The multiple roles of dust in ocean biogeochemistry

Christoph Völker, Ying Ye

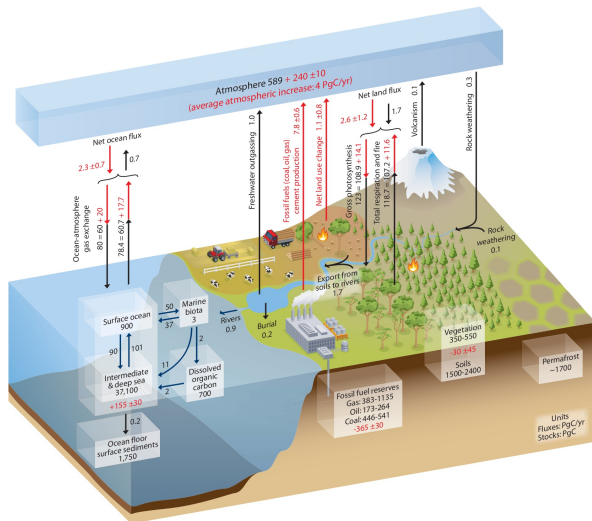Alfred Wegener Institut für Polar- und Meeresforschung
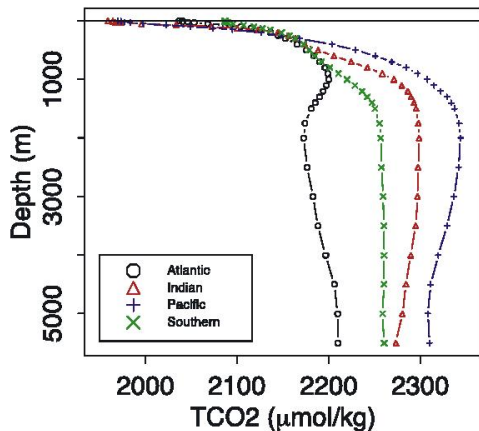
THE OCEAN IS IMPORTANT IN THE CARBON CYCLE

(IPCC AR5)

ocean contains ca. $50\times$ as much carbon as the atmosphere

it currently takes up ca. 1/4 of anthropogenic carbon emissions

CARBON INCREASES WITH DEPTH

(Key et al., 2004)

dissolved inorganic carbon (DIC) is lower at the surface than at depth

this keeps atmospheric $p\mathrm{CO}_2$ lower than for a 'well-mixed' ocean

DIC at depth increases with 'age' from Atlantic to Pacific

THE REASON: BIOLOGICAL CARBON PUMP

biological production in the ocean occurs mostly near the surface (light!)

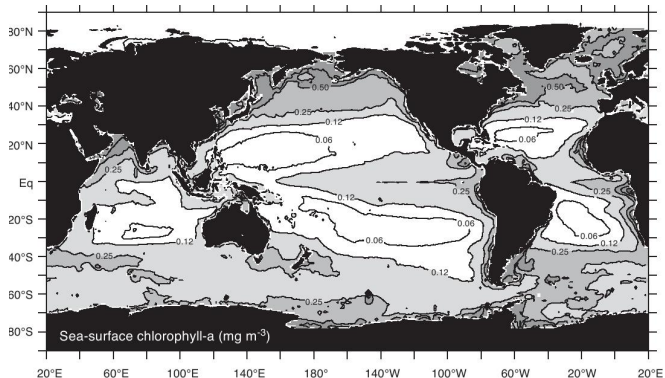aggregation & defecation produce particles that are large enough to sink

at depth, organic material is respired by animals & bacteria, releasing carbon

mixing & circulation bring carbon back to the surface on timescales from 10 to 1000 years
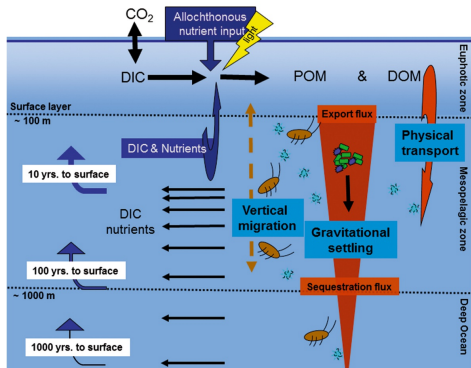
(Passow et al., 2014)

HOW IS BIOLOGICAL ACTIVITY DISTRIBUTED?

(Gruber and Sarmiento, 2006)

• net primary production in the ocean ≈ 50-60 PgC yr^{-1}, same as on land, but biomass lower by a factor of 100!

• biological production is high where mixing and circulation bring nutrients to the surface and there is enough light

HOW CLOSED IS THE SYSTEM?

biological production in the surface ocean requires nutrients (N, P, Fe, Co, Zn, . . .)
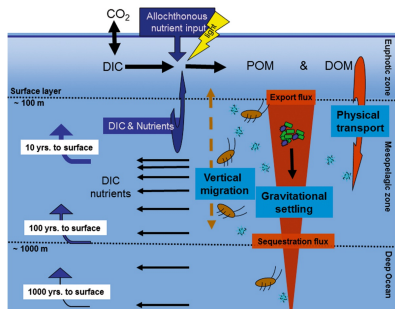
sinking moves then down with carbon

at depth, biomass is remineralized

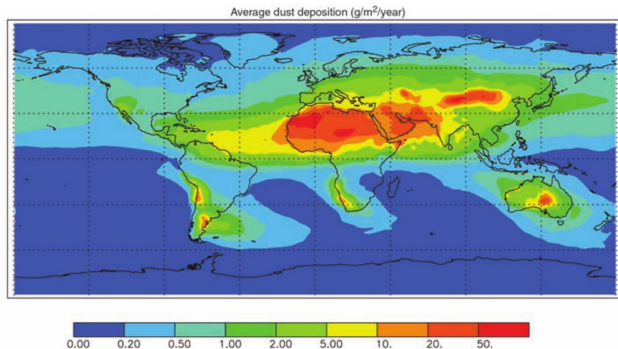return of nutrients to the surface, depends on the residence time of the element

some residence times:
- Phosphorus: 25000 years
- Nitrogen: 3000 years
- Iron: 10-100 years

(Passow et al., 2014)

DUST AS NUTRIENT INPUT

(Jickells et al., 2005)

• dust deposition brings in N (largely anthropogenic), P (from minerals), Fe (also from minerals)
• globally, the input is minor compared to internal recycling for elements with long residence time, such as N and P
• for elements with short residence time, such as Fe, it is important

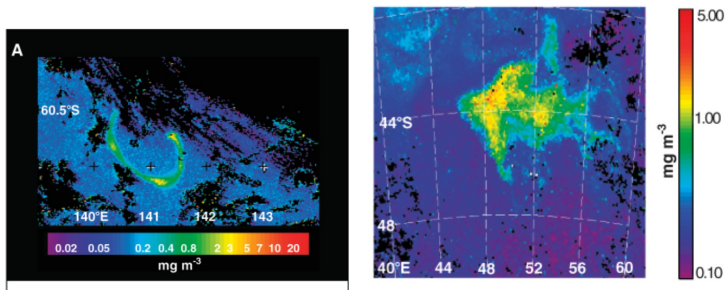## CONSEQUENCE OF THE SHORT RESIDENCE TIME OF FE
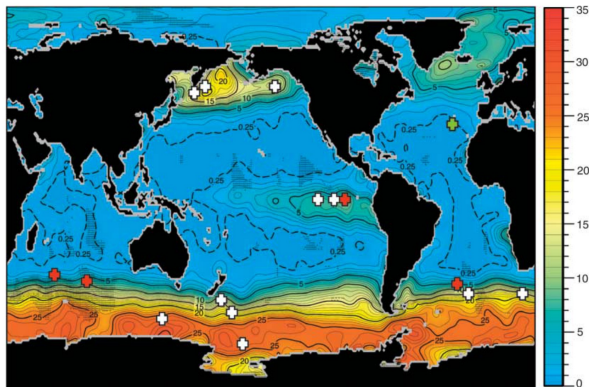
(Boyd et al., 2007)

- High-Nutrient-Low-Chlorophyll regions: despite enough nitrate and phosphate little net primary production
- what is missing is iron; crosses mark *iron fertilization* studies

ARTIFICAL AND NATURAL IRON FERTILIZATION

(Boyd et al., 2007)

• articifial iron fertilization (left, SOIREE): iron is distributed over a patch of ≈ 100 km^2

• natural iron fertilization (right, Crozet island): an island serves as iron source for its otherwise iron-poor surroundings

both have been shown to lead to elevated chlorophyll, NPP, . . .
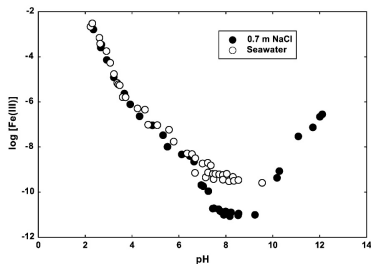
IRON DISTRIBUTION IN THE OCEAN IS COMPLEX
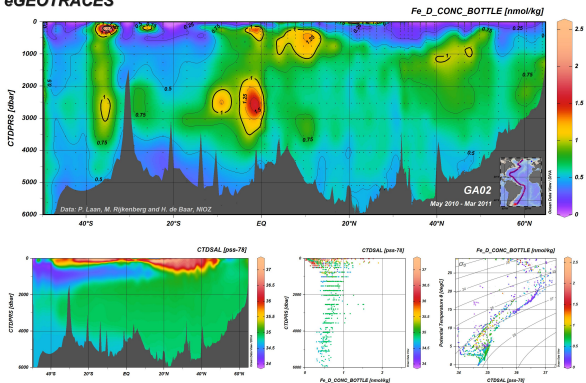
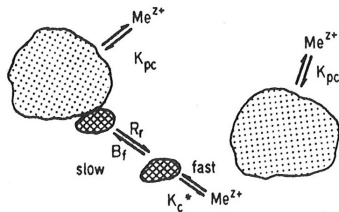iron concentration along a section through the Western Atlantic (Rijkenberg et al., 2014)

due to the short residence time, iron distribution is strongly affected by local sources and sinks

iron is hard to measure in seawater; problem of contamination, reliable measuments start around 1985

IRON IS PARTICLE REACTIVE

(Liu and Millero, 2002)

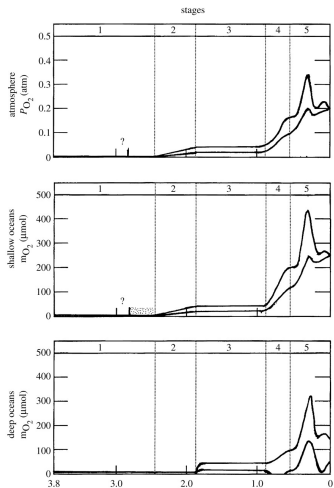(Honeyman and Santschi, 1989)

iron in oxic seawater is mostly Fe(III)

solubility of inorganic Fe(III) is extremely low:
< 0.1 nmol kg^{-1} at typical ocean pH

$\rightarrow$ iron is lost much faster from the ocean than nitrogen or phosphorus

loss proceeds via *scavenging* on particle surfaces, accelerated by aggregation of small colloids

A CRISIS A LONG TIME AGO

Holland, 2006

ocean oxygenation caused iron to precipitate; iron became scarce for marine biology!
many exploited iron ores are created this way; especially 'banded iron formations' e.g. in South Africa

IRON CHEMISTRY IS COMPLICATED

Iron can exist in many different forms in seawater:

• inorganically bound in redox states Fe(III) and Fe(II)
• Fe(II) is soluble, Fe(III) precipitates
• in oxic seawater, Fe(II) is quickly oxidised
• photochemical processes can produce Fe(II)
• strong organic iron-binding substances exist in seawater
• typically, 99% of iron is bound to these ligands

This iron *speciation* greatly affects iron loss, dust iron solubility, iron uptake . . .

FE-BINDING LIGANDS AS NATURES REMEDY

**Phaeophytin (porphyrin)**   **Desferrioxamine (hydroxamate)**
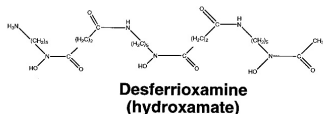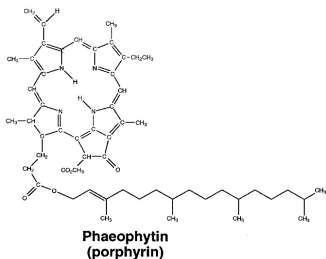
Witter et al., 2000

binding of iron to organic ligands prevents rapid scavenging
two main types of ligands proposed: degradation products, such as
porphyrins, and siderophores, produced by bacteria under iron
limitation
production / degradation pathways probably as varied as ligand
origins

IT IS EVEN WORSE..
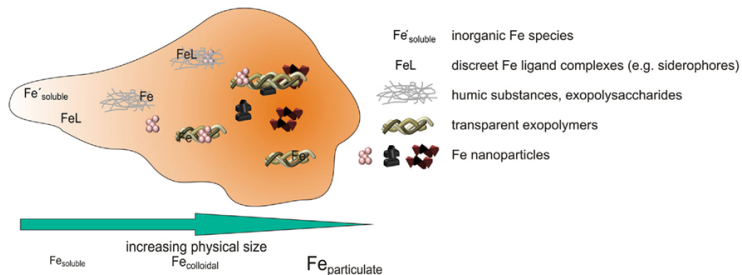
Gledhill et al., 2012

besides redox speciation and organic complexation, iron species can be anything between dissolved, colloidal and small particles

speciation influences residence time

modelling iron cycling in the ocean is not trivial! Iron model intercomparison (FEMIP) (Tagliabue et al. 2016)

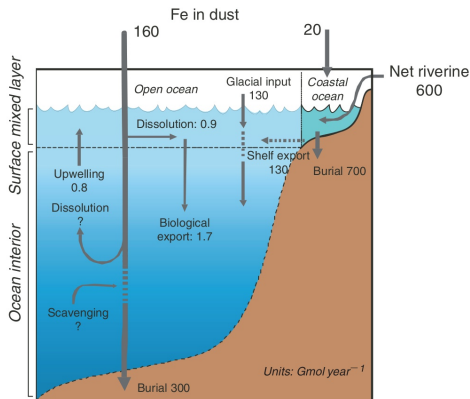# THE MAIN EXTERNAL IRON SOURCE: DUST DEPOSITION
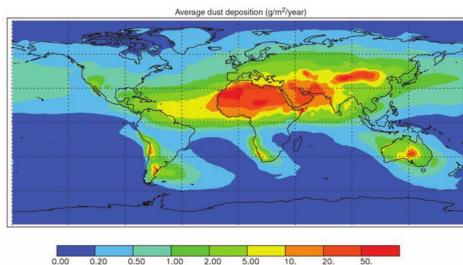
(Jickells et al., 2005)

- dust carries lots of iron into the ocean
- but only a small (and variable) fraction dissolves!
- dissolution depends on wet/dry deposition, atmospheric history, but especially iron chemistry in the water
- but: dust also brings in particle surfaces → scavenging!

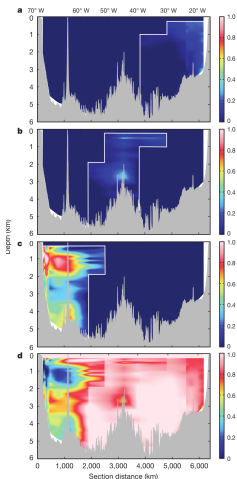## OTHER SOURCES OF IRON

(Hunter, 2007)

besides lithogenic dust, there are also other sources of iron:
• rivers
• sediment diagenesis
• hydrothermalism
• cosmic dust . . .

but for all of them, most of the iron is lost as particles close to the source.

quantification of different iron sources is ongoing, large uncertainties so far!

# TROPICAL ATLANTIC: DOMINATED BY DUST

(Conway et al, 2014)

relative role of the different iron sources along a section across the subtropical/tropical Atlantic estimated from isotopic composition of dissolved iron
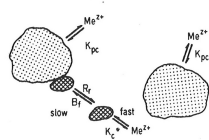
- sediment diagenesis
- hydrothermalism
- suspended sediment particles
- saharan dust

$\rightarrow$ in the tropical and subtropical Atlantic, dust dominates as source of iron

BUT: DUST ALSO SCAVENGES DISSOLVED IRON

(Wagener et al. 2010)
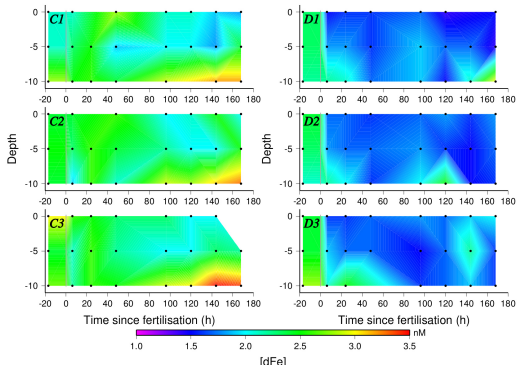
dissolved iron decreases after dust addition in mesocosms;
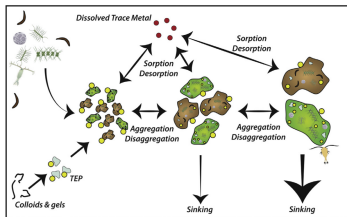dust can act as dFe sink

(Honeyman & Santschi 1989)
colloidal pumping mechanism

is that important in the open Atlantic, where often biogenic particles dominate?
needs understanding & modelling of particle dynamics!
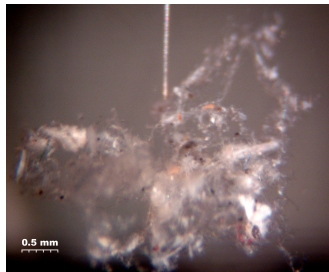
PARTICLE DYNAMICS

aggregation processes (Jackson and Burd 2015)

typical marine aggregate (Iversen, pers. comm.)

- dust brings in mostly micrometer-sized particles
- these hardly sink on their own
- sinking dominated by larger, mixed organic/inorganic aggregates

LITHOGENIC MATERIAL IN THE ATLANTIC
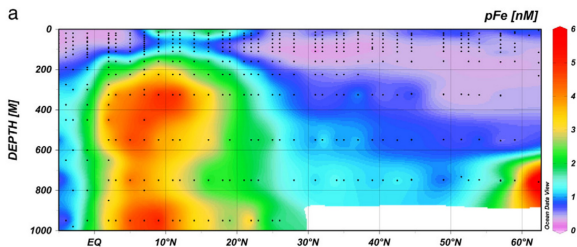
particulate Fe along section A16N (Barrett et al. 2012)

much new information on lithogenic particles from A16N and US Geotraces Atlantic Zonal Transect (Barrett at al. 2012, 2015, Lam et al. 2015, Ohnemus et al. 2015)

• increased pFe under dust plume
• high pFe at the surface, mimimum around 100m depth, then again increase
• deep lithogenic particle concentration dominated by small particles
• large fraction of lithogenics highest around 100 m depth, higher towards African coast

indicates dynamic aggregation / disaggregation cycle

MODEL SETUP

global biogeochemical model REcoM including the iron cycle (Hauck et al. 2013, Völker and Tagliabue 2015)
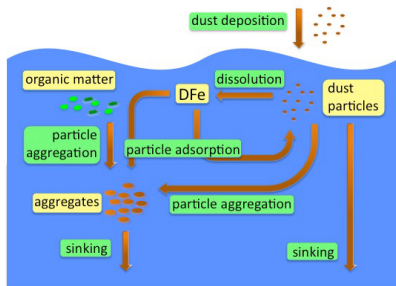
added model for lithogenic particles with two size classes (fine dust and faster-sinking aggregates)

quadratic aggregation and linear disaggregation of particles

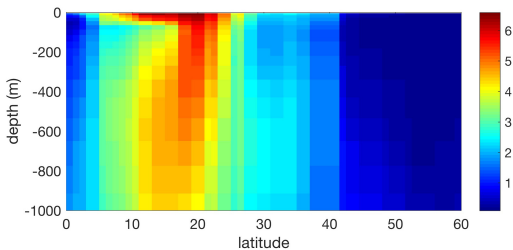lithogenic particles included as additional scavenging agents for dissolved iron

scavenging proportional to particle concentration
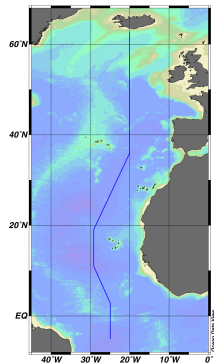
rate equal for organic and lithogenic particles
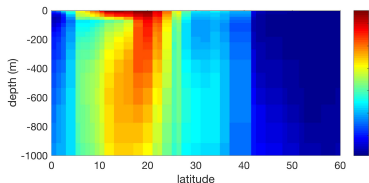
MODELLED VS. OBSERVED PARTICULATE Fe
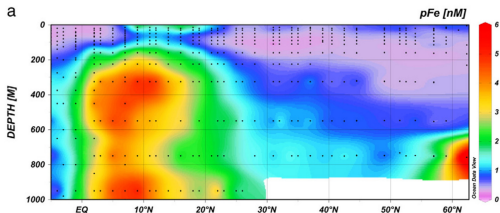
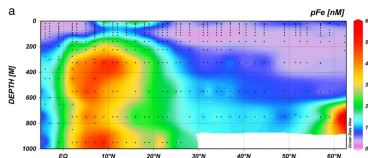particulate Fe along section A16N (Barrett et al. 2012)

modelled particulate Fe (nM) along section A16N

# MODELLED VS. OBSERVED PFE

modelled pFe (nM) along A16N

obs'd pFe along A16N (Barrett et al. 2012)

some agreement, but also some disagreement:

+ pFe concentration in the right order of magnitude
+ minimum in particle concentration around 100m depth
+ size-class distribution consistent with Ohnemus et al. (2015)
− surface pFe concentration somewhat high → aggregation rate?
− deep pFe maximum too deep → variable disaggregation?
− deep pFe maximum too far north → dust deposition?
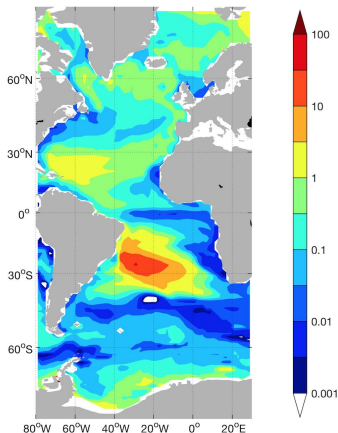− shelf-derived nepheloid layers absent

EFFECT ON DISSOLVED Fe
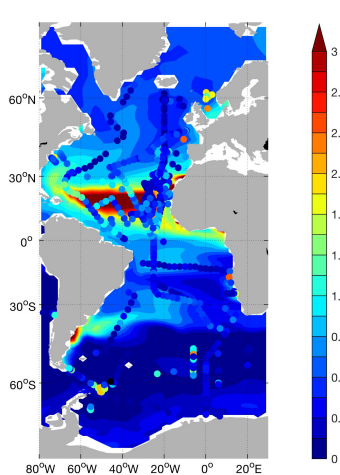
dFe with dust only as Fe source
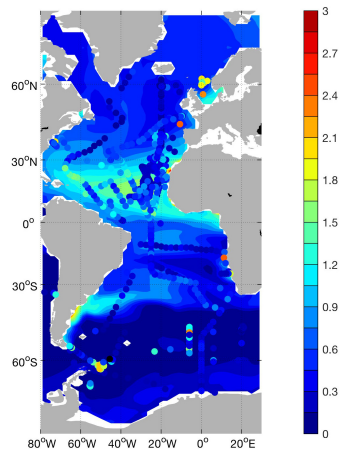
dFe with dust as Fe source and as additional scavenging
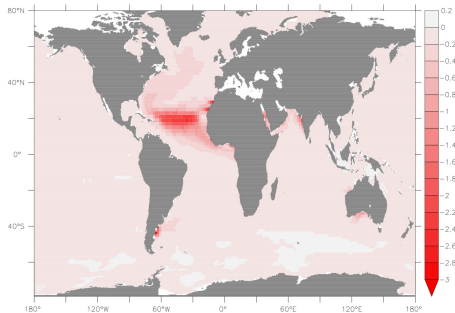
WHY THE REDUCTION? RESIDENCE TIME OF dFe

residence time (stock/total loss rate in years) of dissolved iron varies by several orders of magnitude

affected by scavenging on dust/biological particles and biological uptake

distribution of residence time agrees quite well with data-based estimates (Usher et al. 2013)

GLOBAL EFFECT AT SURFACE
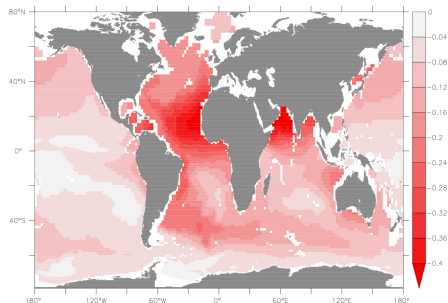

surface dFe difference between a run with/without
lithogenic particles present as scavenging agent

scavenging by lithogenic
particles
• reduces surface dFe
directly in high-deposition
regions
• but hardly everywhere
else

GLOBAL EFFECT AT DEPTH

dFe difference (2000 m depth) between a run
with/without lithogenic particles

- dFe reduction more widespread at depth
- 1st cause: lateral transport of fine lithogenic material
- 2nd cause: downstream effect of localized scavenging
- reduces deep water dFe Atlantic – Pacific gradient

caveats: strength of effect depends on scavenging residence time, at
present highly tuned in ocean iron models (Tagliabue et al., 2016)
also affected by ligand excess (Völker and Tagliabue, 2015)

SO, IS DUST A SOURCE OR A SINK OF DFE?
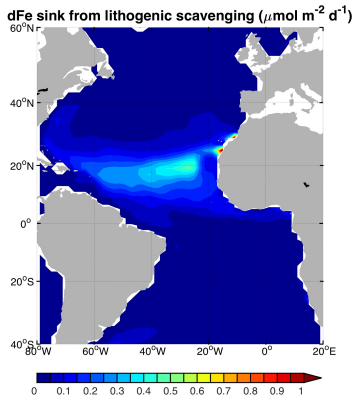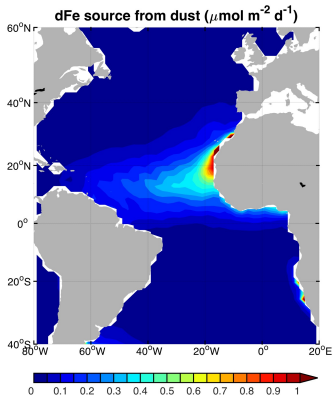
so: how much source, how much sink?
generally, dFe source stronger than vertically integrated sink; but depends somewhat where you look!

SOME CONCLUSIONS

- lithogenic particles in the Atlantic modeled with a 2-size-class model
- both aggregation and disaggregation important
- reproduces some features of observed distributions of lithogenic particles
- brings surface dFe distributions under the dust plume more in line with observations
- affects on the global deep dFe distribution through lateral transport
- allows to quantify the role of scavenging and compare it to local sources
- need to go further in developing more process-oriented iron models, making use of the available and coming GEOTRACES data