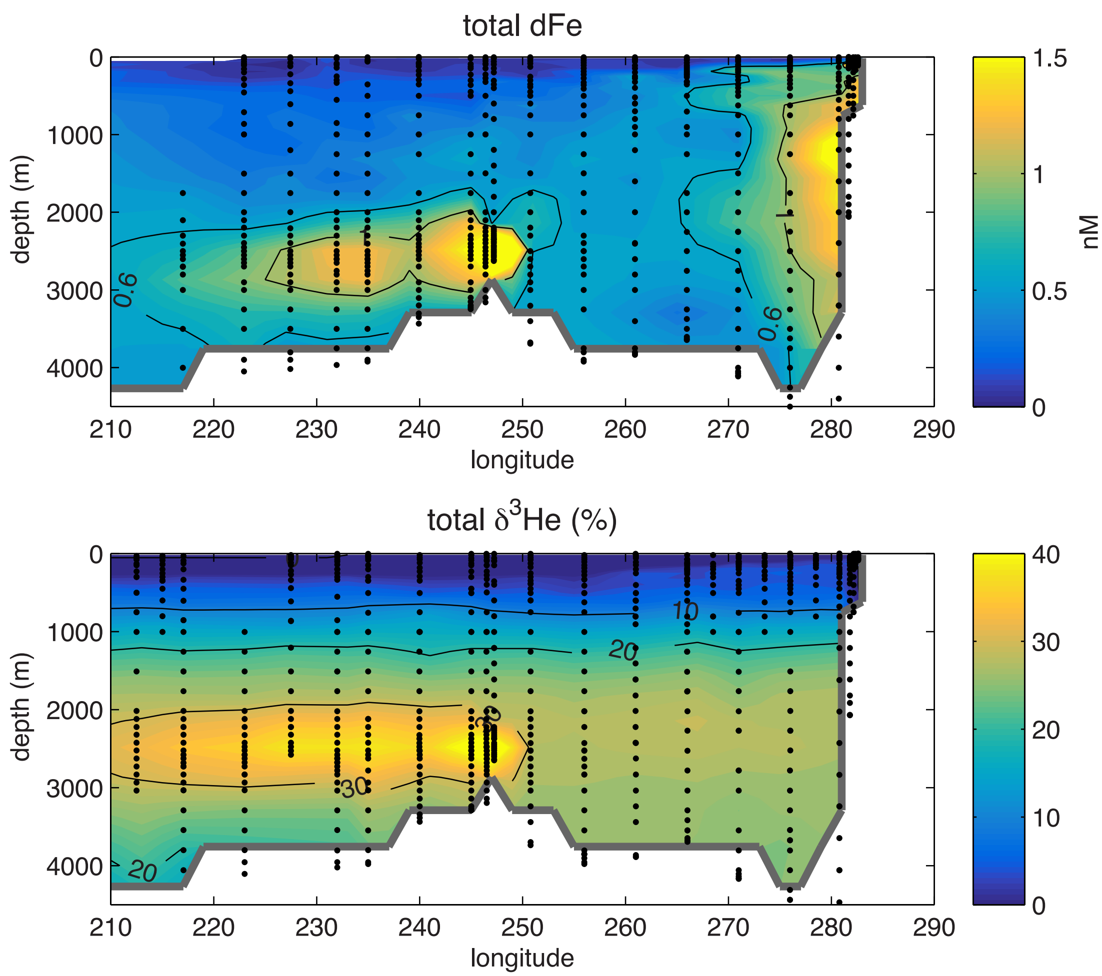
Data-assimilating models





- A model that maximizes data use, *without over-relying on it*
  - Doesn't allow unrealistic parameter choices (we might just have the wrong model!)
- A model whose fluxes/rates are most consistent with data
  - Back out fluxes from section data

Rates: Lifetime of hydrothermal Fe

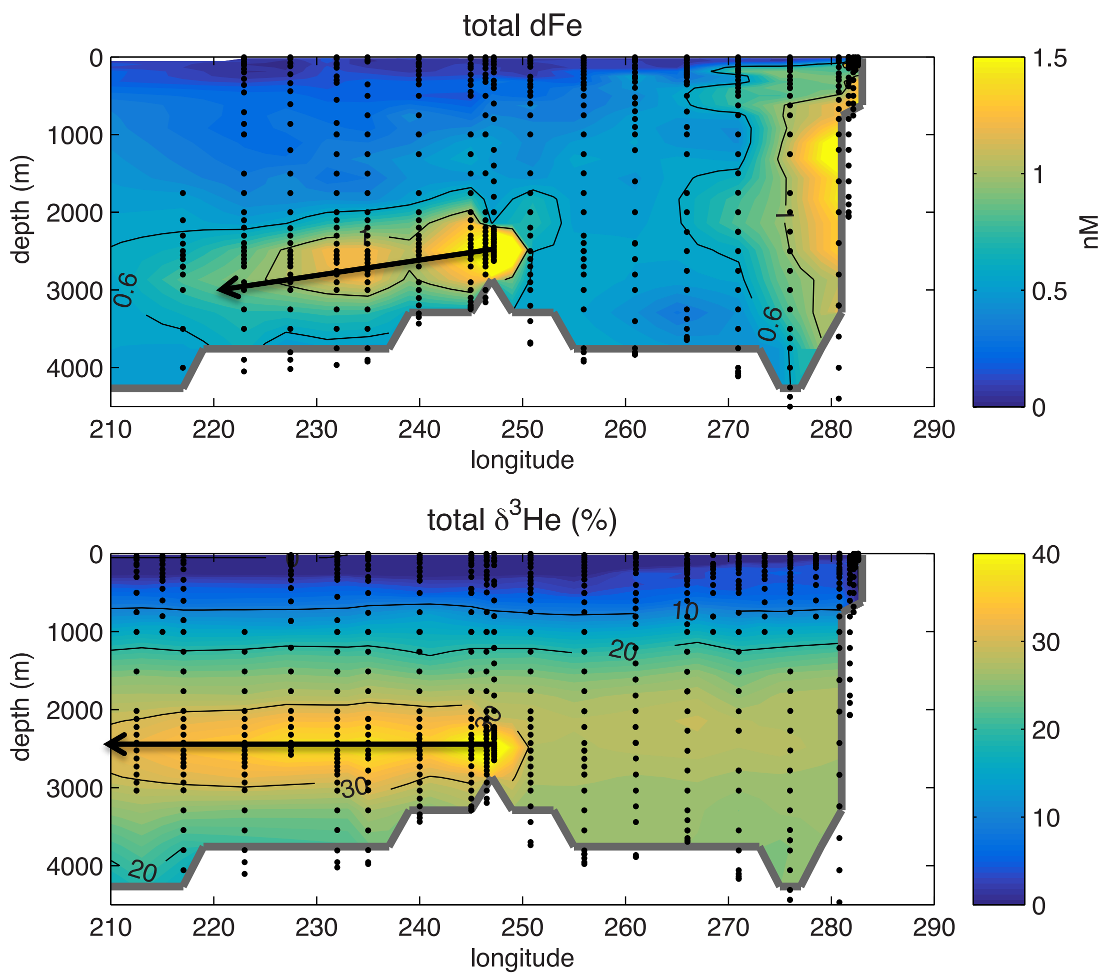


EPZT hydrothermal vent

- Fe plume transported long distances across the basin (slow scavenging)

Resing et al 2015

Rates: Lifetime of hydrothermal Fe

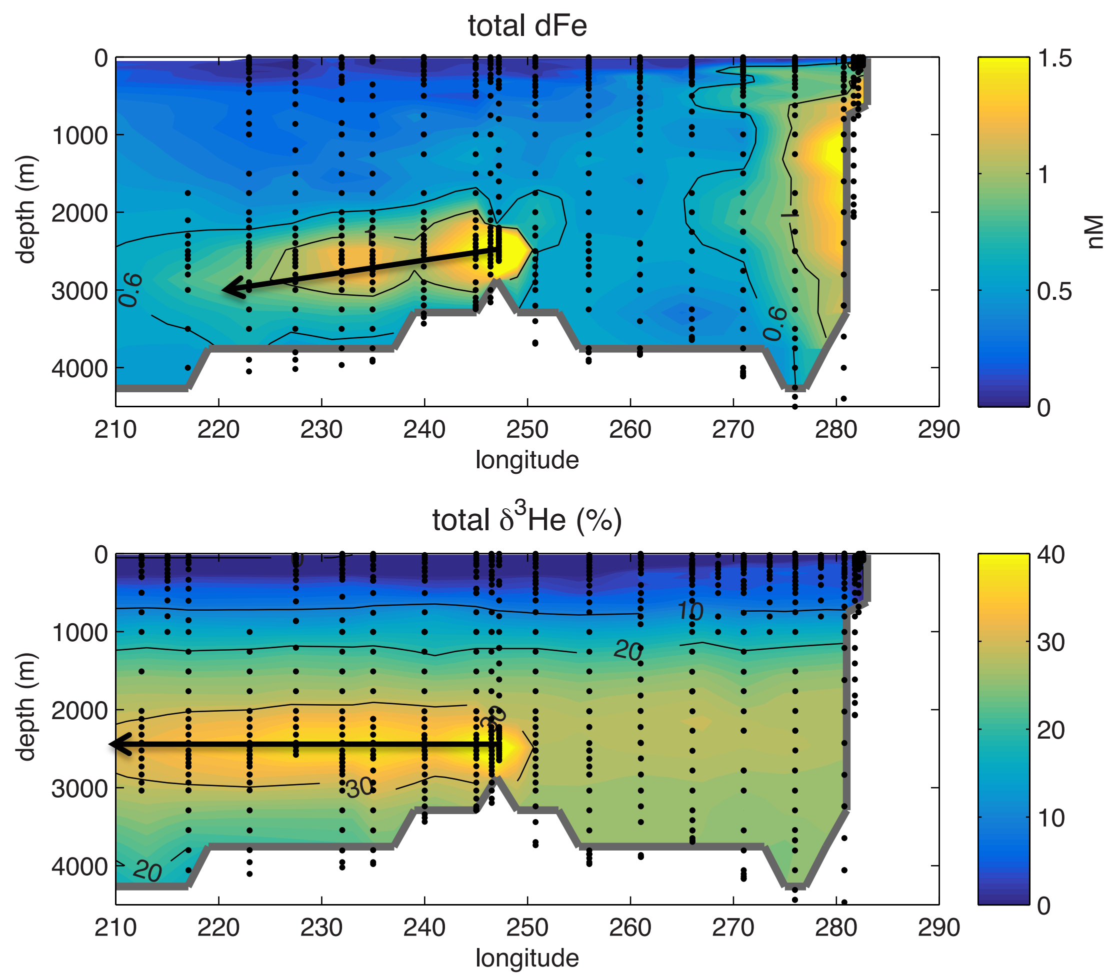


EPZT hydrothermal vent

- Fe plume transported long distances across the basin (slow scavenging)
- Slumping of plume relative to passive tracer

Resing et al 2015

Rates: Lifetime of hydrothermal Fe

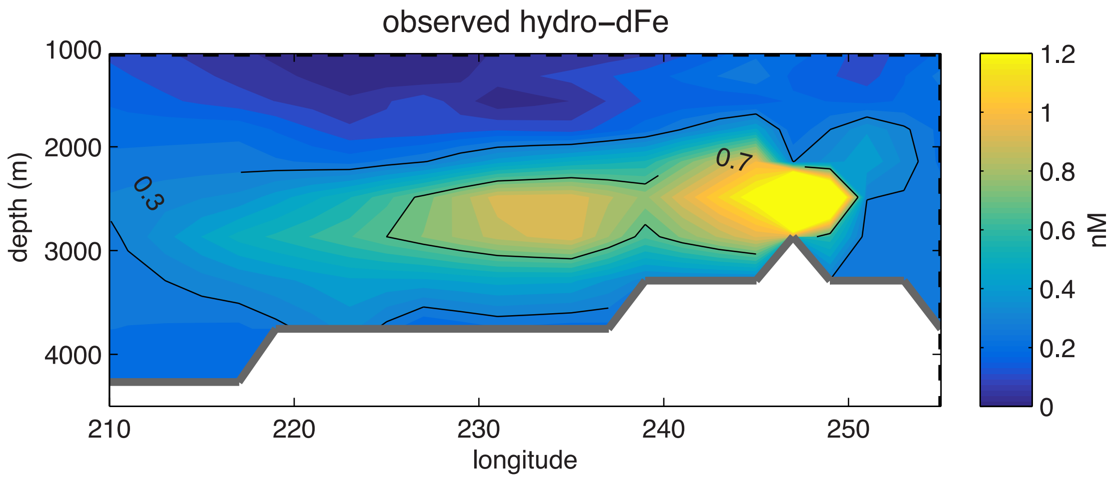


EPZT hydrothermal vent

- Fe plume transported long distances across the basin (slow scavenging)
- Slumping of plume relative to passive tracer
- Rates of Fe sinking and scavenging?
- Lifetime of hyrdrothermal Fe, and supply to surface?

Resing et al 2015

A simple "hydro-dFe" model



<u>hydro-dFe</u>
dFe in plume region, minus "background" concentration (advected, ligand-bound Fe)

$$\frac{d(\mathrm{Fe})}{dt} = circ.(\mathrm{Fe}) + R_{Fe:He} J_{hydro}(^{3}\mathrm{He}) - k_{sc}\mathrm{Fe} - \frac{\partial}{\partial z}(w_{\mathrm{sink}}\mathrm{Fe})$$

Circulation
2°x2° Ocean model (OCIM)

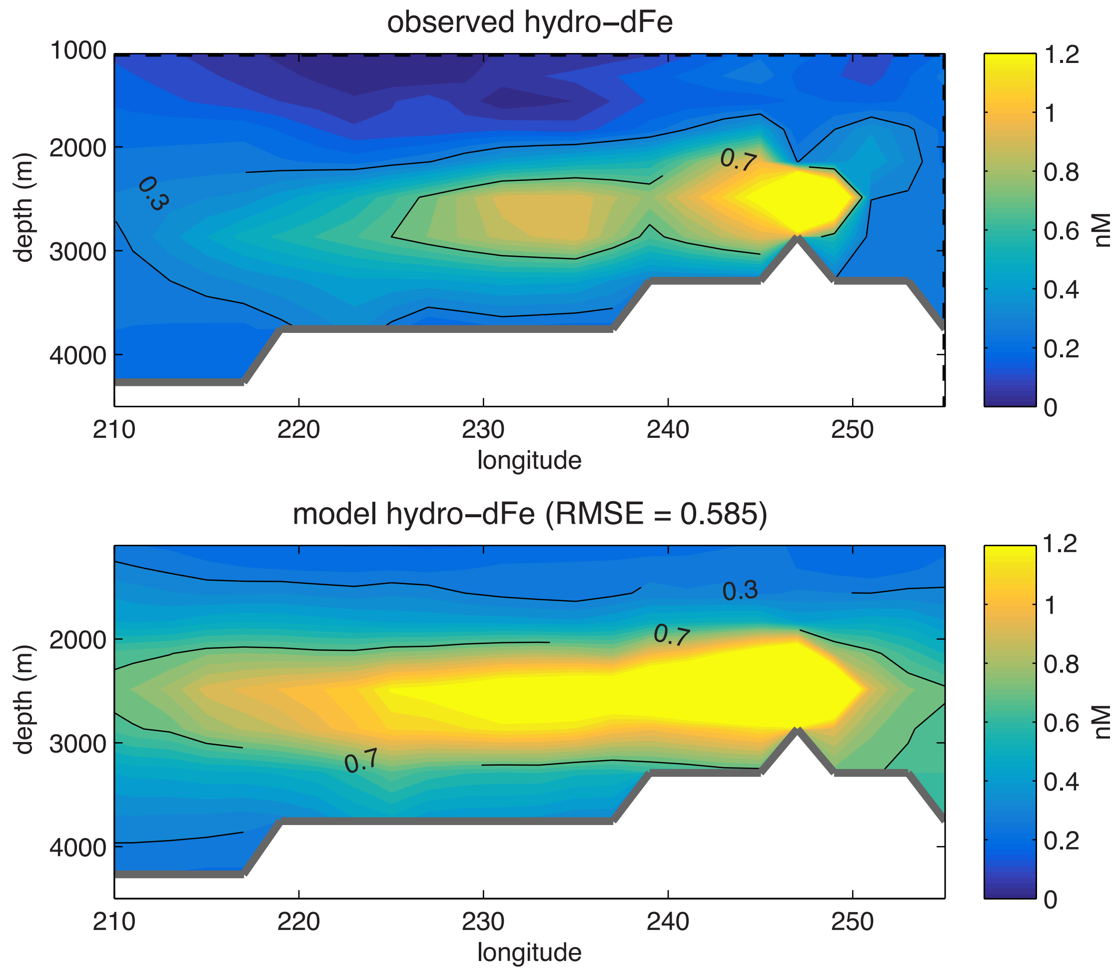
DeVries et al 2011

Vent source
Coupled to ^{3}He input

Scavenging
First-order removal

Sinking
At constant sinking rate

A simple “hydro-dFe” model

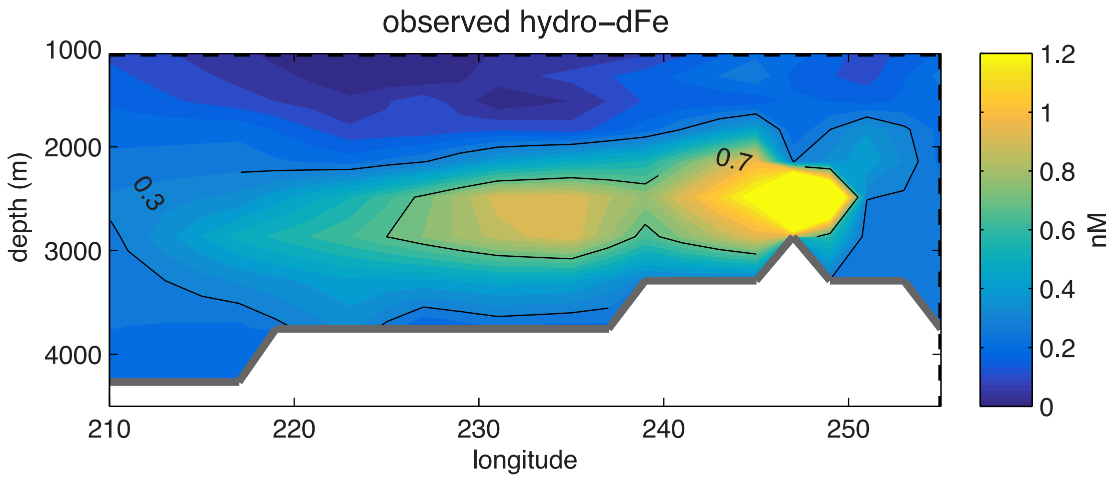


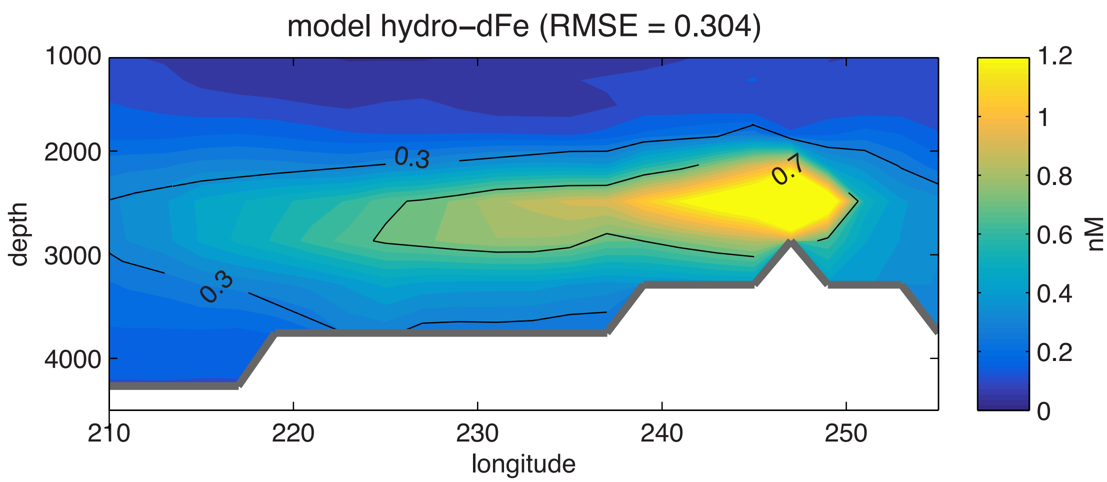
<u>hydro-dFe</u>
dFe in plume region, minus “background” concentration (advected, ligand-bound Fe)

<u>Initial guess:</u>

- $Fe/^3He = 10^8$ mol/mol
- w_{sink} = 10 m/yr
- k_{sc} = 0.01yr^{-1}

Optimized "hydro-dFe" model





<u>hydro-dFe</u>

dFe in plume region, minus "background" concentration (advected, ligand-bound Fe)

<u>Optimum (~200 iterations):</u>

- $Fe/^3He = 5.5\times10^7$ mol/mol
- $w_{sink} = 33$ m/yr
- $k_{sc} = 0.02 yr^{-1}$

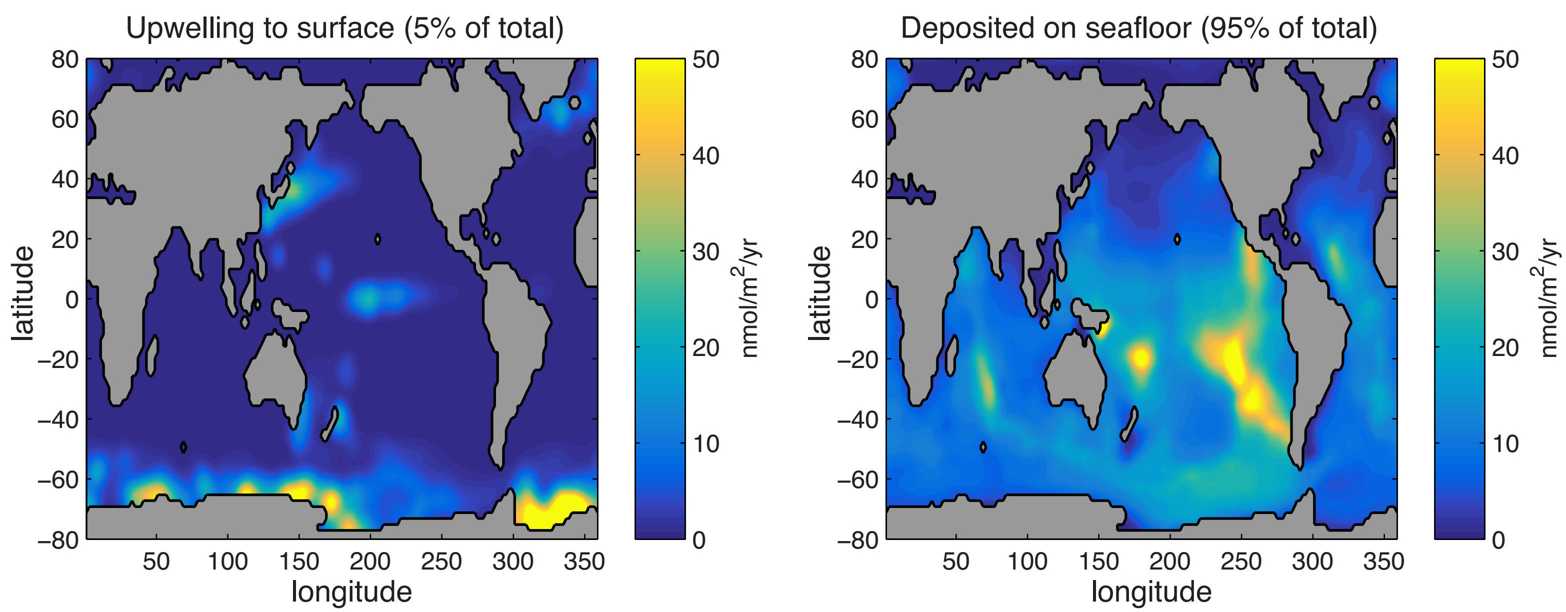
Limitations and implications

Limitations:

- Unresolved process (*data-assimilating models are often necessarily simplified*)

Implications (extrapolation):

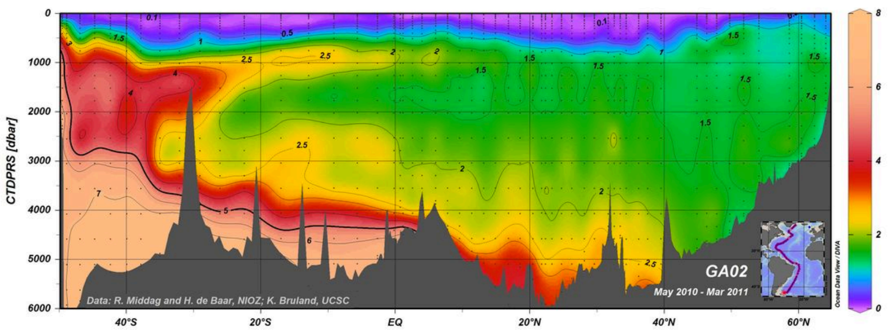
- Total hydrothermal source of 4.5Gmol/yr, lifetime of ~30yrs
- Sinking and scavenging remove 95% of hydrothermal before it reaches the surface



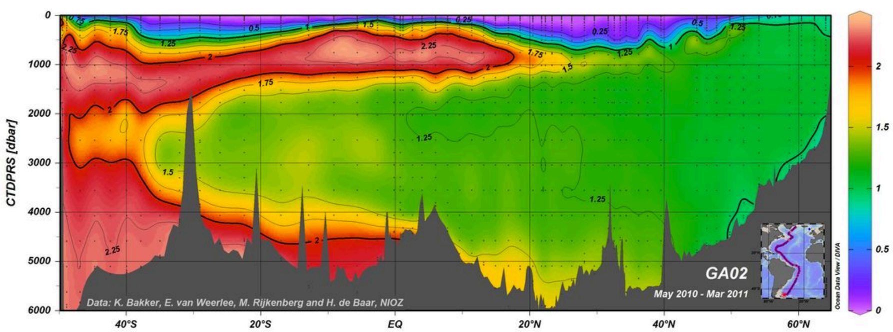
<u>Processes</u>: Global Zn/Si covariation

<u>Oceanic distribution (GA02)</u>

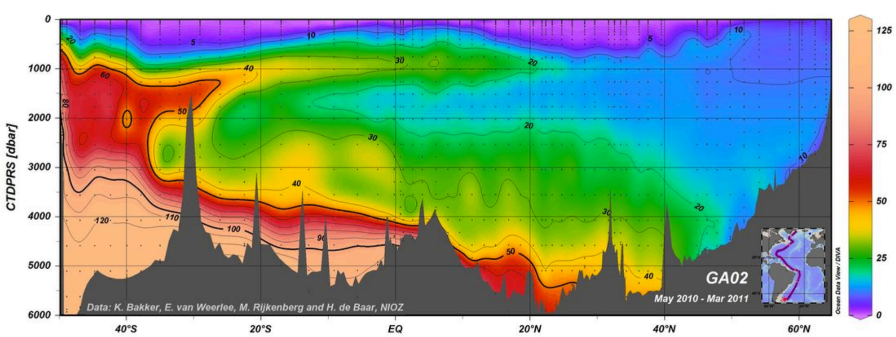
Zn



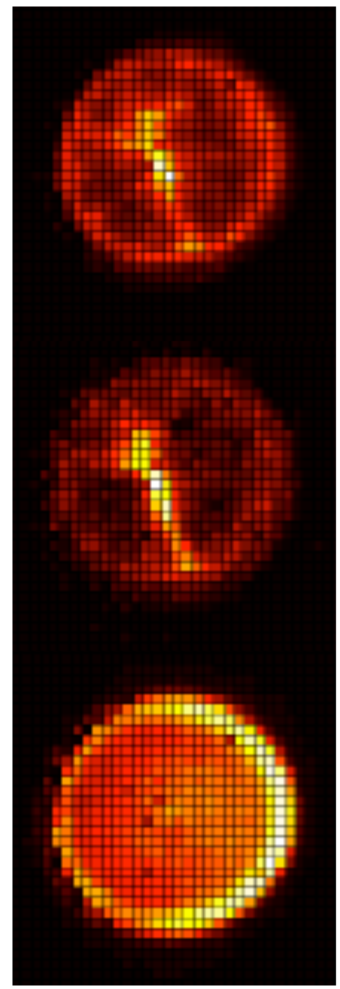
PO_4



$Si(OH)_4$



<u>Cellular distribution (SXRF)</u>



Zn

P

Si

Twining et al 2003

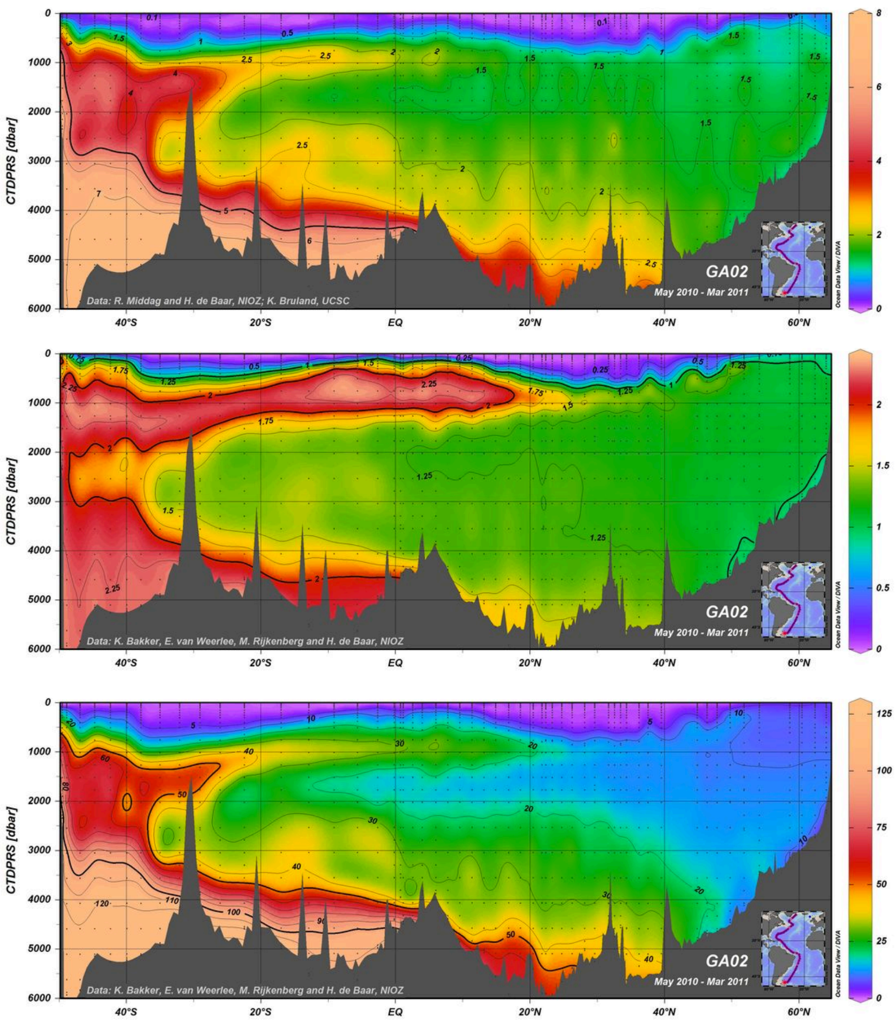
<u>Processes</u>: Global Zn/Si covariation

<u>Oceanic distribution (GA02)</u>

Zn

PO_4

$Si(OH)_4$



<u>Three hypotheses</u>

1. **Preformed**: Rapid Southern Ocean uptake leaves surface distribution similar to $Si(OH)_4$
2. **Frustules:** Incorporation of some Zn into diatom frustules results in deeper remineralization than other soft-tissue nutrients
3. **Scavenging:** Zn adsorbed onto organic particles, hitches a ride to the deep ocean (*John & Conway 2014*)

Model 1: Preformed Zn

$$\frac{\mathrm{dZn}}{\mathrm{dt}} = circ.(\mathrm{Zn}) - J_{up}(\mathrm{Zn}) - J_{rem}(\mathrm{POZn})$$

Circulation
2°x2° Ocean Circulation model (OCIM)

Uptake
Rapid uptake when Zn abundant (Southern Ocean)

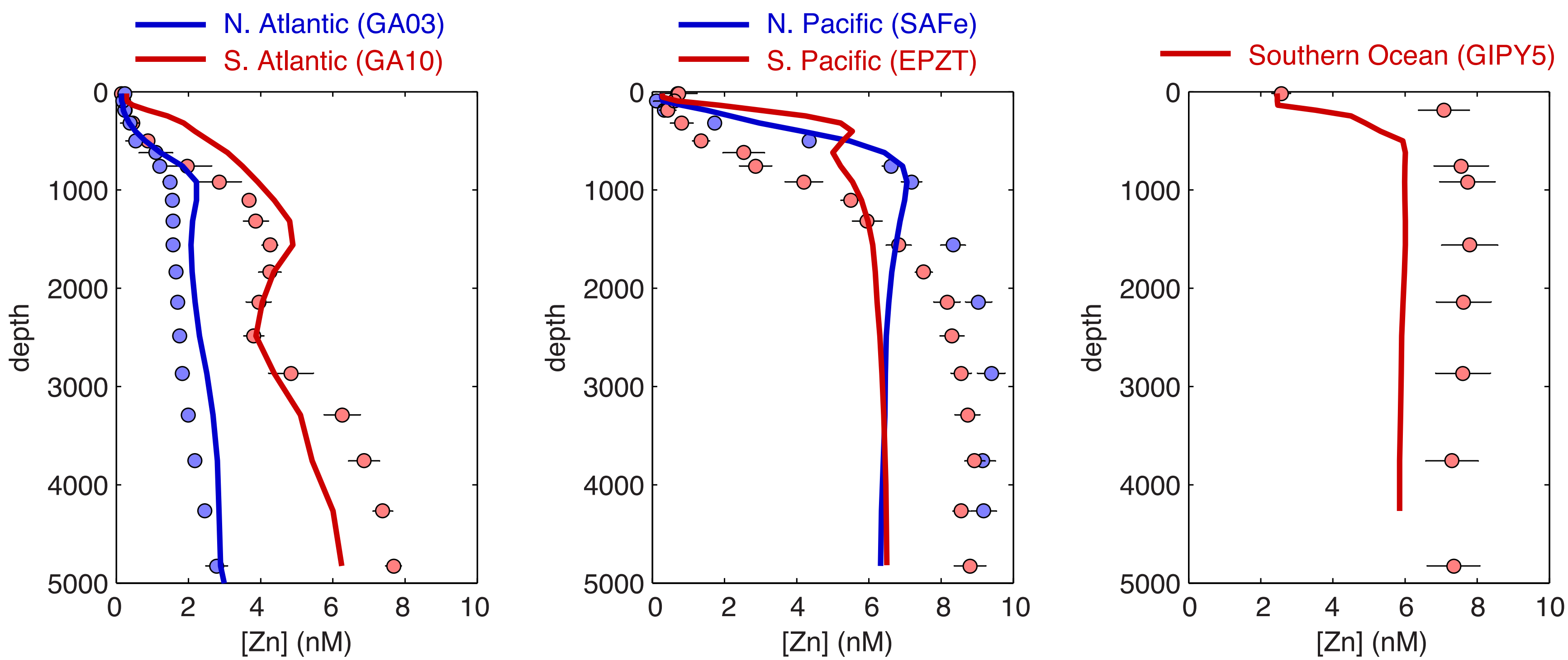
Organic Remin.
Depth scale as PO_4 (derived in inverse P-cycle model)

<u>Why data-assimilating model?:</u>

- Rule out model "failure" due to bad parameters.
- Fairest way to eliminate hypotheses.

Model 1: Preformed Zn

$$\frac{\mathrm{dZn}}{\mathrm{dt}} = circ.(\mathrm{Zn}) - J_{up}(\mathrm{Zn}) - J_{rem}(\mathrm{POZn})$$



Model 2: Frustrule-associated Zn

$$\frac{dZn}{dt} = circ.(Zn) - J_{up}(Zn) - J_{rem}(POZn) - J_{rem}(Zn_{frust})$$

Circulation
2°x2° Ocean
Circulation model
(OCIM)

Uptake
Rapid uptake
when Zn abundant
(Southern Ocean)

Organic Remin.
Depth scale as PO_4
(derived in inverse
P-cycle model)

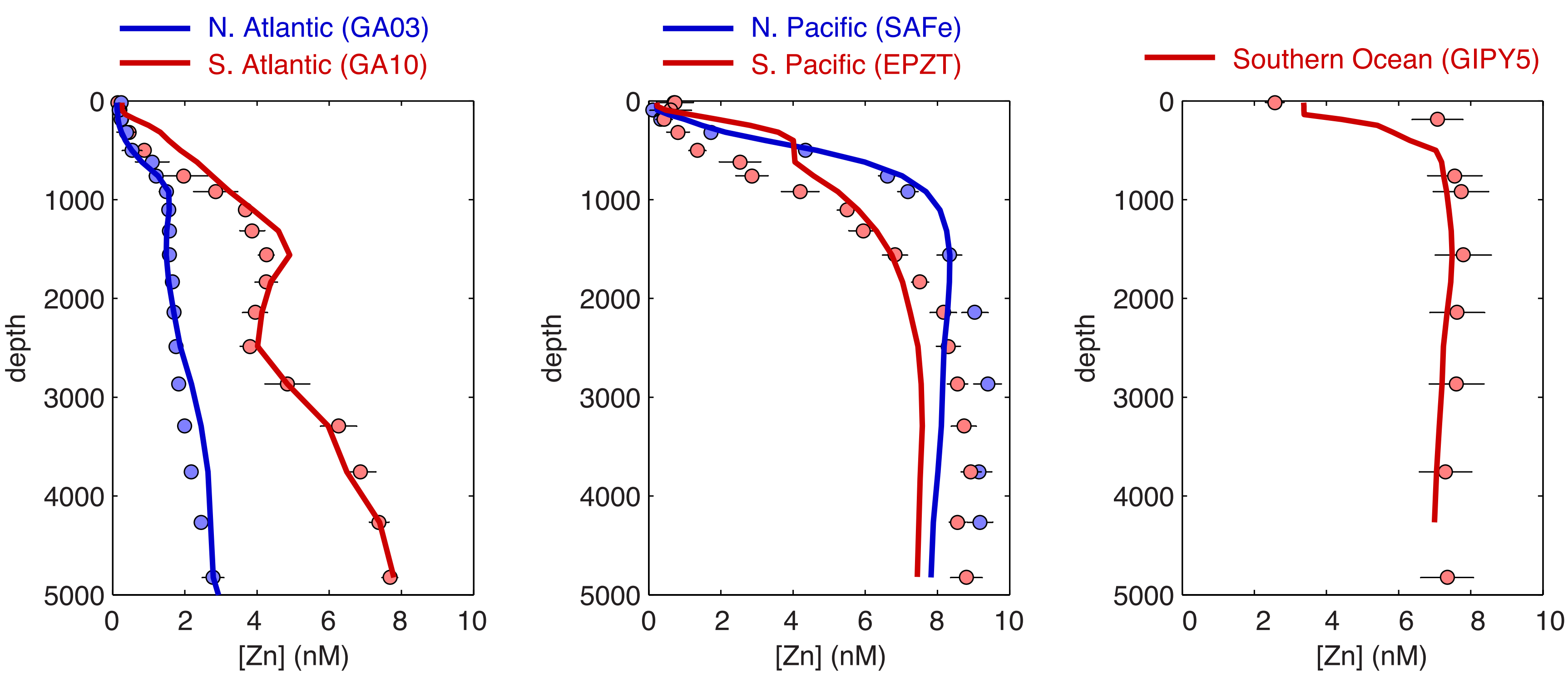
Opal Remin.
Depth scale as Si
(derived in inverse
Si-cycle model)

Additional constraints:

- 1-3% directly incorporated into frustules (*Ellwood & Hunter 2000*)
- <40% co-located with frustule (*SXRF*)

Model 2: Frustrule-associated Zn

$$\frac{dZn}{dt} = circ.(Zn) - J_{up}(Zn) - J_{rem}(POZn) - J_{rem}(Zn_{frust})$$



Wants >40% Zn in diatom frustules

Model 3: Scavenging

$$\frac{\mathrm{dZn}}{\mathrm{dt}} = circ.(\mathrm{Zn}) - J_{up}(\mathrm{Zn}) - J_{rem}(\mathrm{POZn}) - \frac{\partial}{\partial z} w\mathrm{Zn}_{\mathrm{ads}}$$

Circulation
2°x2° Ocean
Circulation model
(OCIM)

Uptake
Rapid uptake
when Zn abundant
(Southern Ocean)

Organic Remin.
Depth scale as PO_4
(derived in inverse
P-cycle model)

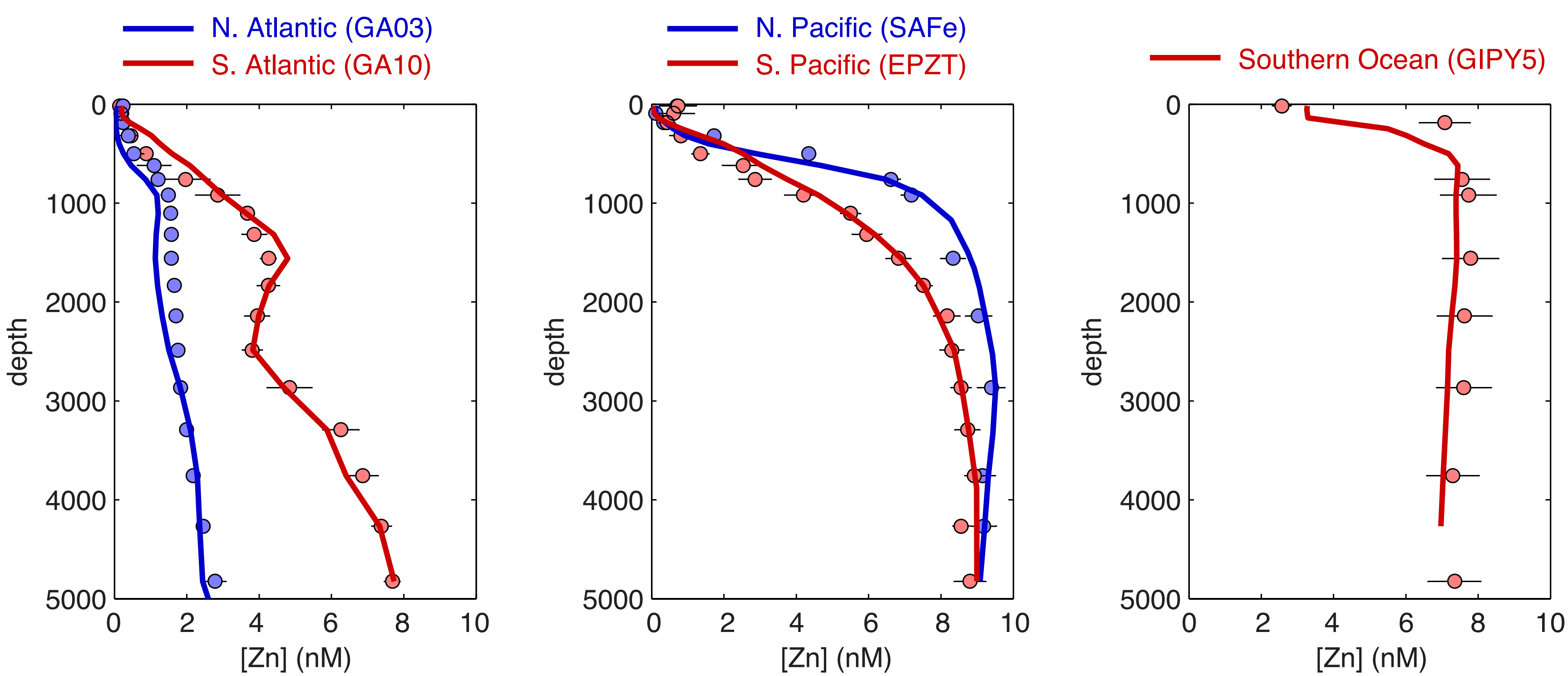
Scavenging
Depth scale as Si
(derived in inverse
Si-cycle model)

Reversible scavenging model:

$$\mathrm{Zn}_{\mathrm{ads}} = \frac{K_{sc}[\mathrm{particles}]}{K_{sc}[\mathrm{particles}]+1}\mathrm{Zn}$$

Model 3: Scavenging

$$\frac{\mathrm{dZn}}{\mathrm{dt}} = circ.(\mathrm{Zn}) - J_{up}(\mathrm{Zn}) - J_{rem}(\mathrm{POZn}) - \frac{\partial}{\partial z} w\mathrm{Zn}_{\mathrm{ads}}$$

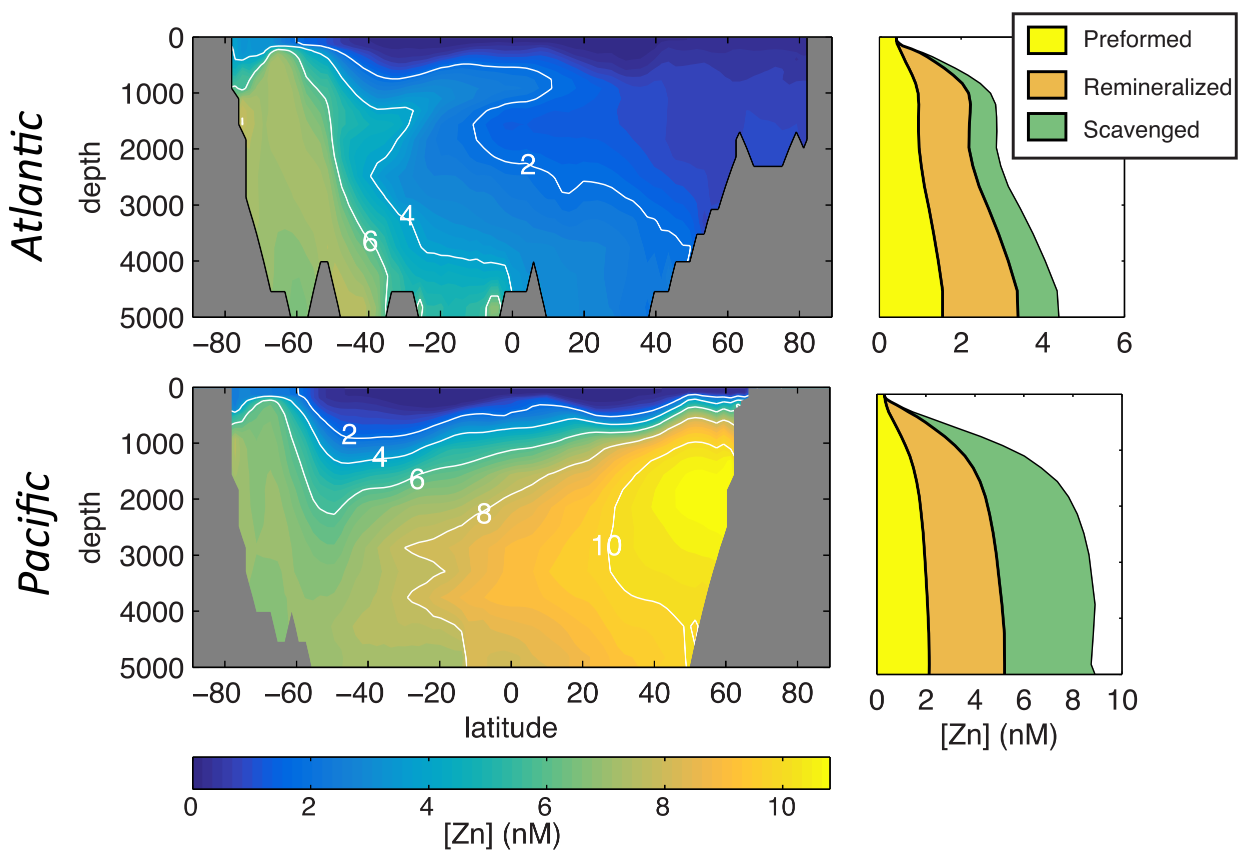


Predicts between 0.01% (deep) and 1% (surface) in adsorbed phase

Limitations and implications

<u>Limitations:</u>

- Lack of direct constraints on adsorbed fraction
- Cannot unravel combination of frustule/scavenging mechanisms

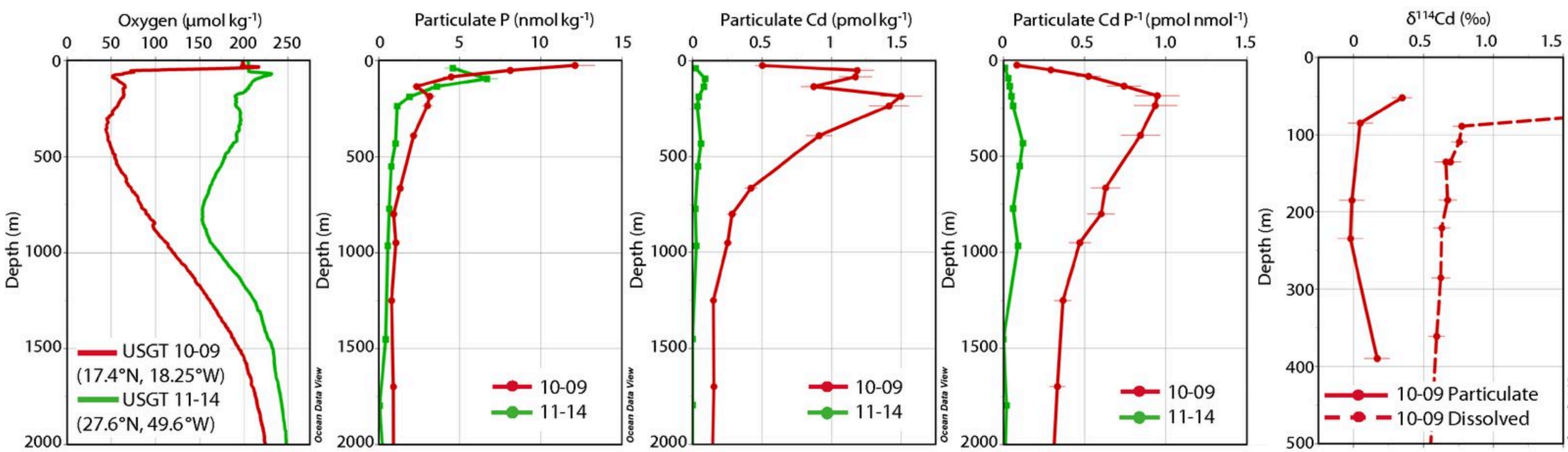


<u>Implications:</u>

- Power of reversible scavenging: <1% in adsorbed phase results in major transfer from intermediate to deep water
- Zn/Si covariance not caused by close mechanistic coupling of their cycles

Mechanisms: Cd scavenging in ODZ

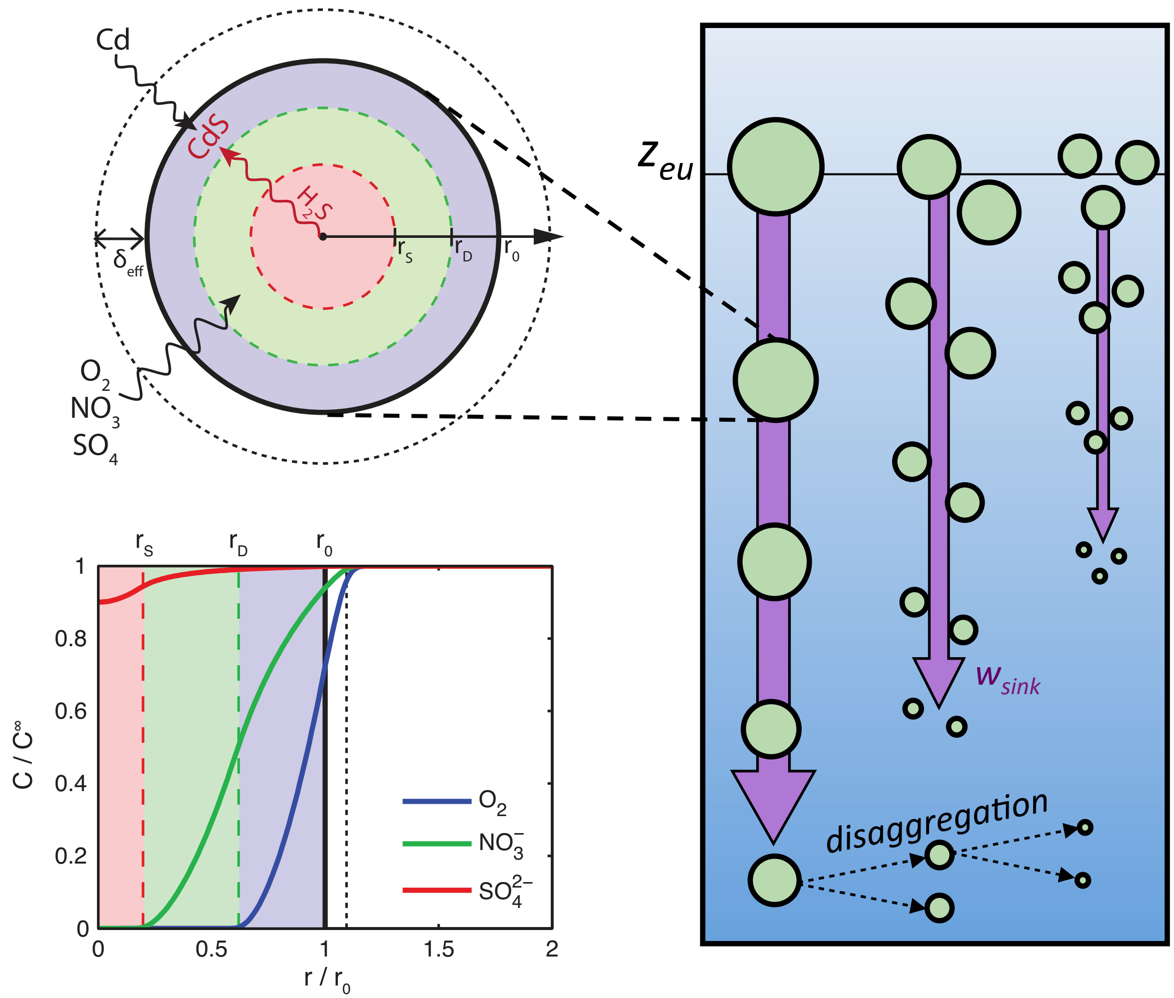
Observation: Scavenging of "light" Cd from dissolved to particulate phase in ODZ in east of GA03 transect.



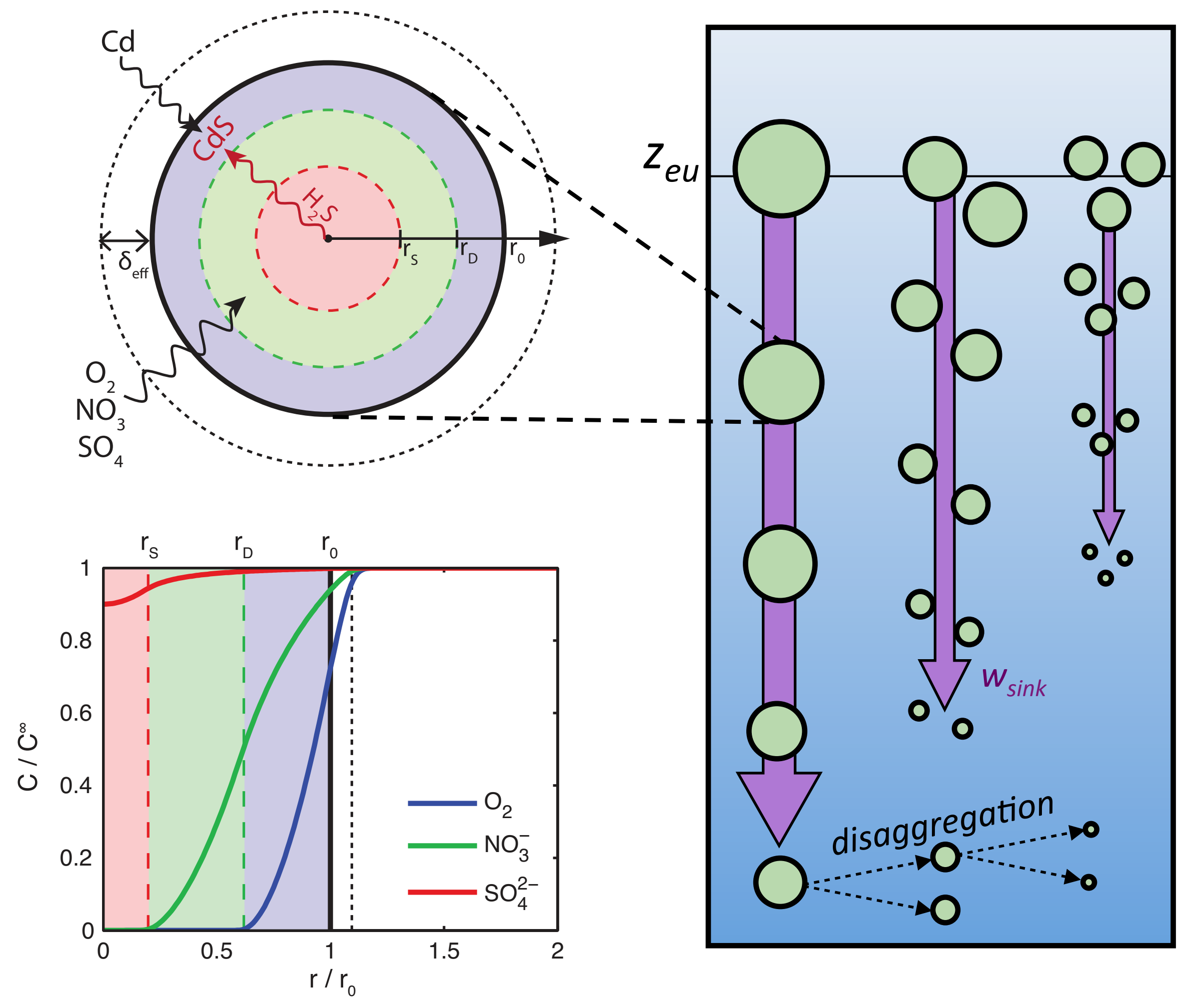
Janssen et al 2014

Hypothesized Mechanism: CdS precipitates in sulfidic "microzones" inside organic particles undergoing rapid respiration

Mechanistic model



Mechanistic model



<u>Boundary conditions:</u>

- Surface particle size spectrum (UVP-*TARA*)
- Chemical environment (*GEOTRACES*)

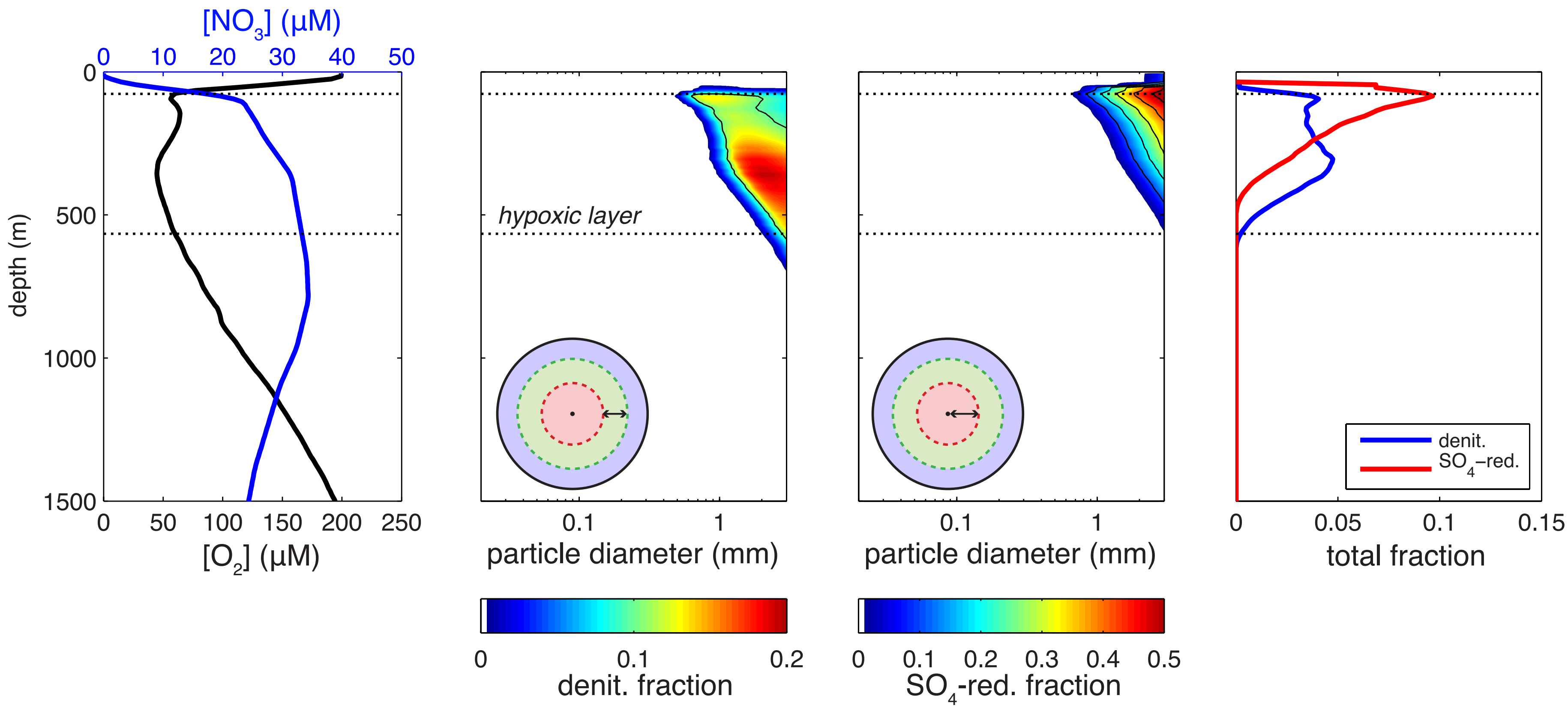
<u>Parameters (and ranges)</u>

- Sinking (*Smayda 1971*)
- Respiration rates (*McDonnell 2015*)
- Disaggregation rates
- Fractionation factors

<u>Constraints</u>

- Particulate P, Cd, δ^{114}Cd (Janssen 2014)
- Particle size spectrum (UVP-*TARA)*

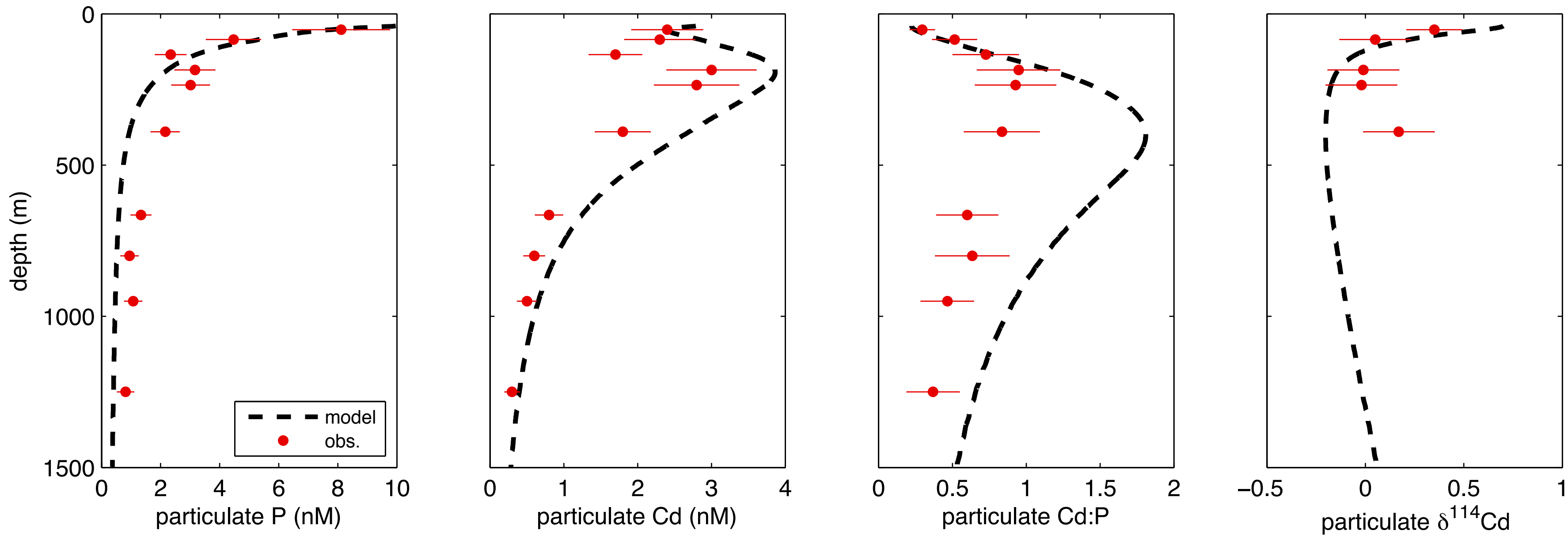
Trop. Atlantic particle microzones



Predictions from model with **prior parameters** ("best-guess" from observations)

Paticles >1mm can precipitate CdS (and then disaggregate)

Trop. Atlantic particle chemistry



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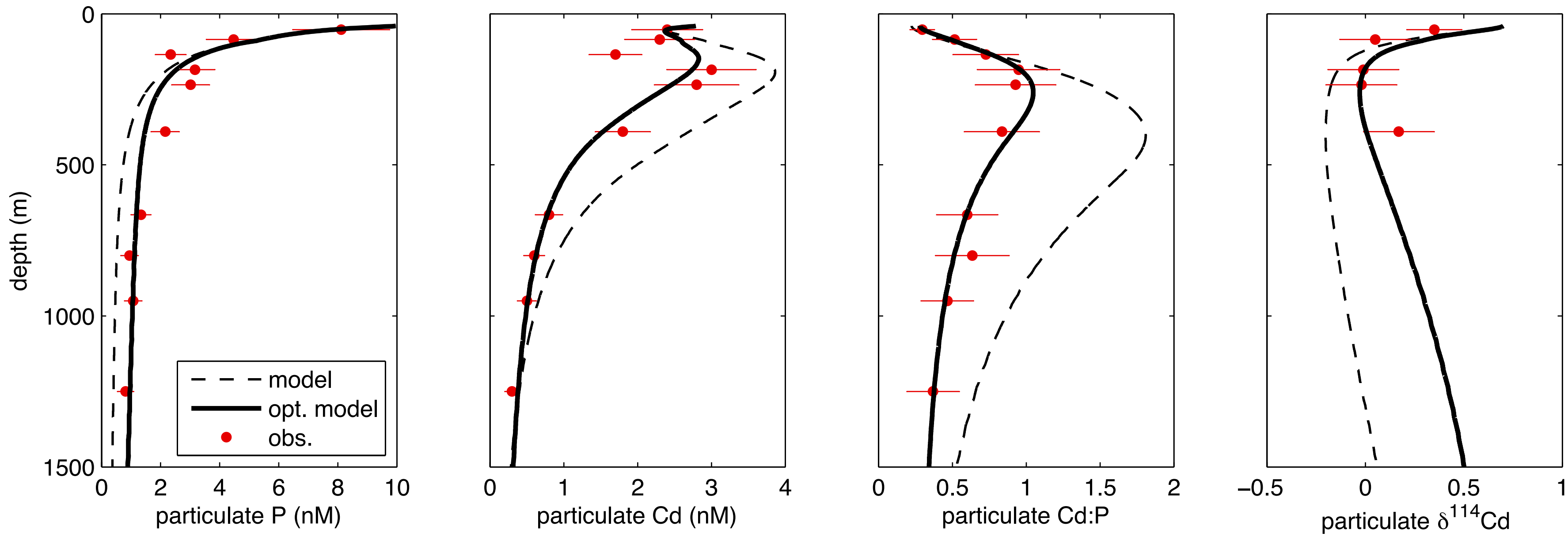
Trop. Atlantic particle chemistry



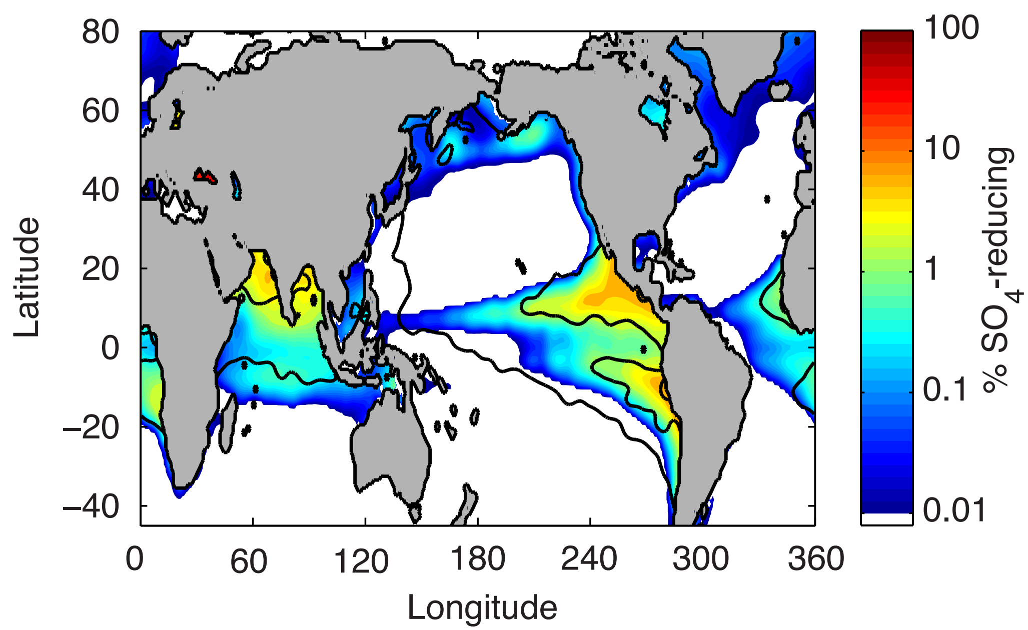
Predictions from model with **optimized parameters**

(Requires minor reduction in respiration rates, remain within observed range)

Limitations and implications

Limitations:

- Highly idealized model particles (spherical geometry, “fast” communities)
- *Cannot prove* the CdS-precipitation mechanism (need new observations), can only show that it *is consistent with observations* and other constraints.



Implications:

- Potential for CdS precipitation through tropics and N.Pacific (identifies new regions for observations)
- Major sink and redistribution process for all chalcophile trace metals?

Concluding remarks

- New scavenging insights from data-constrained models:
  - Hydrothermal Fe lifetime of ~35yrs (limited supply to surface)
  - Reversible scavenging can explain global covariation of Zn and Si
  - Particulate observations in Tropical Atlantic are consistent with CdS precipitation mechanism

- Important take-homes:
  - Inverse modeling methods can be applied to wide range of datasets to answer a wide array of questions
  - Can help *you* test *your* ideas, and interpret *your* observations
  - Best outcomes from observationalist-modeler collaboration!