Equilibrium or kinetics: What controls the distribution of Fe isotopes in the global ocean?

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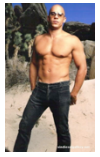
Consider a phytoplankter the size of two 53’ intermodal freight containers

5 tons CO_2

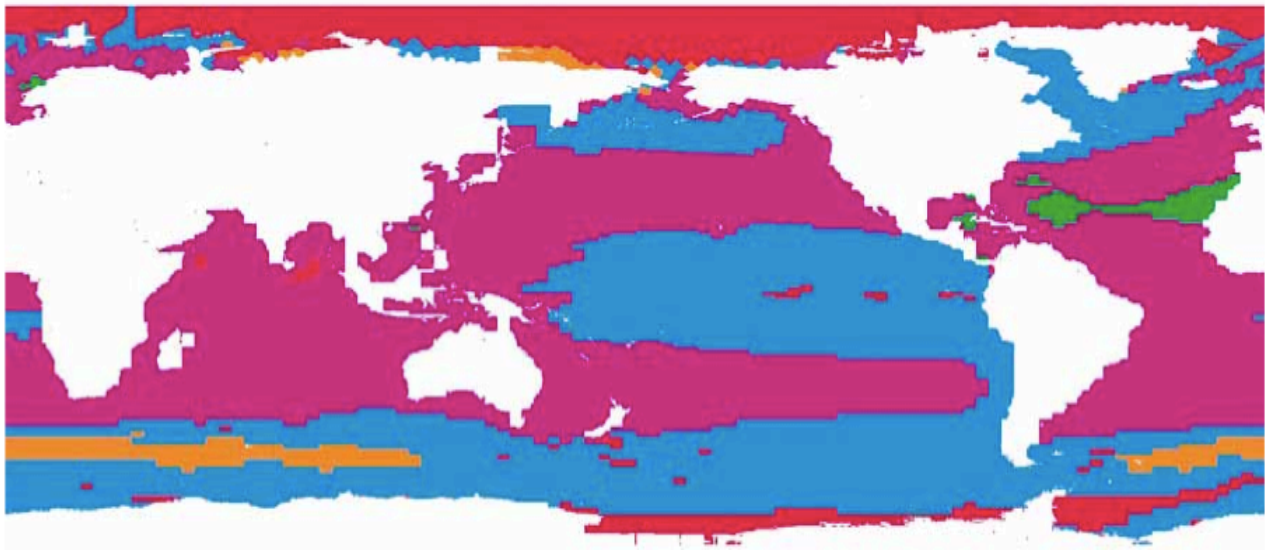
1000 kg NO_3^-



100 kg PO_4^-

160 g Fe

Model predicted ultimate-limiting nutrient

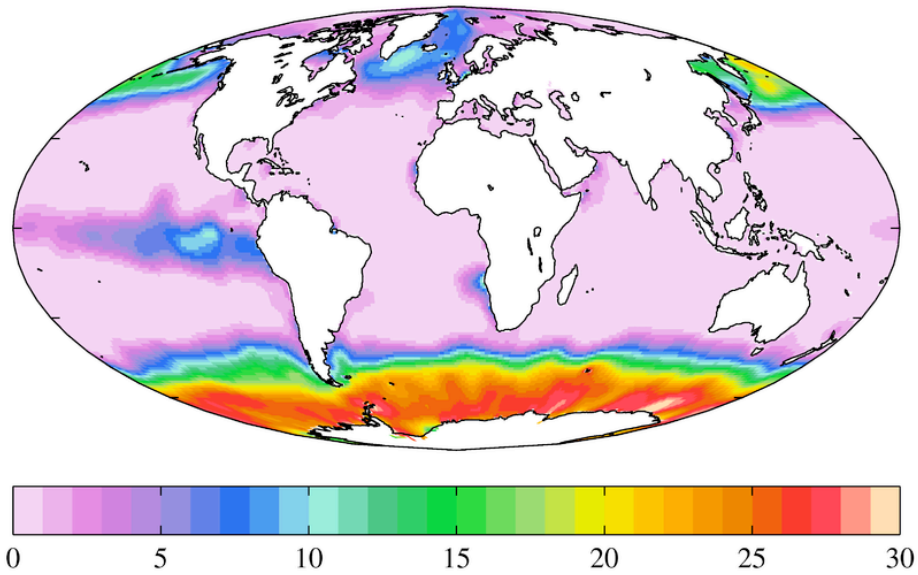


Small Phytoplankton Nutrient Limitation

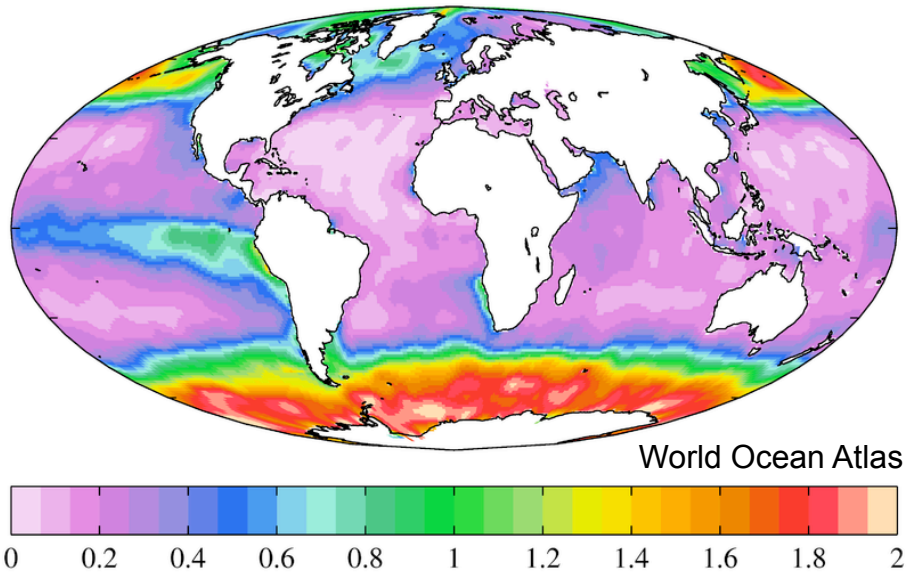
- Nitrogen 55.9 %
- Iron 36.3 %
- Phosphorous 1.4 %
- Replete 2.6 %
- Light 3.8 %

Adapted from Moore et. al., GBC, 2004.

What happens if you add more nutrients to the ocean?



Sea-surface nitrate (mM)



Sea-surface phosphate (mM)

Forcing

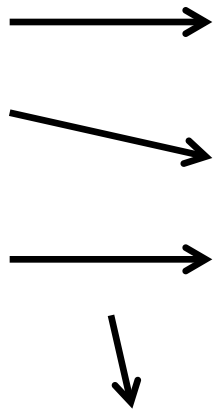
2x increase in riverine NO_3^- flux

2x increase in riverine PO_4^{3-} flux

2x increase in gyre upwelling

2x increase in HNLC Fe flux

Atmospheric CO_2

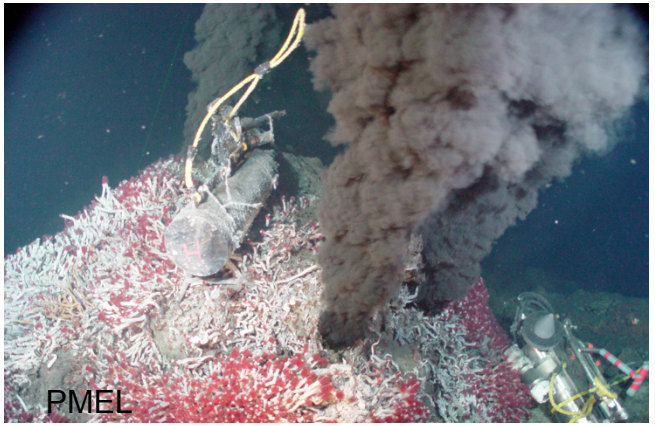


Possible sources of iron to the ocean

Dust

Porewater Fe(II)

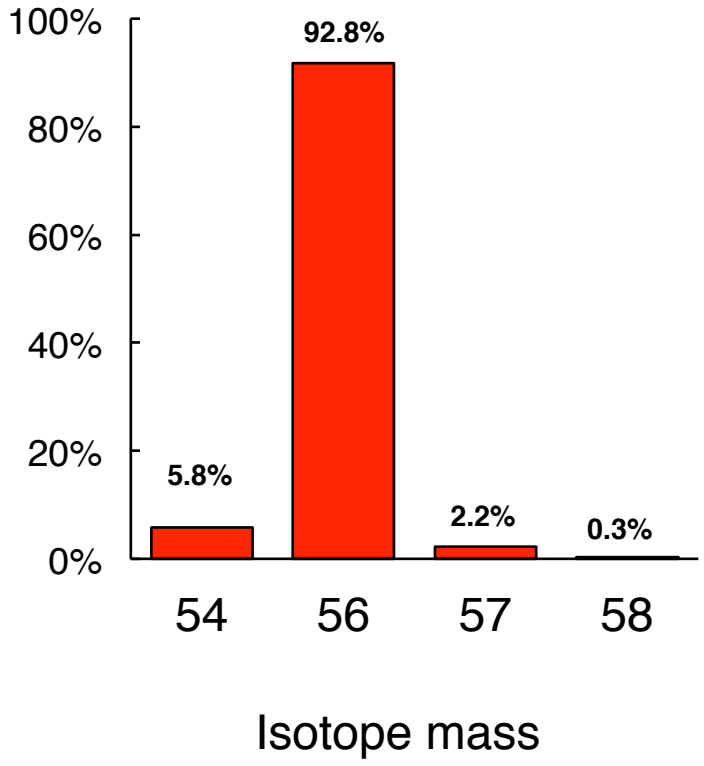
“Non-reductive” dissolution



Hydrothermal vents

Fe stable isotopes

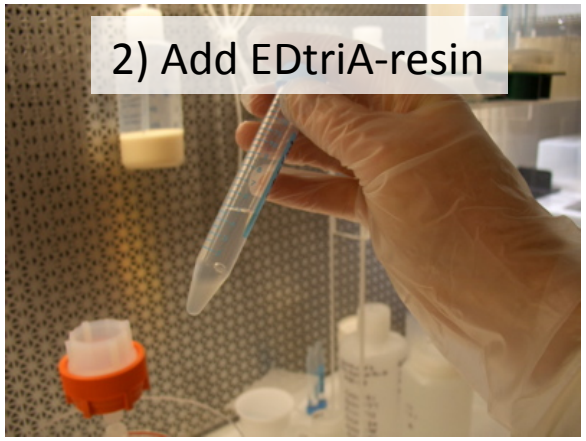
Relative abundance of natural Fe stable isotopes

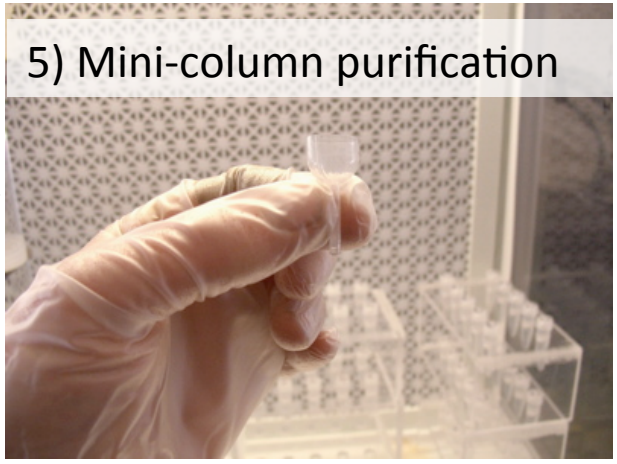


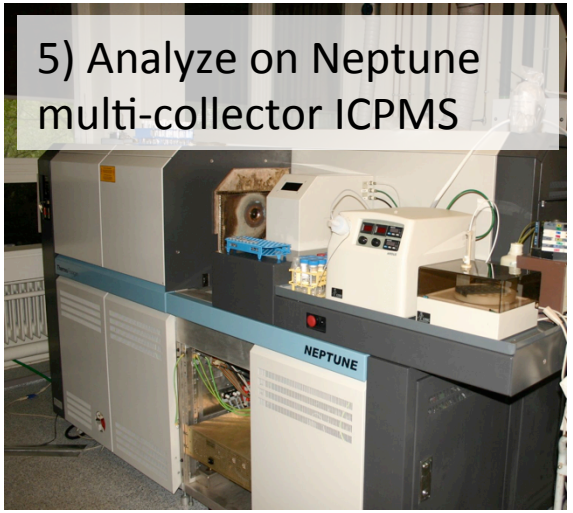
'Permil' notation (‰)

$$1) \quad \delta^{56}Fe = \left(\frac{\left(\frac{^{56}Fe}{^{54}Fe} \right)_{sample}}{\left(\frac{^{56}Fe}{^{54}Fe} \right)_{standard}} - 1 \right) \bullet 1000$$

US GEOTRACES: Analysis of Fe, Zn, and Cd isotopes in seawater



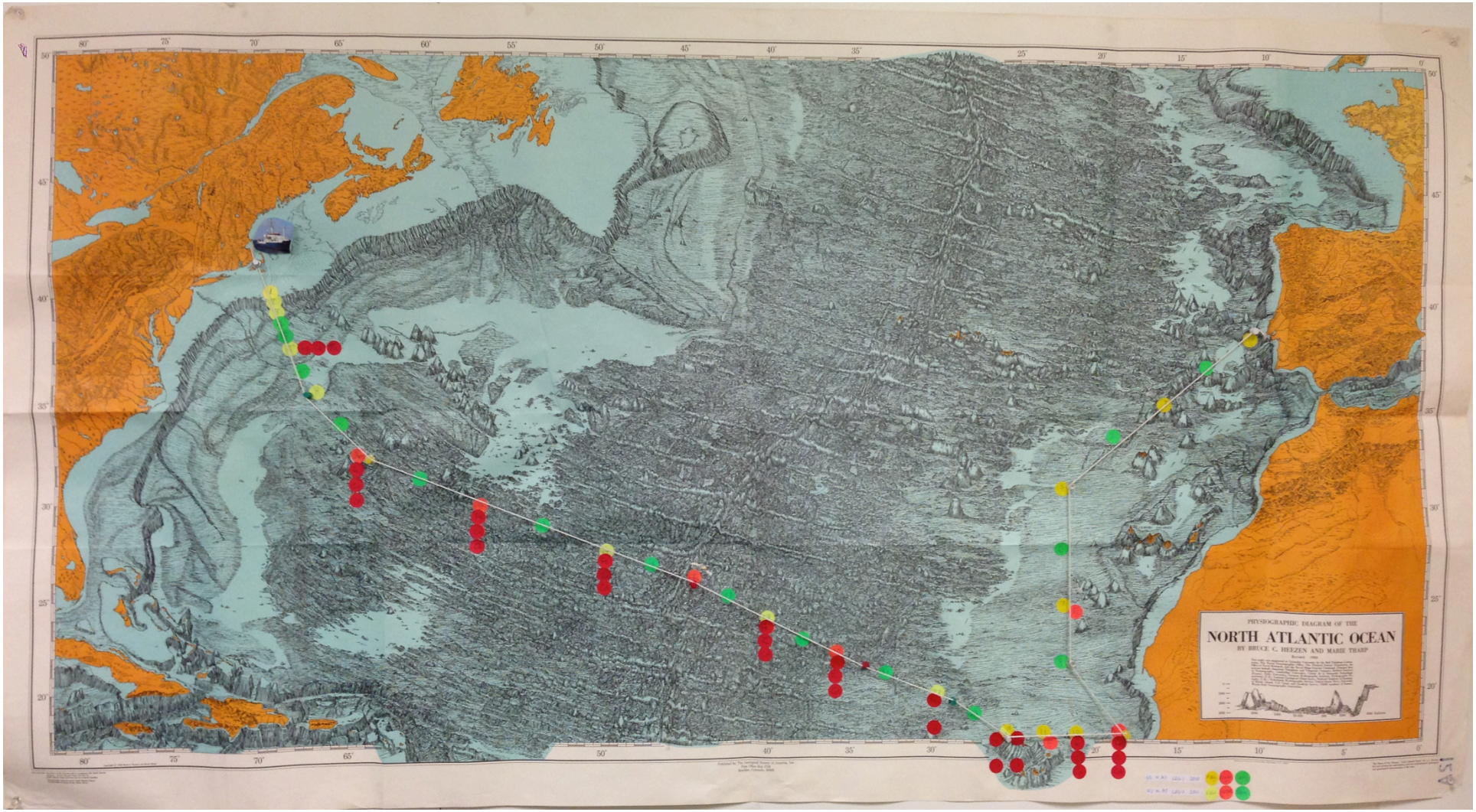




- Low blanks.
- 2-3 hours per sample.
- No isotope fractionation during processing.

US GEOTRACES sample processing

GEOTRACES NAZT Fe, Cd, Zn isotope profiles



Project goal: Use $\delta^{56}Fe$ to calculate Fe sources to the N. Atl.

Dust

$\delta^{56}Fe_{dust}$ = +0.1 ‰

$\delta^{56}Fe_{input}$ = +0.7 ‰ (??)

Porewater Fe(II)

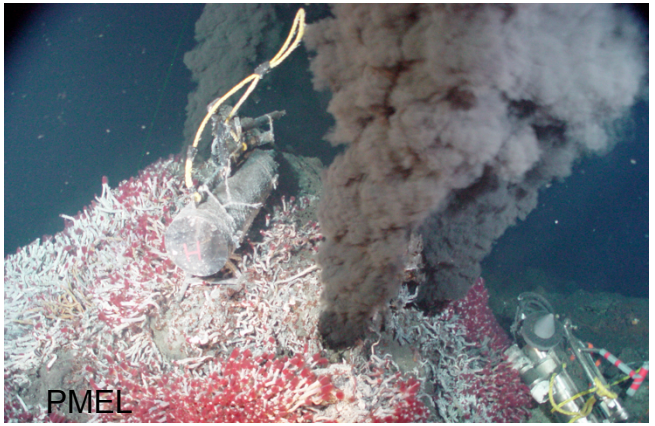
$\delta^{56}Fe_{porewater}$ = -2-3 ‰

$\delta^{56}Fe_{input}$ = -2-3 ‰

“Non-reductive” dissolution

$\delta^{56}Fe_{sediments}$ = +0.1 ‰

$\delta^{56}Fe_{input}$ = +0.3 ‰ (??)



Hydrothermal vents

$\delta^{56}Fe_{fluids}$ = -0.5 - 0 ‰

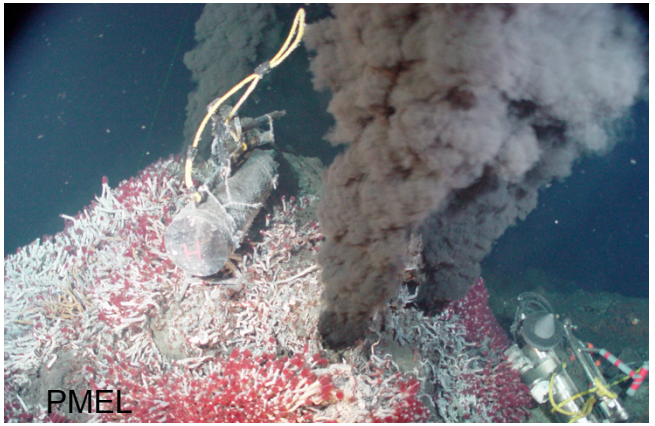
$\delta^{56}Fe_{input}$ = -1.5 ‰ (??)

What constitutes a “source” of Fe to the oceans?

Dust

“Reductive dissolution” (porewater Fe(II))

“Non-reductive” dissolution

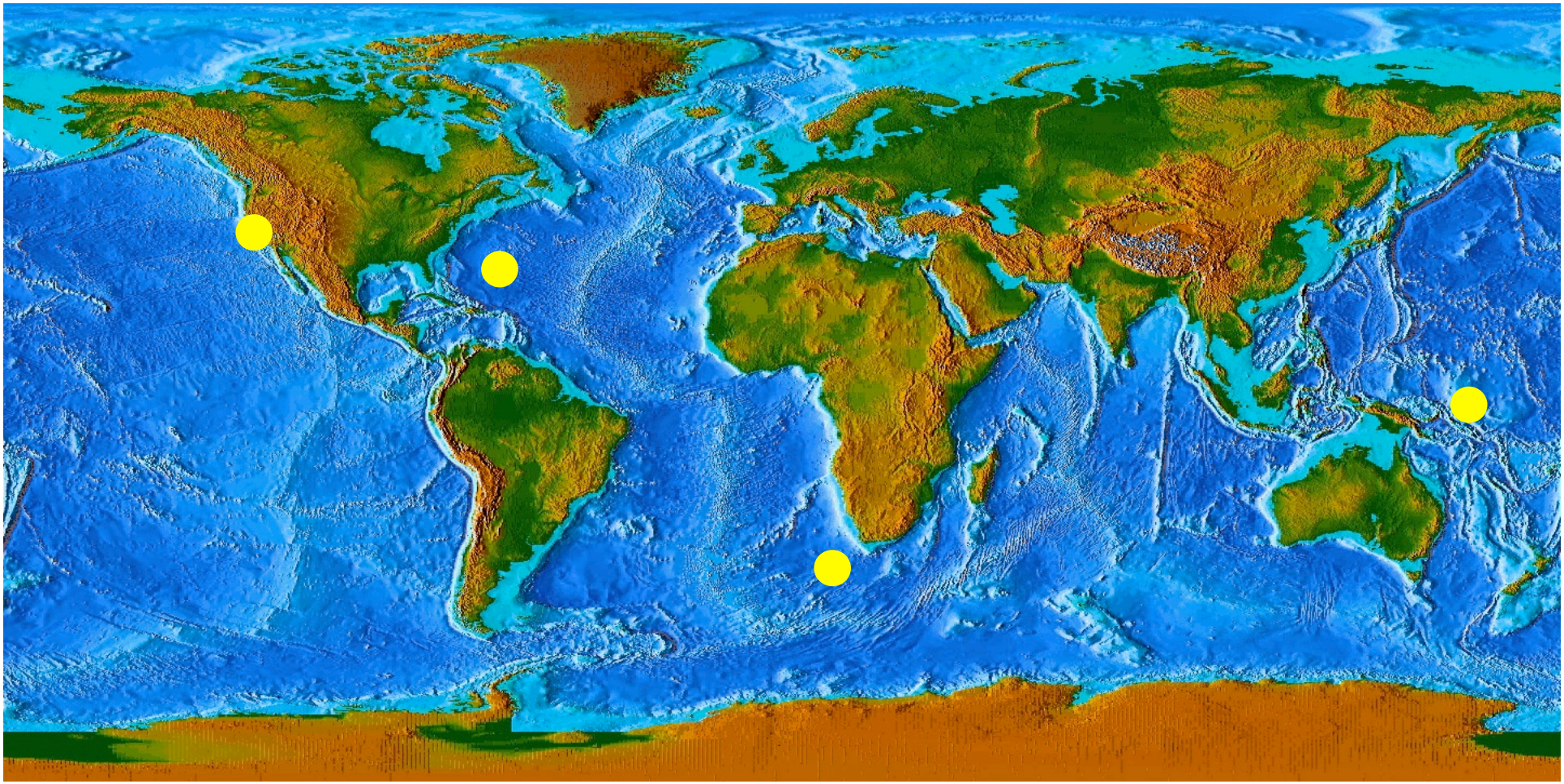


Hydrothermal vents

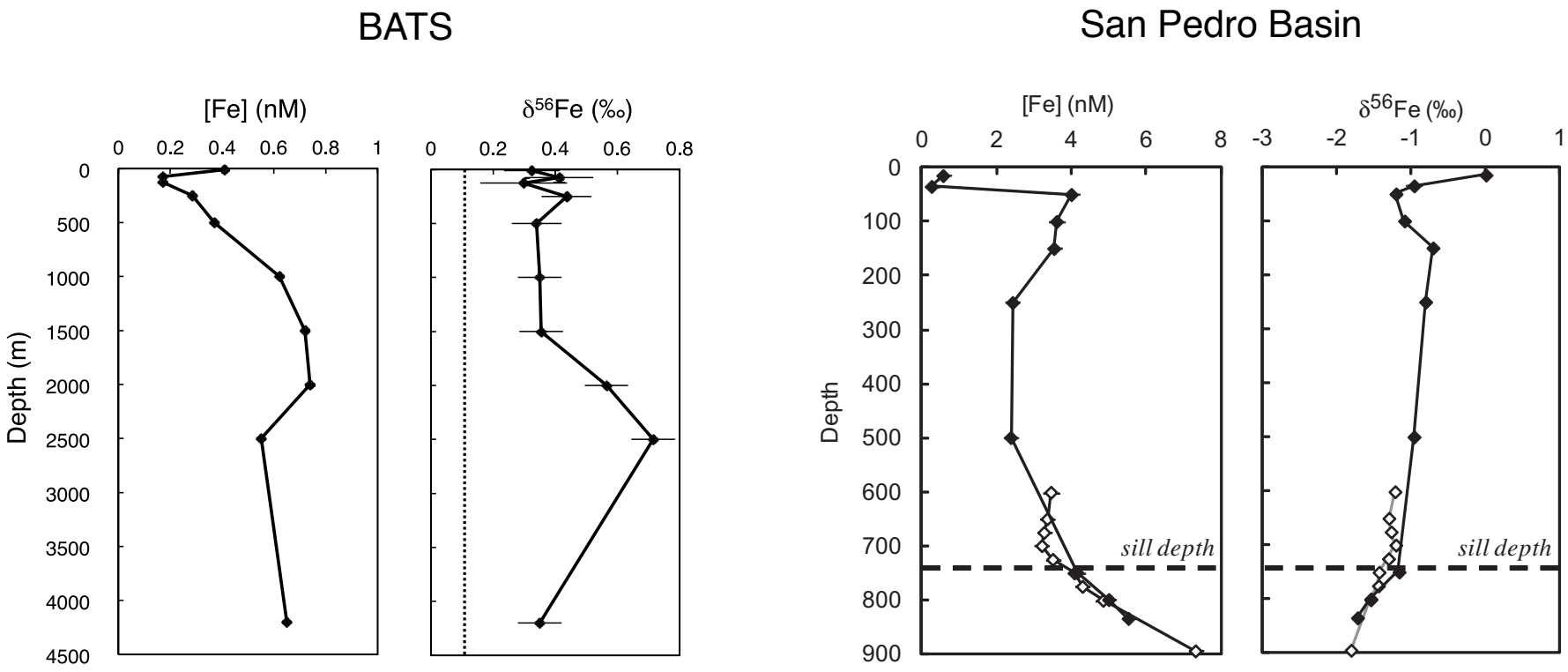
If you add Fe to the ocean, but it doesn't increase the iron concentration in seawater…

was it ever really there?

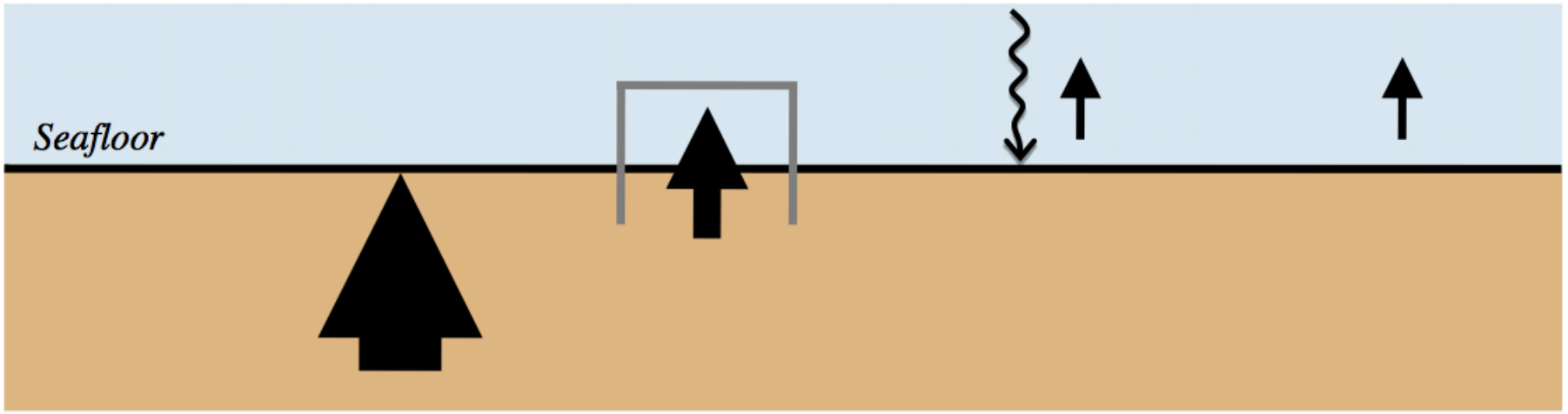
Published Fe isotope profiles



Flux of reduced Fe into the San Pedro Basin water column

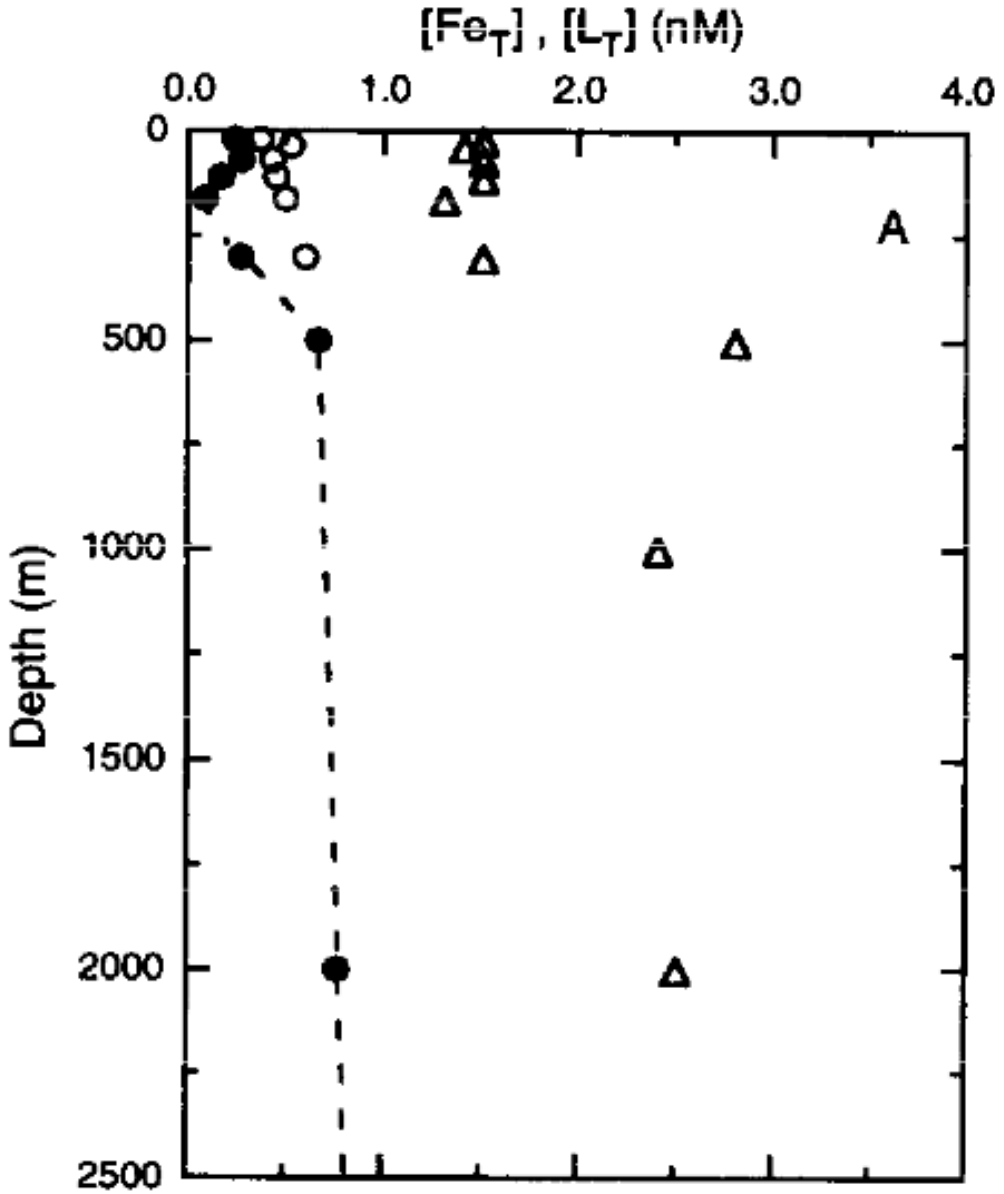


Comparing approaches to predicting Fe and δ^{56}Fe fluxes



	Sediment Porewaters	Benthic flux chambers	Organic carbon fluxes	Water column measurements
F_{sed} (µmol m^{-2} d^{-1})	140 *	14 to 568 *†	0.72*	0.32 to 1.14 ‡
$\delta^{56}Fe_{sed}$ (‰)	-1.8 to -3.6 †	-3.3 to -4.2 †		-2.4 ‡

Iron in the ocean is bound to organic ligands

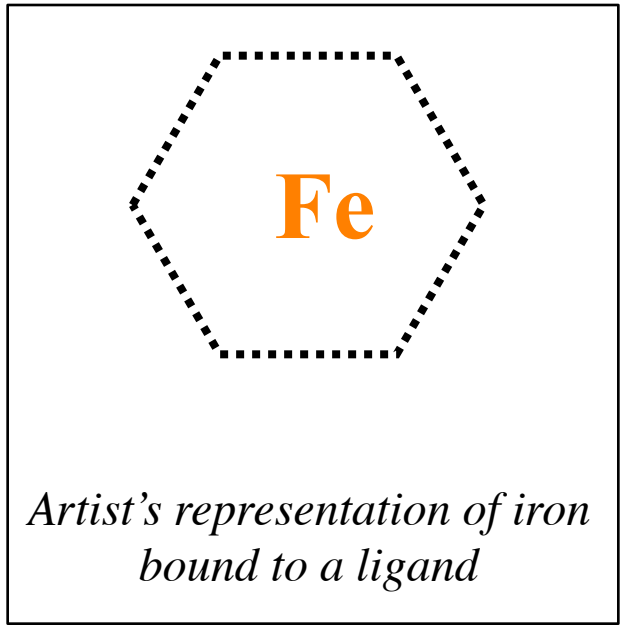


Rue and Bruland, 1995

● Dissolved Fe

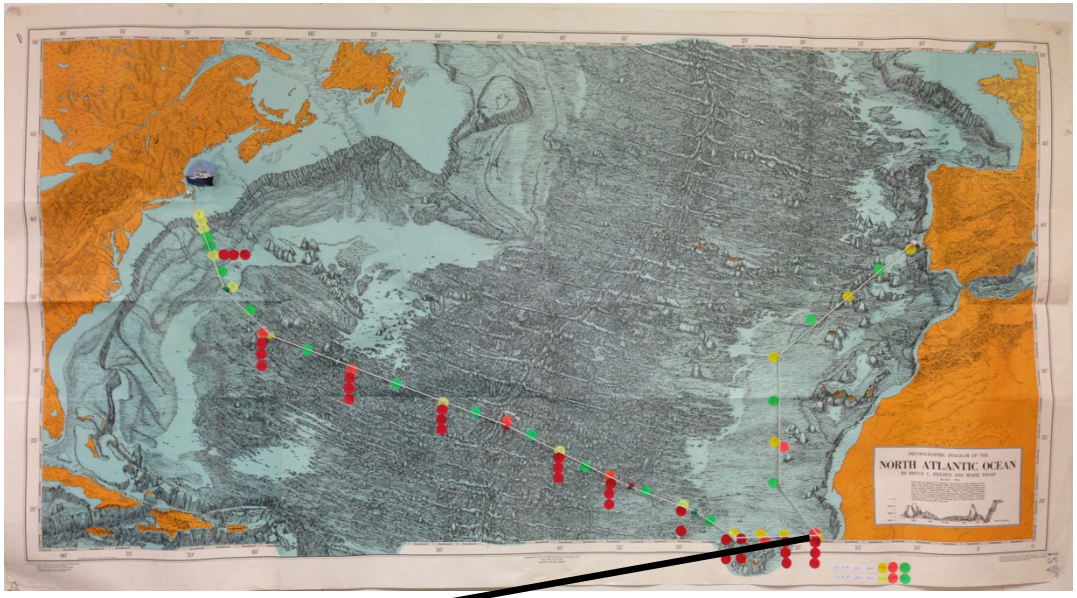
○ Strong ligands

△ Weak ligands

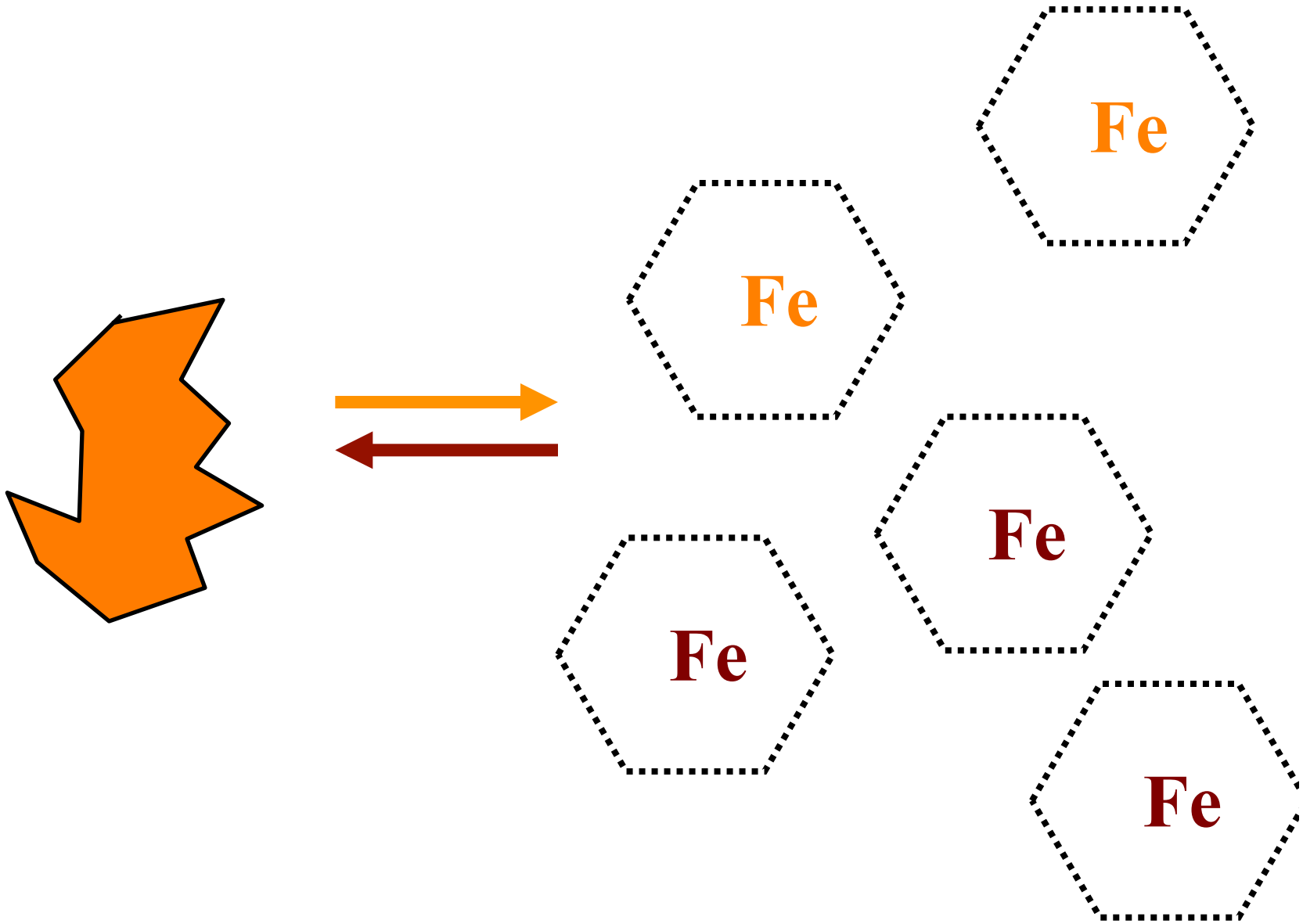


Artist's representation of iron bound to a ligand

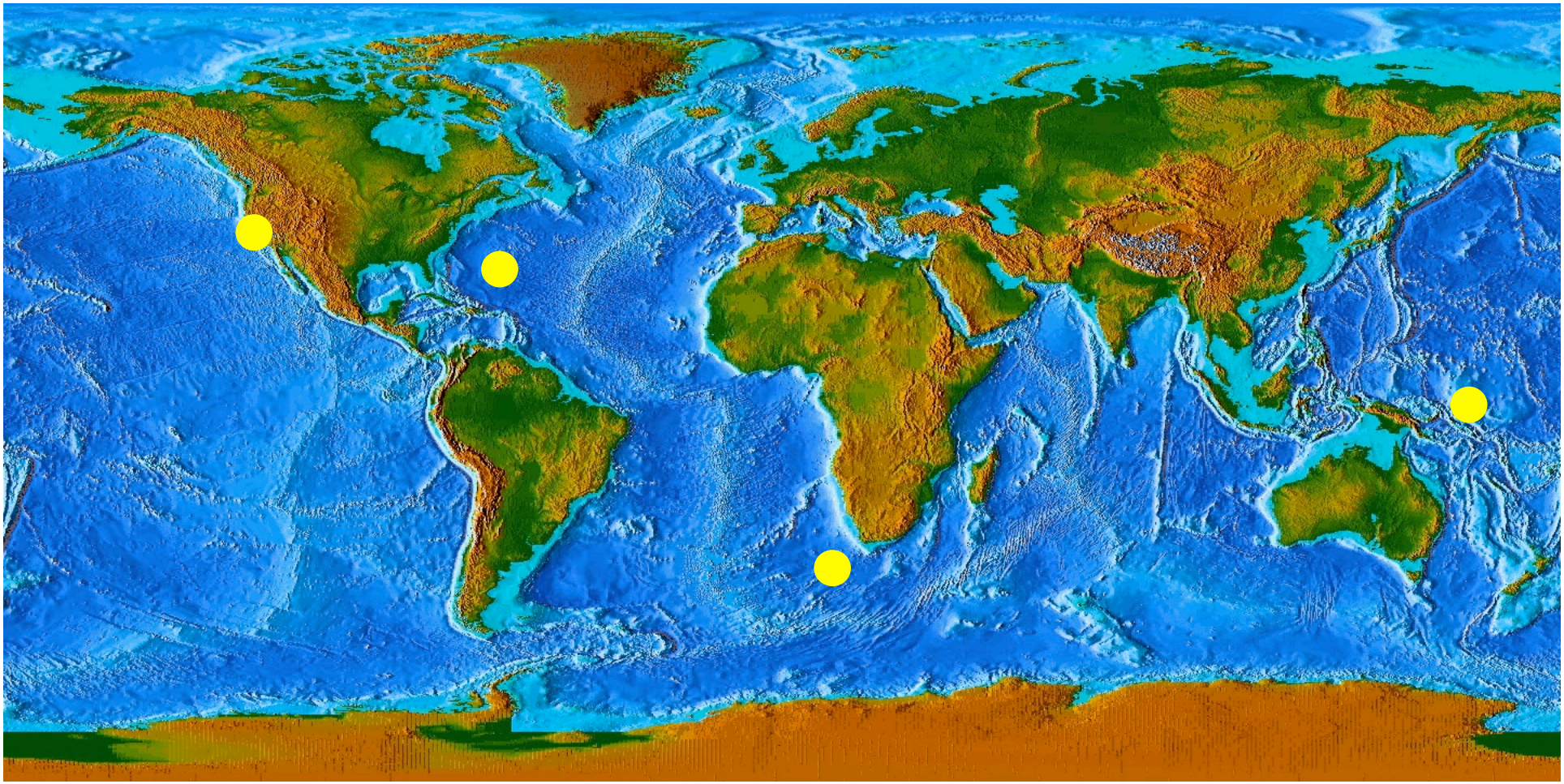
Large variations in nephloid layer dissolved δ^{56}Fe, little change in [Fe].



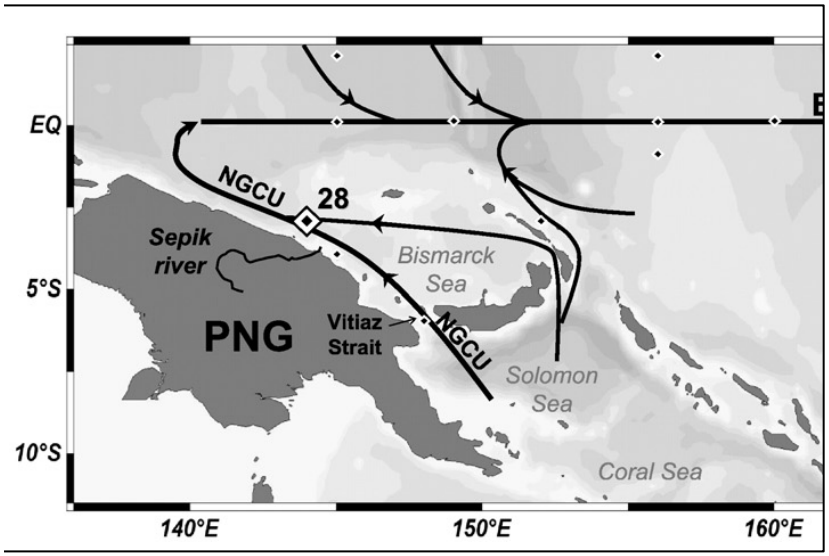
Iron exchange between particles and the dissolved phase

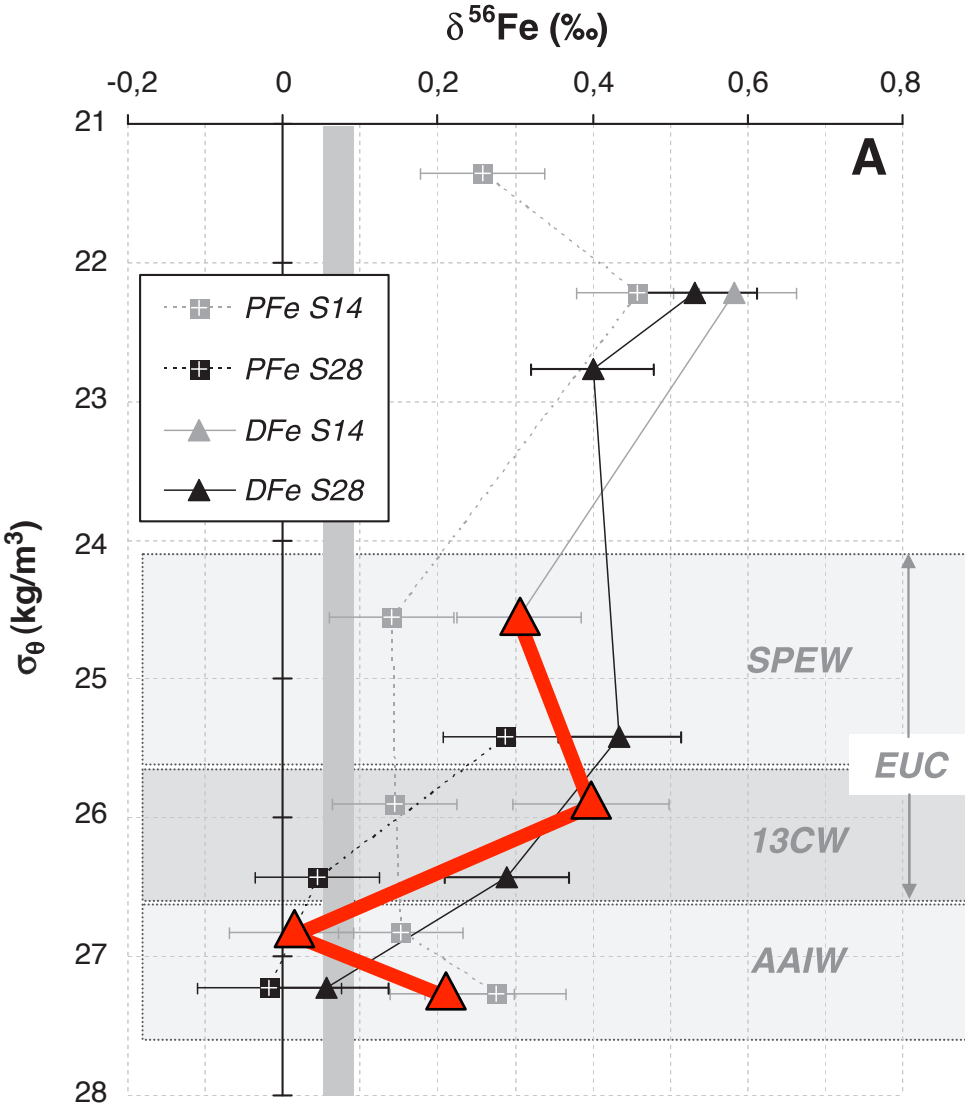


Published Fe isotope profiles



Non-reductive dissolution and Fe isotopes in the Eastern Pacific

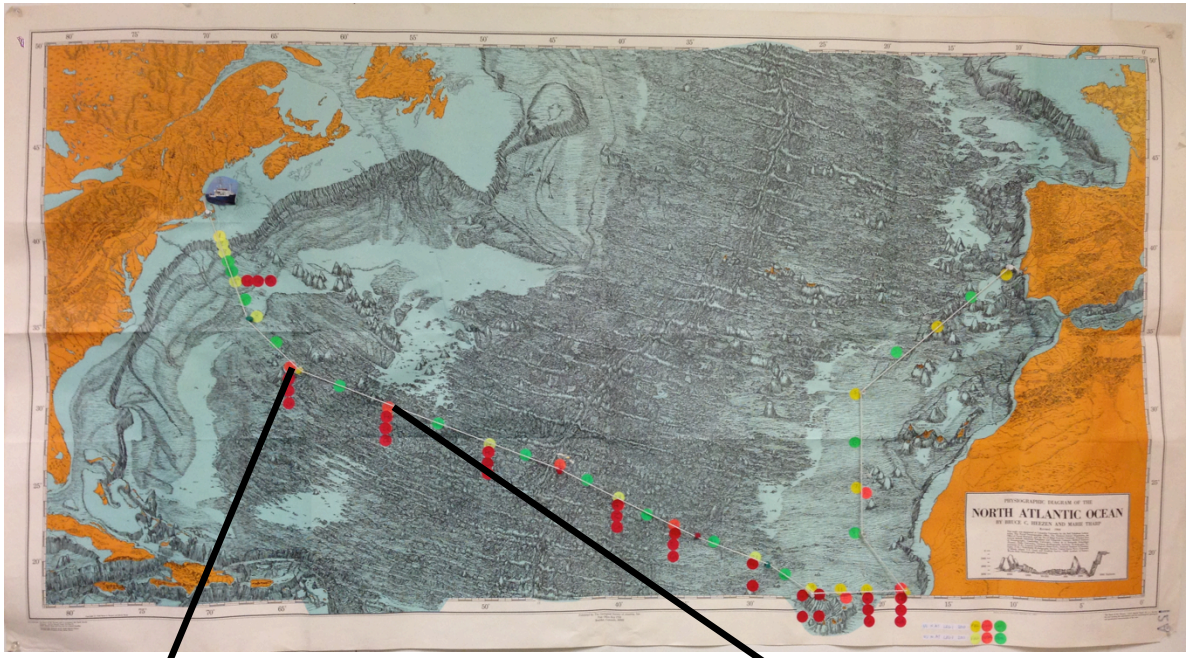


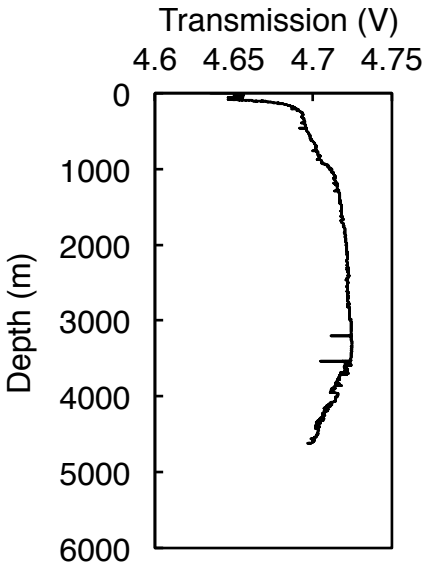


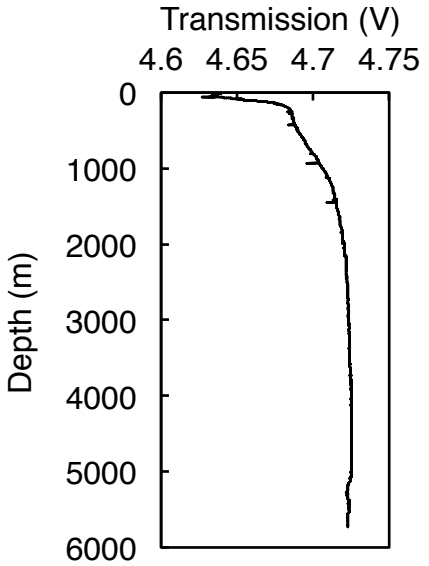
Dissolved $\delta^{56}Fe$ after non-reductive sedimentary interactions

Radic et al., EPSL, 2012.

A 1000 m nephloid layer is present near Bermuda



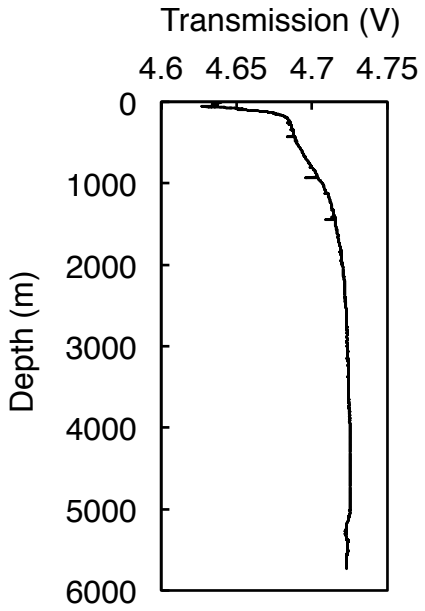




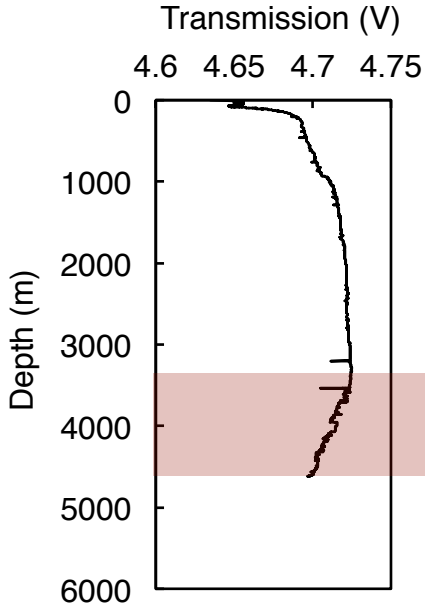
A very “typical” North Atlantic Fe isotope profile

“Rapid” exchange of Fe within the nephloid layer

Mid-Basin



Near Bermuda



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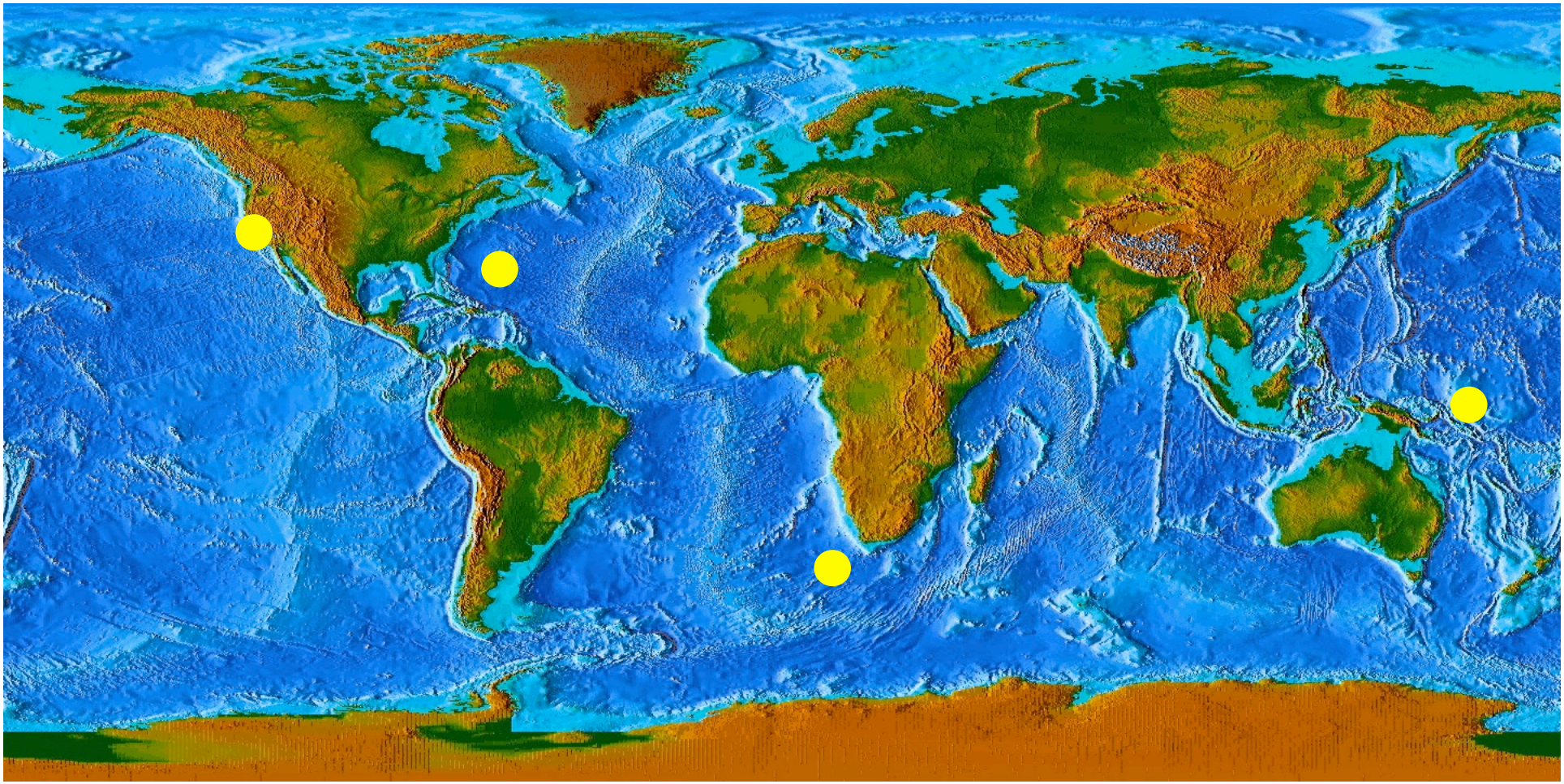
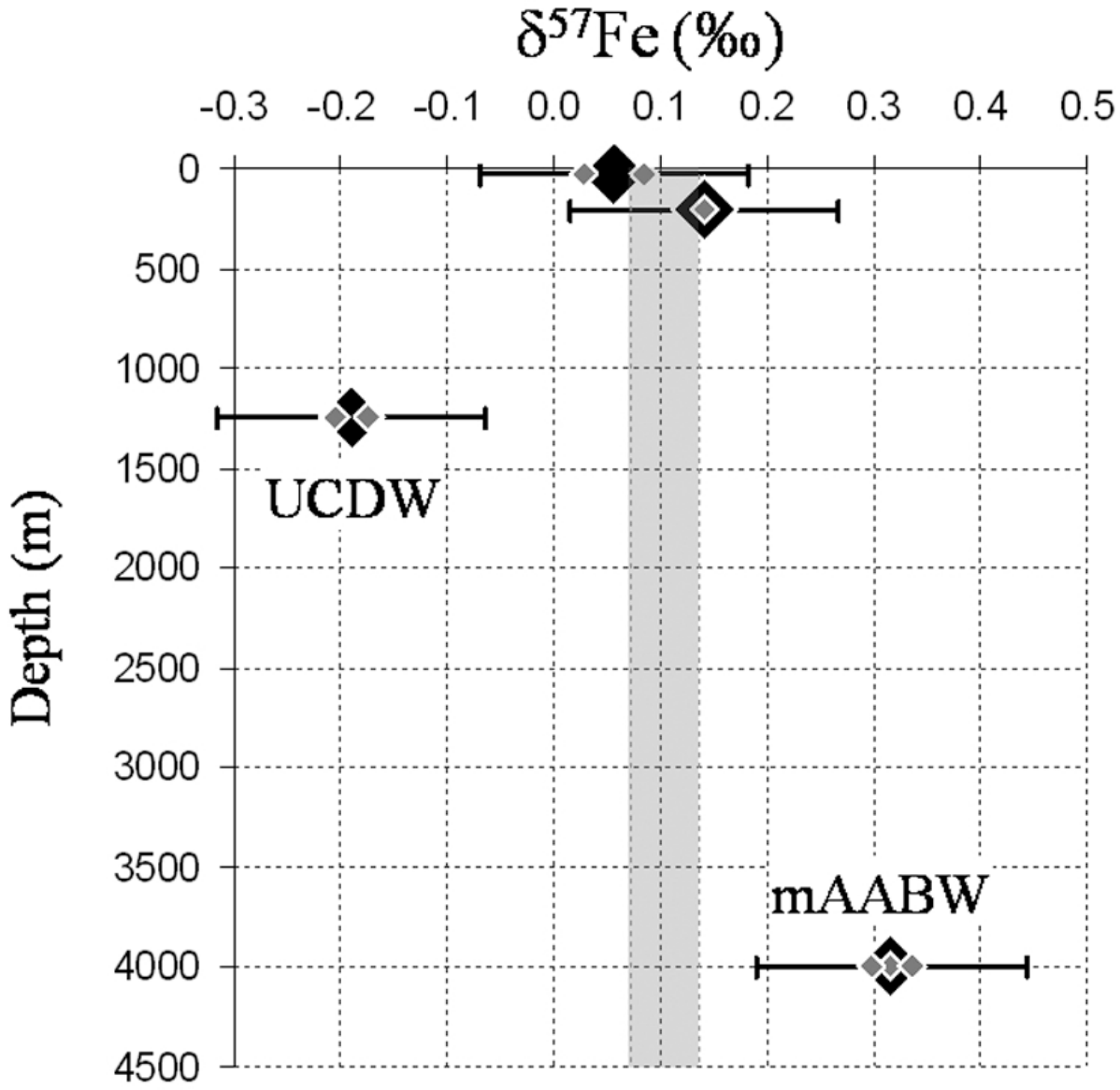


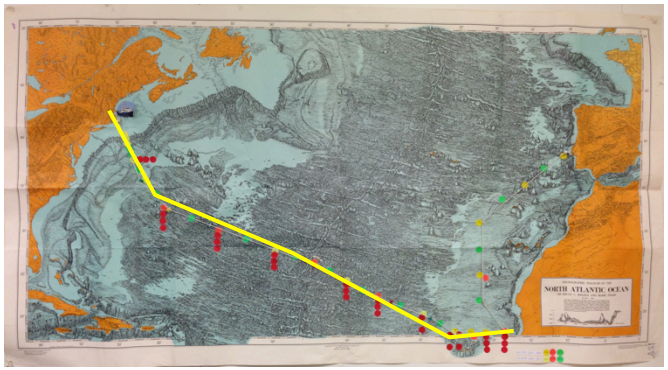
Southern Ocean Fe isotopes



"Typical" North Atlantic Fe isotopes

Lacan et al., EPSL, 2008.

North Atlantic GEOTRACES particulate Fe isotopes



Conclusions

- Iron inputs to the ocean impact the global carbon cycle
- δ^{56}Fe shows “sources” of marine Fe which do not necessarily lead to an increase in dissolved Fe concentrations.
- This hilights the importance of iron isotope exchange between particles and ligands.
- Equilibrium plays an important role in marine Fe biogeochemical cycling.