1st August 2017
NOC, Southampton

Adding anthro CO2 to the ocean … accidentally and deliberately

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National Oceanography Centre
NATURAL ENVIRONMENT RESEARCH COUNCIL

Overview

- Background / recap on the ocean carbon cycle
- Anthropogenic CO_2
- Ocean Acidification
- Geoengineering

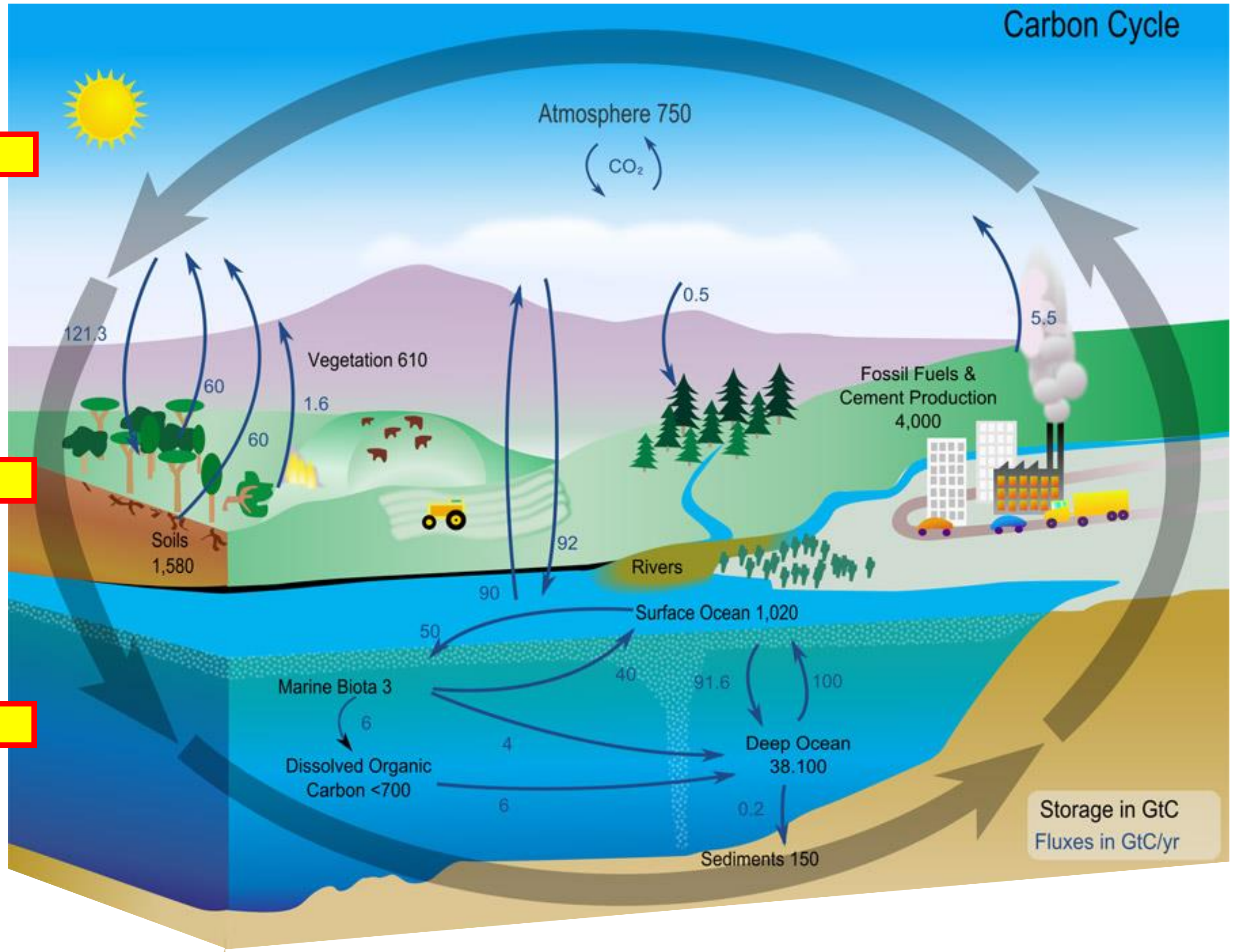
Where is the carbon?

750
(1.8%)

2190
(5.2%)

39120
(93%)

Gt C



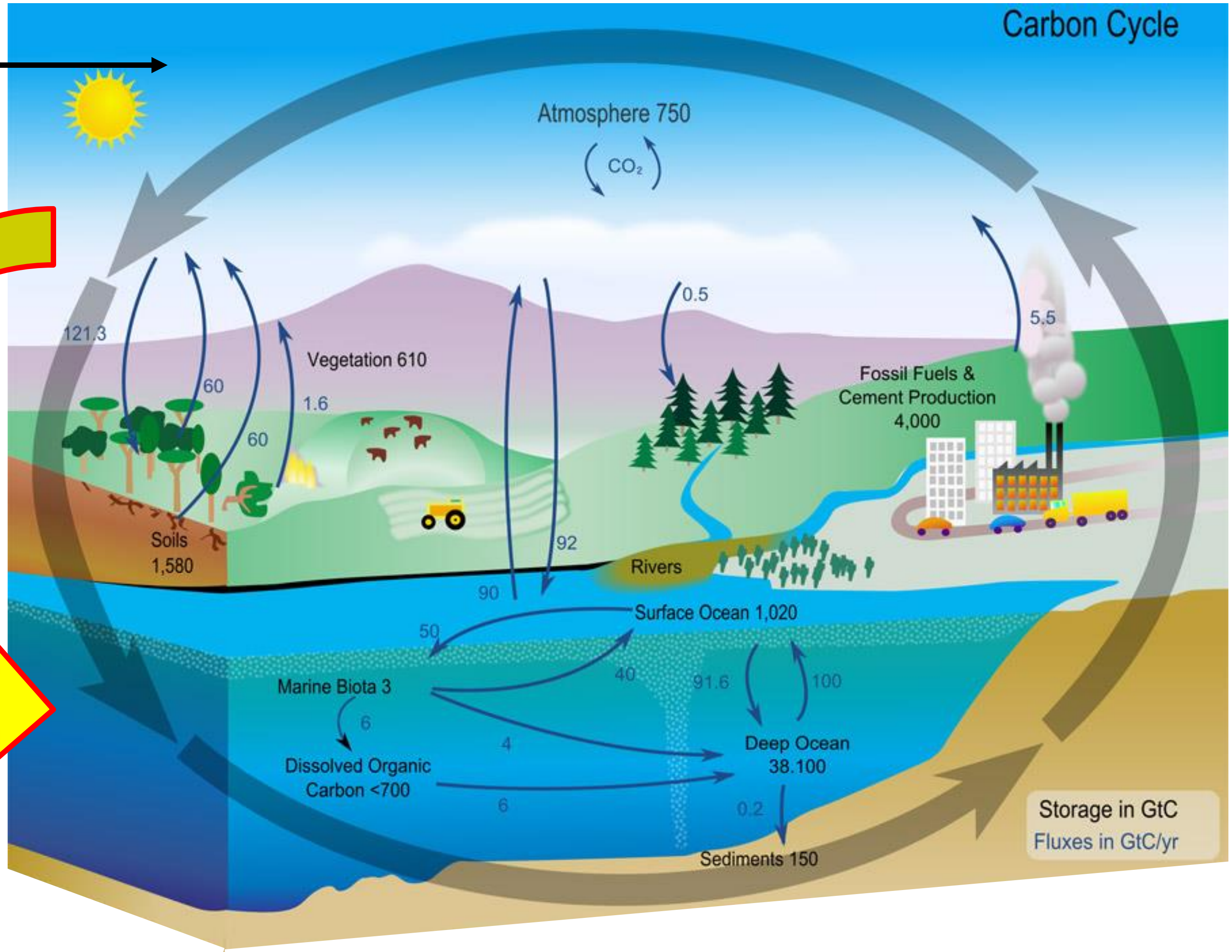
NASA

Where is *our carbon* going?

About ½ here

~2

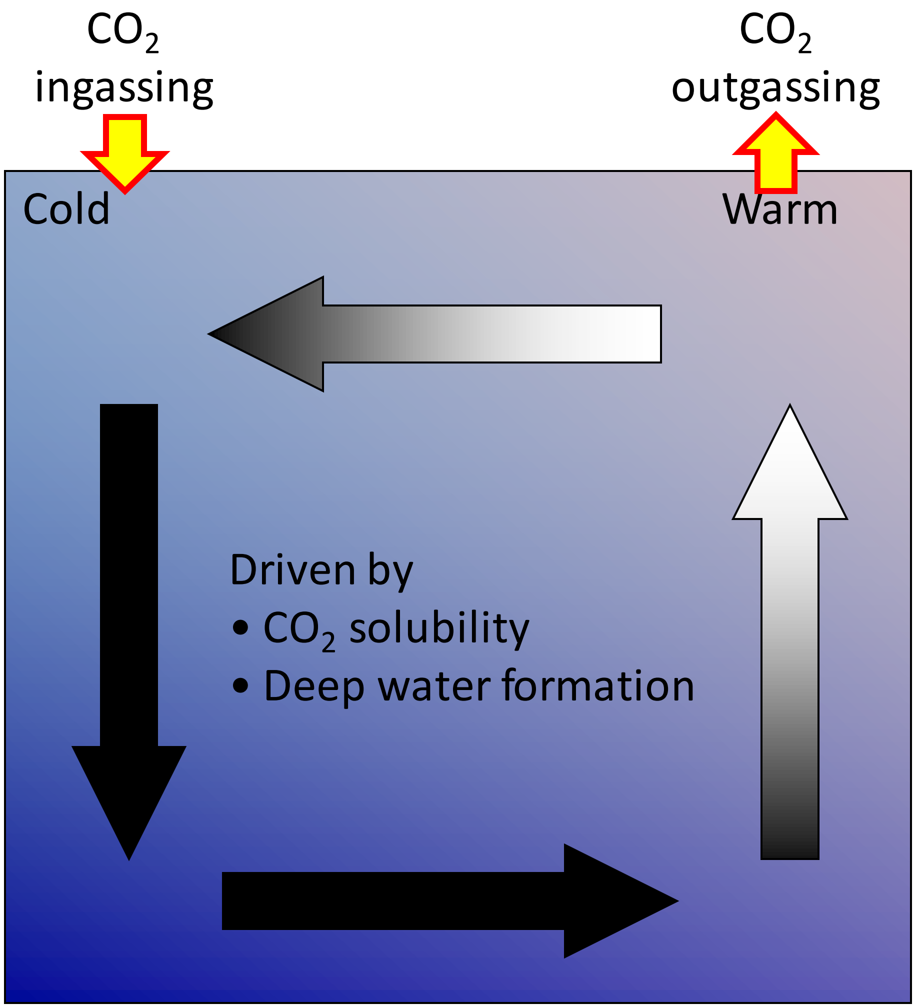
Gt C / y



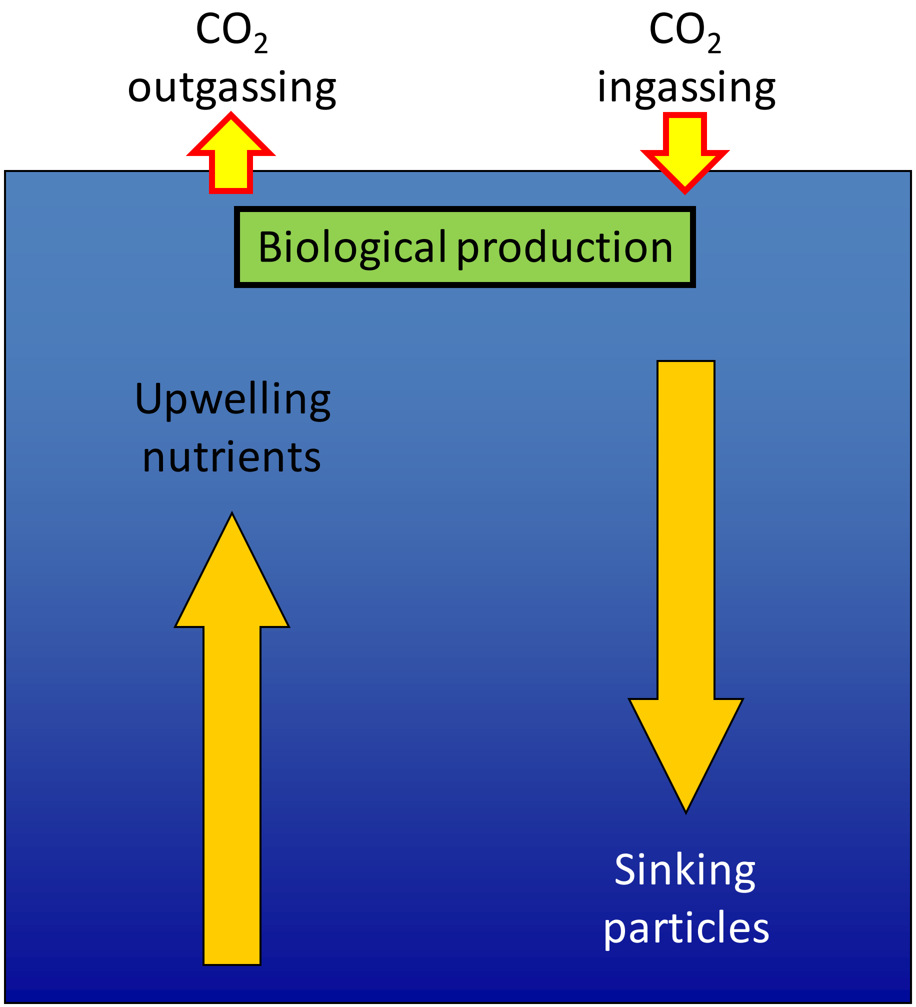
NASA

How does it get there?

Solubility pump

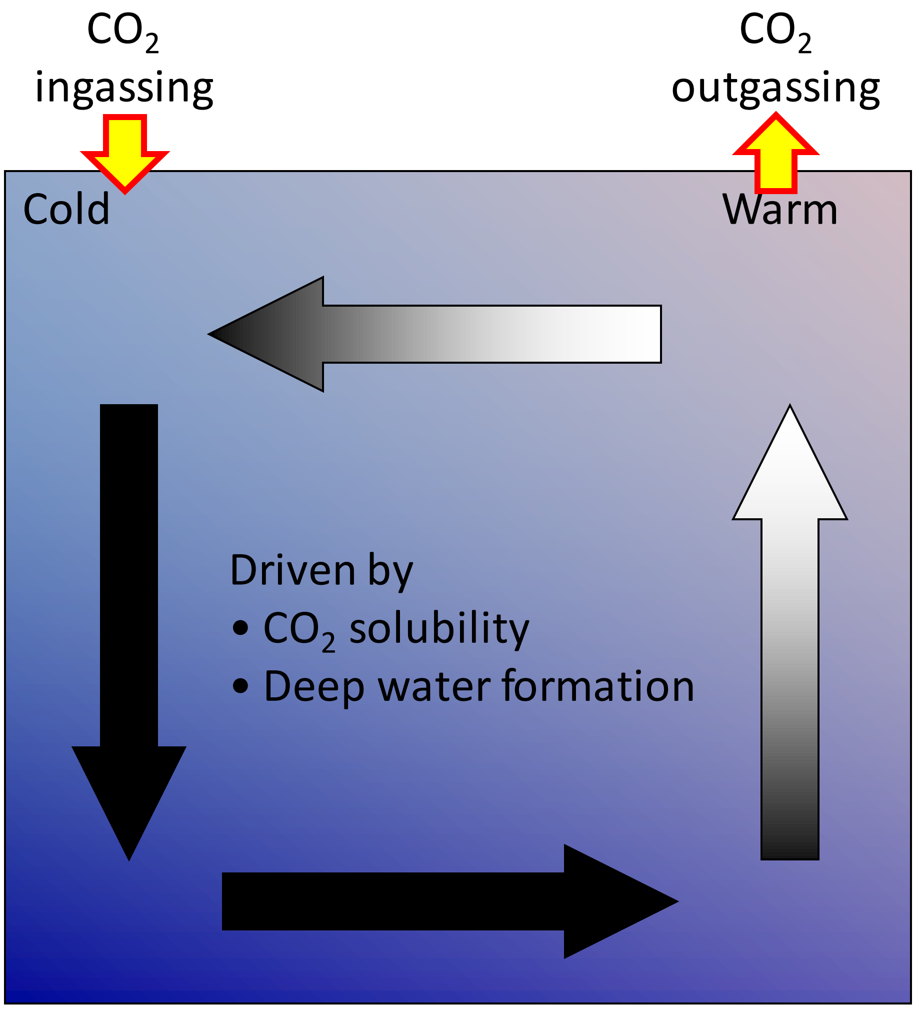


Biological pump

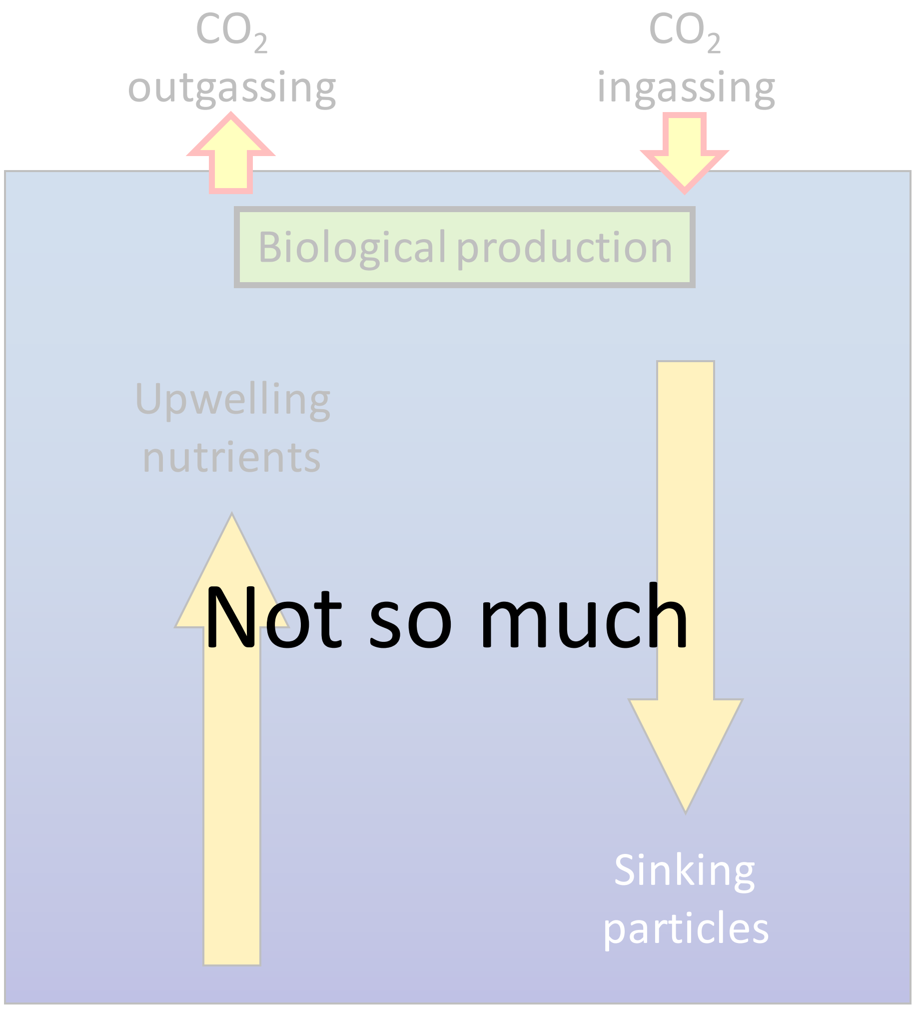


How is *our CO2* getting there?

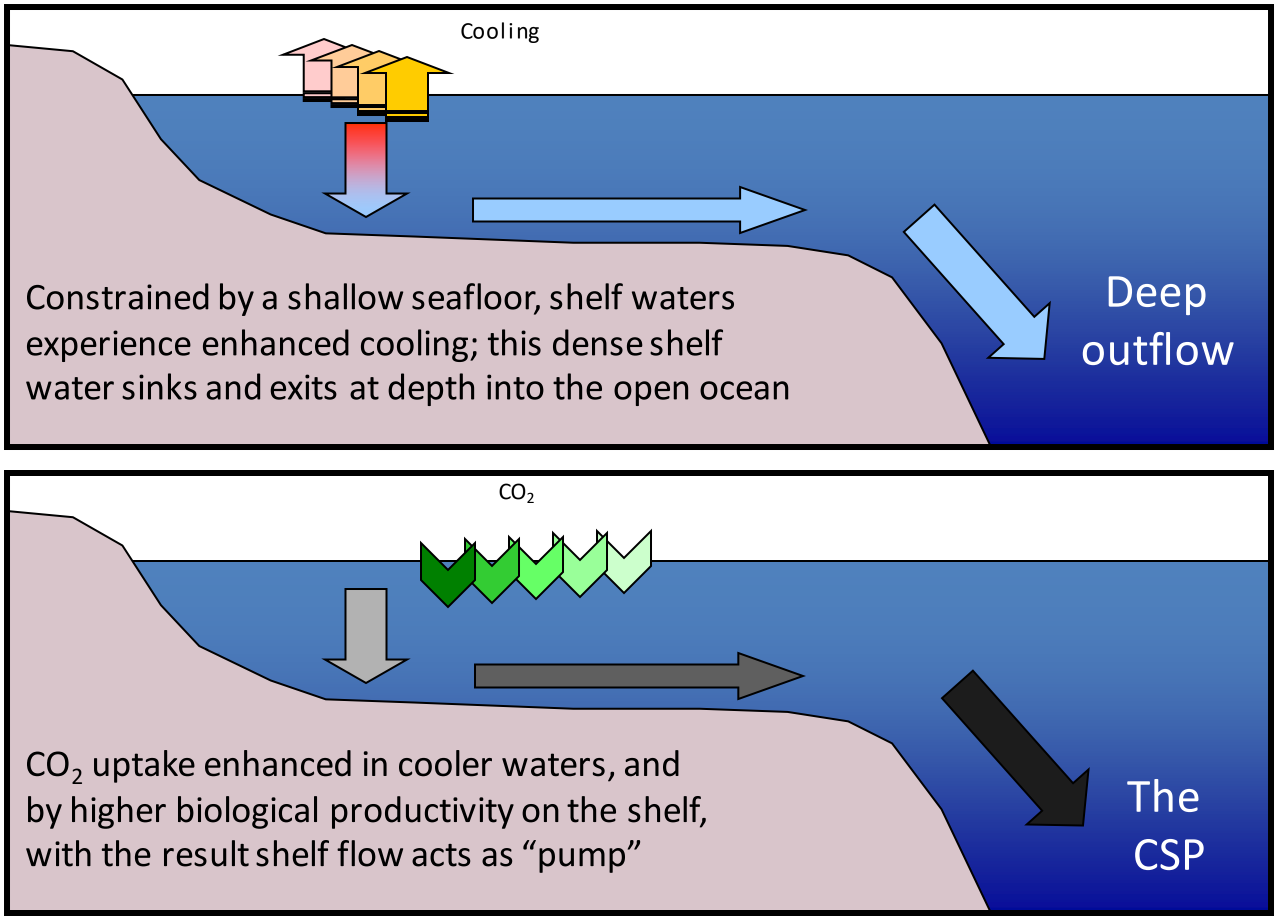
Solubility pump



Biological pump

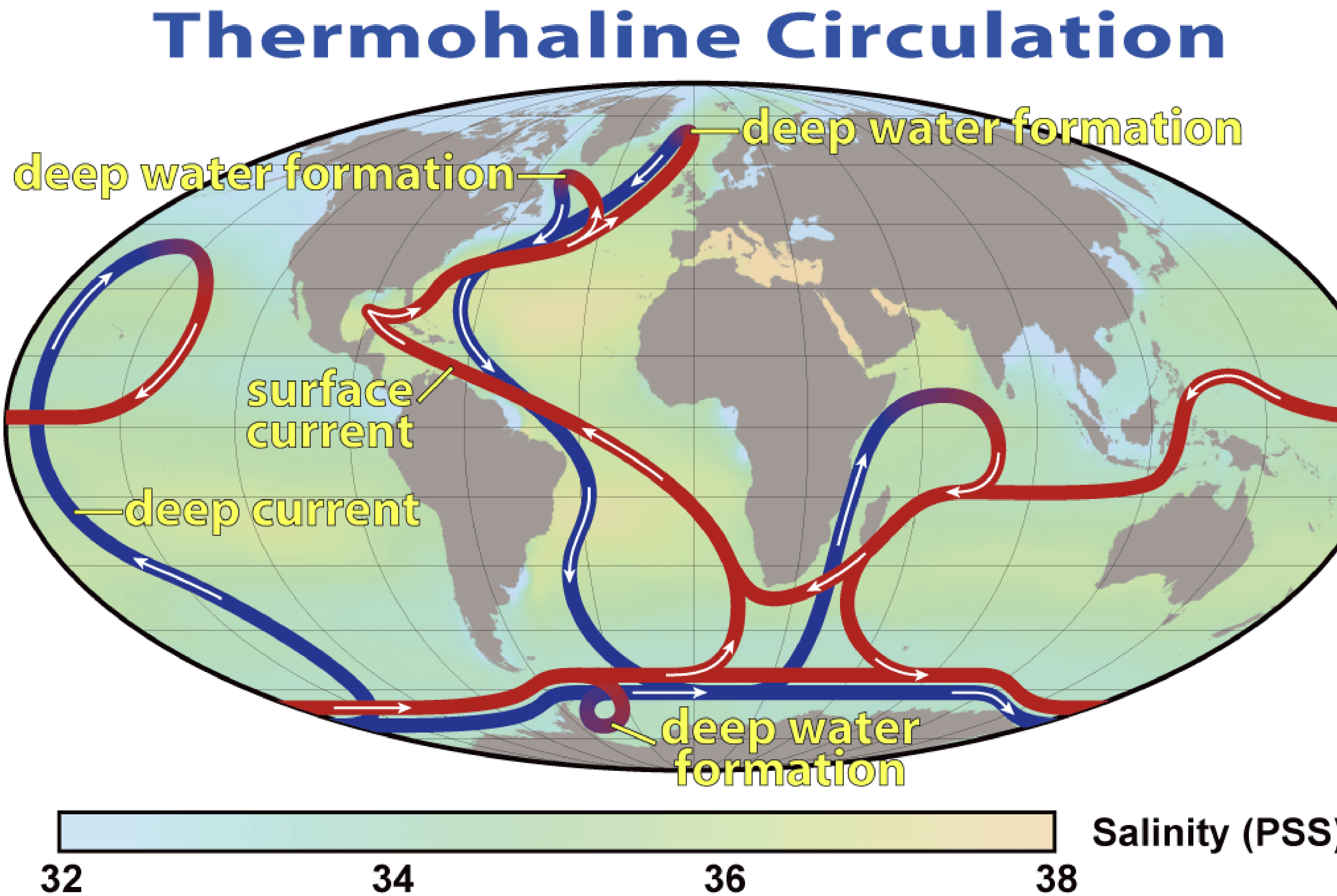


Continental shelf pump



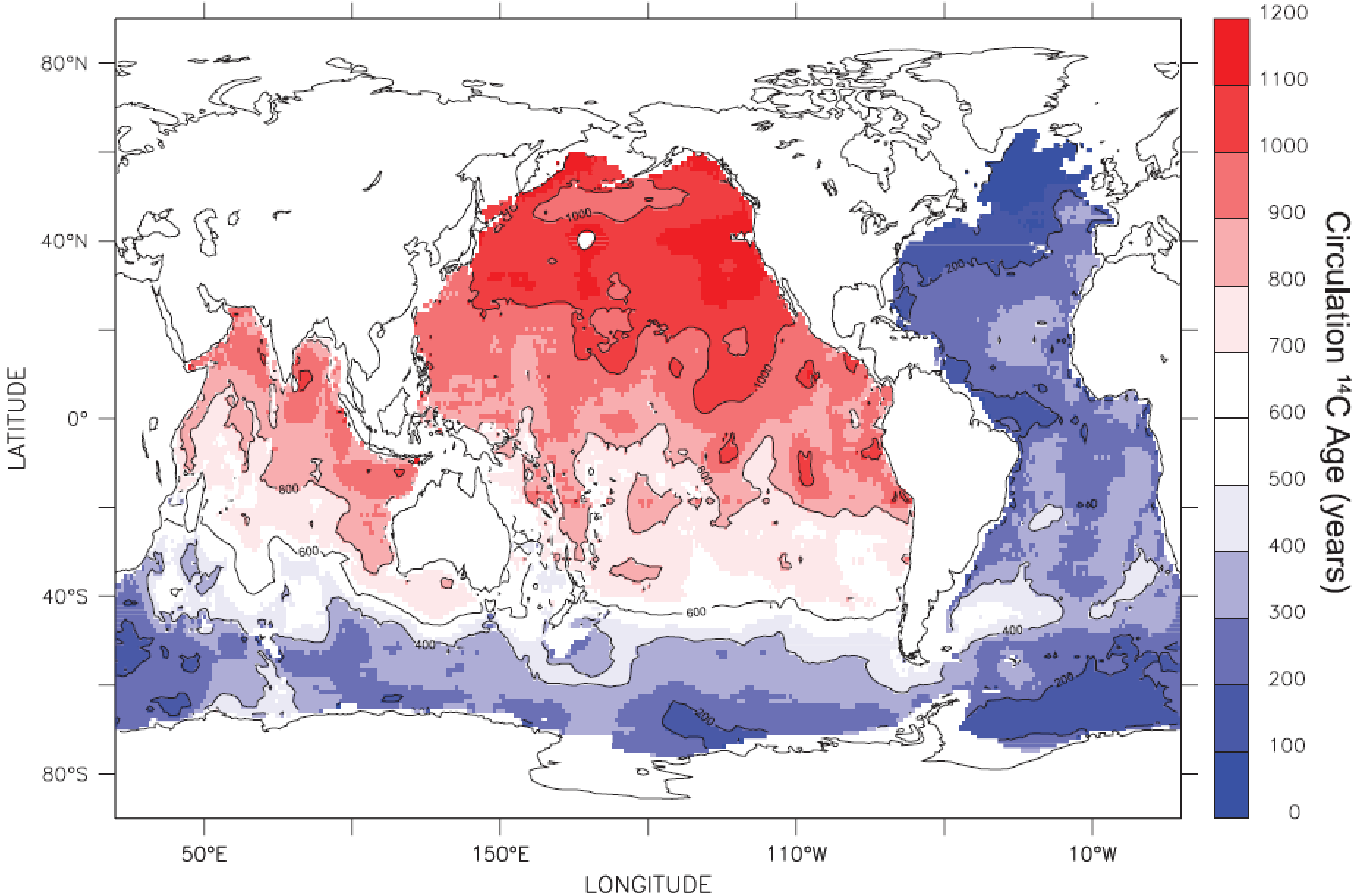
Tsunogai et al., *Tellus B*, 1999

Inside the ocean



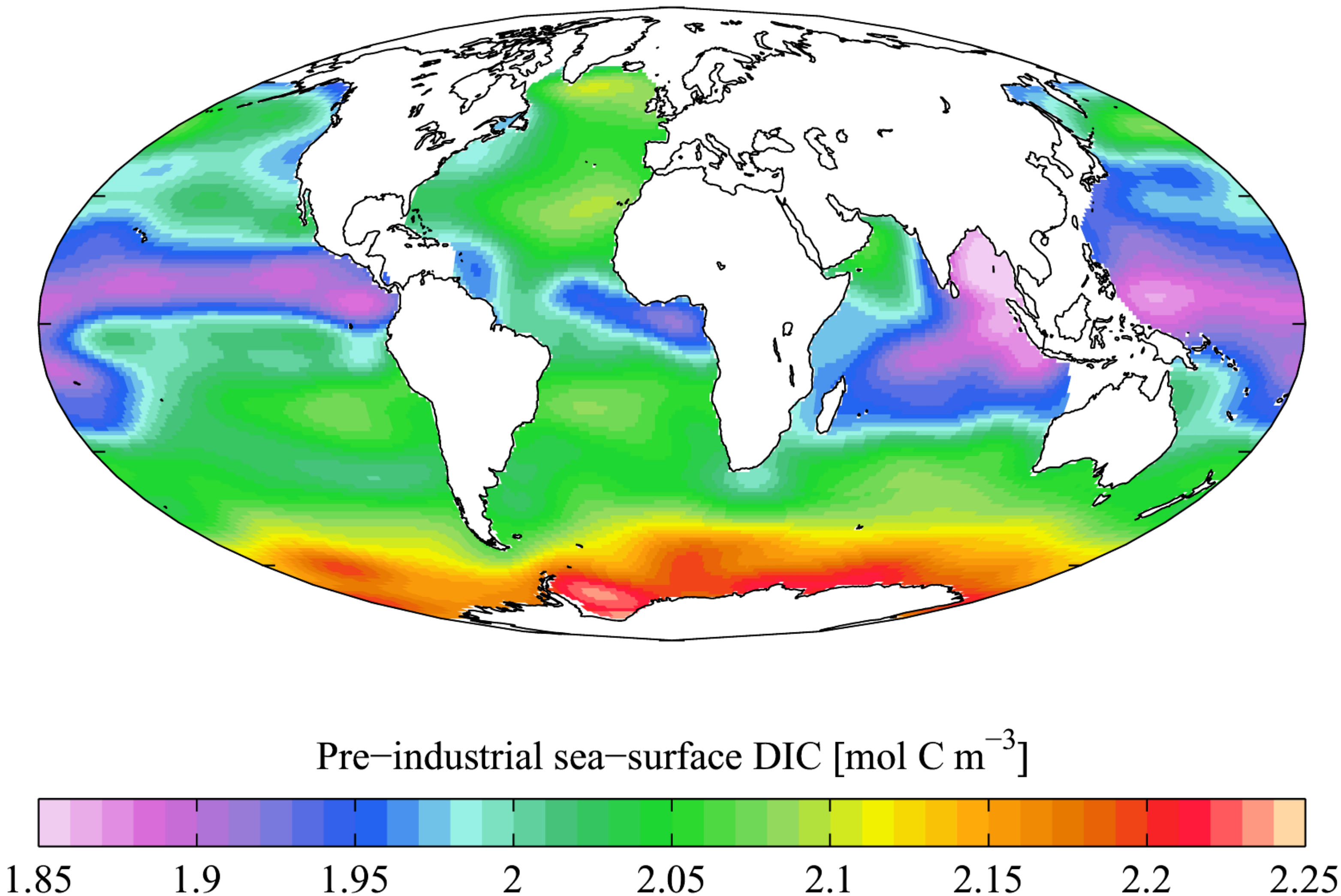
Wikipedia

A long memory



Matsumoto, JGR, 2007

Carbon isn't isotopic



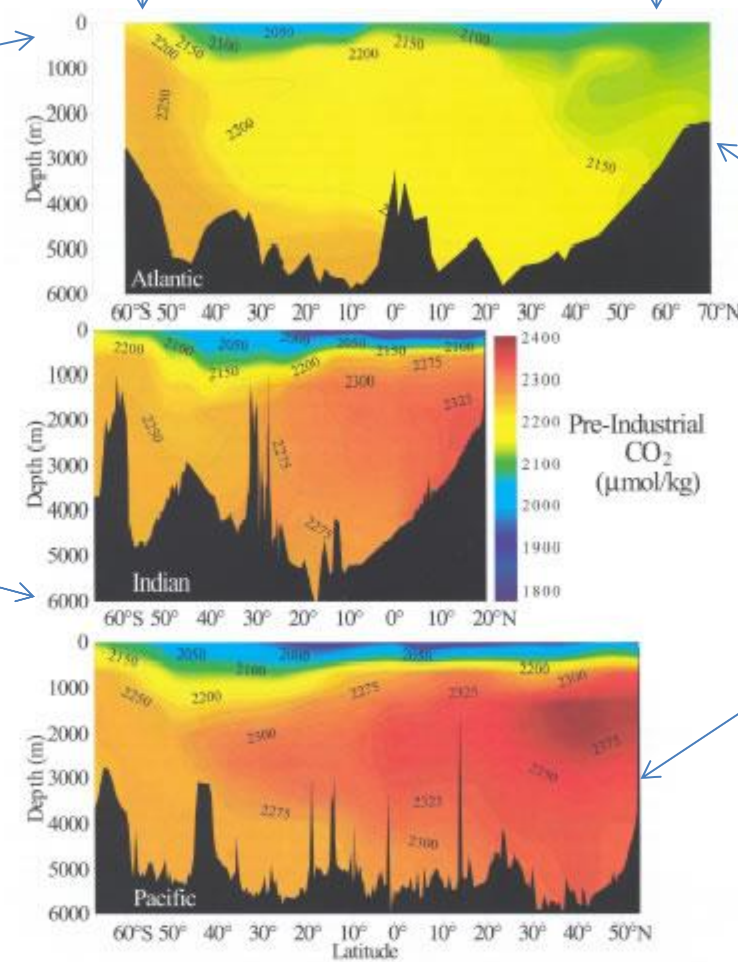
Key et al., GBC, 2004

Not in depth either

North / south gradients

Top / bottom gradients

Between basins



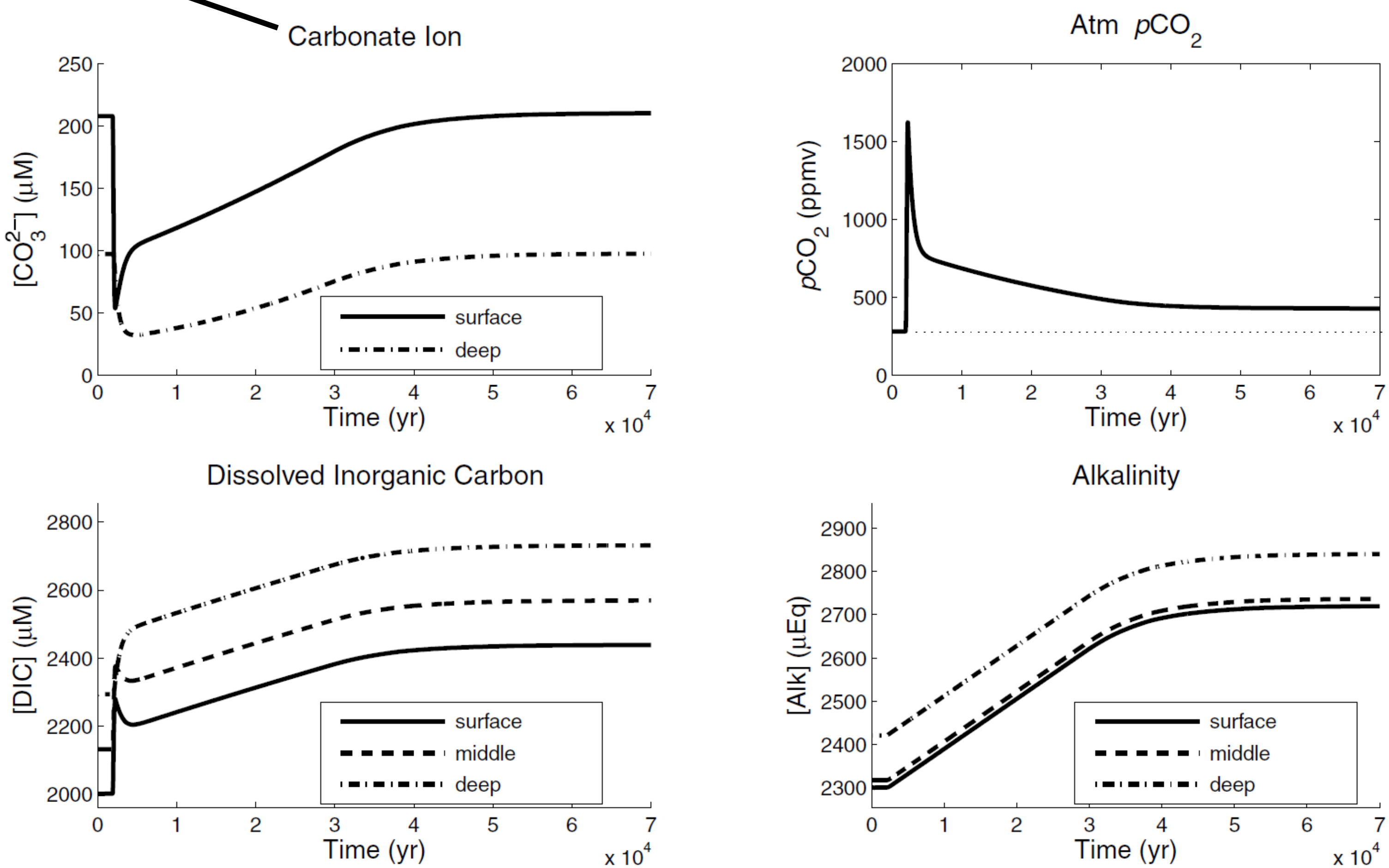
Feely et al., Oceanogr., 2001

The big picture

- CO_2: < 2% in the atmosphere; ~5% in the land and soil; ~93% in the ocean
- Ocean distribution governed by physico-chemical and biological processes
- Since the start of the industrial revolution (and arguably from before then; e.g. deforestation), civilisation has been a source of CO_2
- About half has remained in the atmosphere, with similar amounts in the ocean and land
- In the far future, the majority will end up in the ocean; the near future is more uncertain

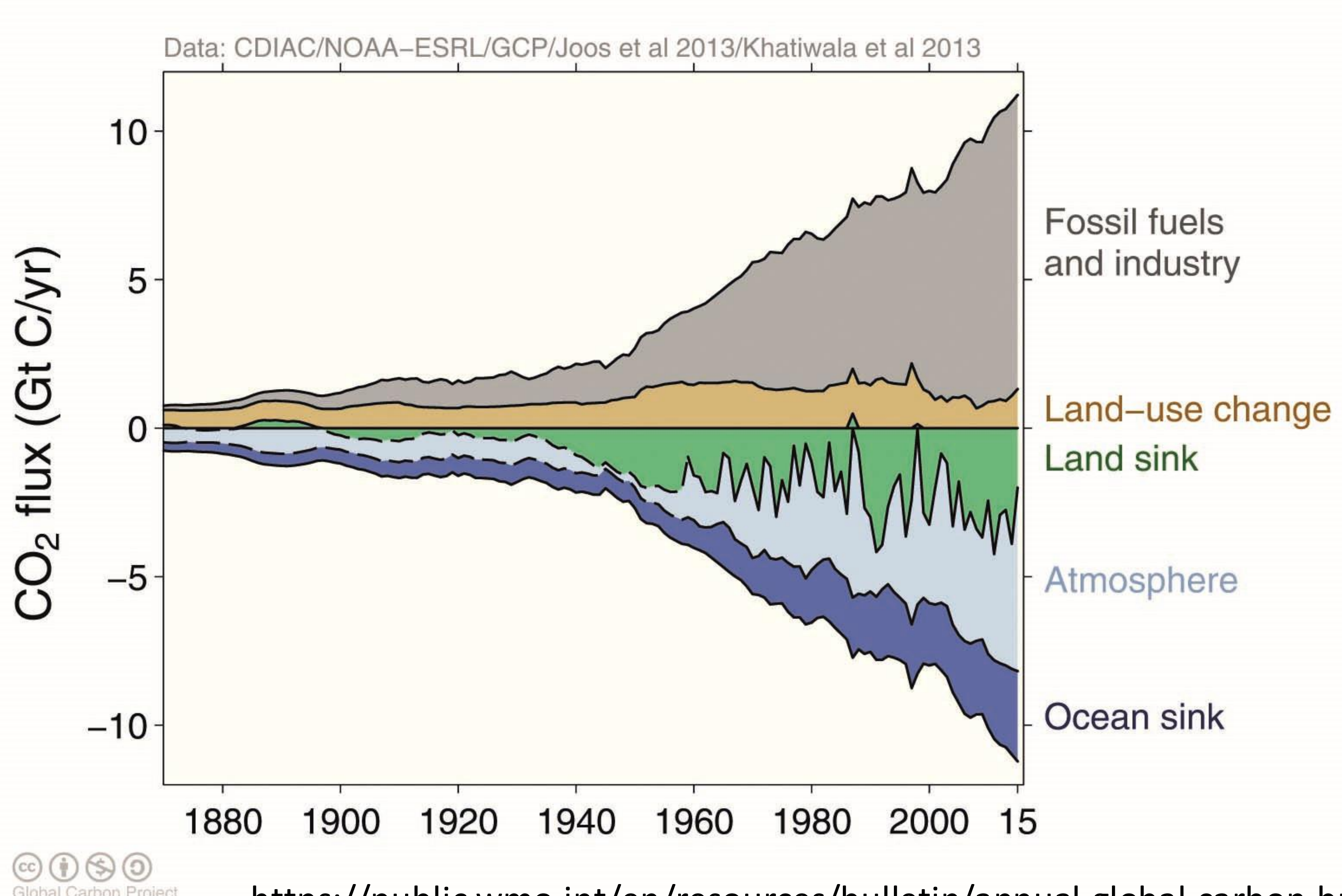
“300 years, plus 25% that lasts forever”

Plus Si weathering



Archer, JGR, 2005
Tyrrell et al., Tellus, 2007

The near future



https://public.wmo.int/en/resources/bulletin/annual-global-carbon-budget

Anthro CO_2

- A key part of carbon cycle budgeting is knowing how much CO_2 the ocean has taken up from the atmosphere
- While we have many measurements of ocean carbon content, we are hampered by the fact that anthro CO_2 is chemically indistinguishable from natural CO_2
- To attempt to circumvent this a range of methods have been developed to estimate anthro CO_2 from total DIC

Back-calculation methods

- The longest-standing class of methods use so-called "back-calculation" …

  Total DIC = equilibrium DIC (T, S)
  + biological pump DIC
  + anthro CO2

- Equilibrium DIC can be estimated from T, S
- Biological pump DIC can be estimated from known nutrient, alkalinity, oxygen relationships
- Anthro DIC is then estimated as a delta

Redfieldian biological pump

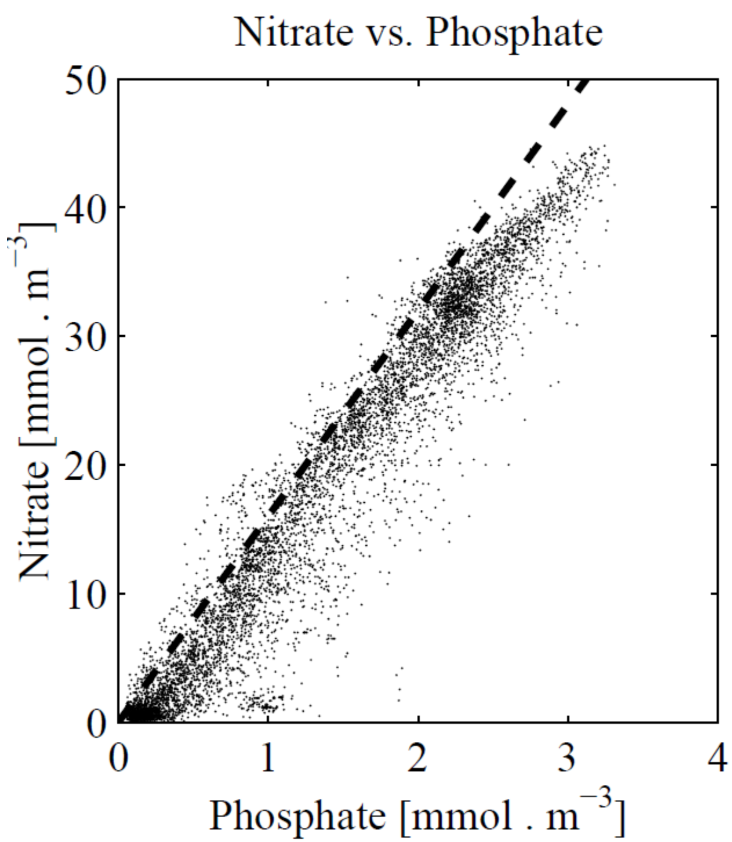
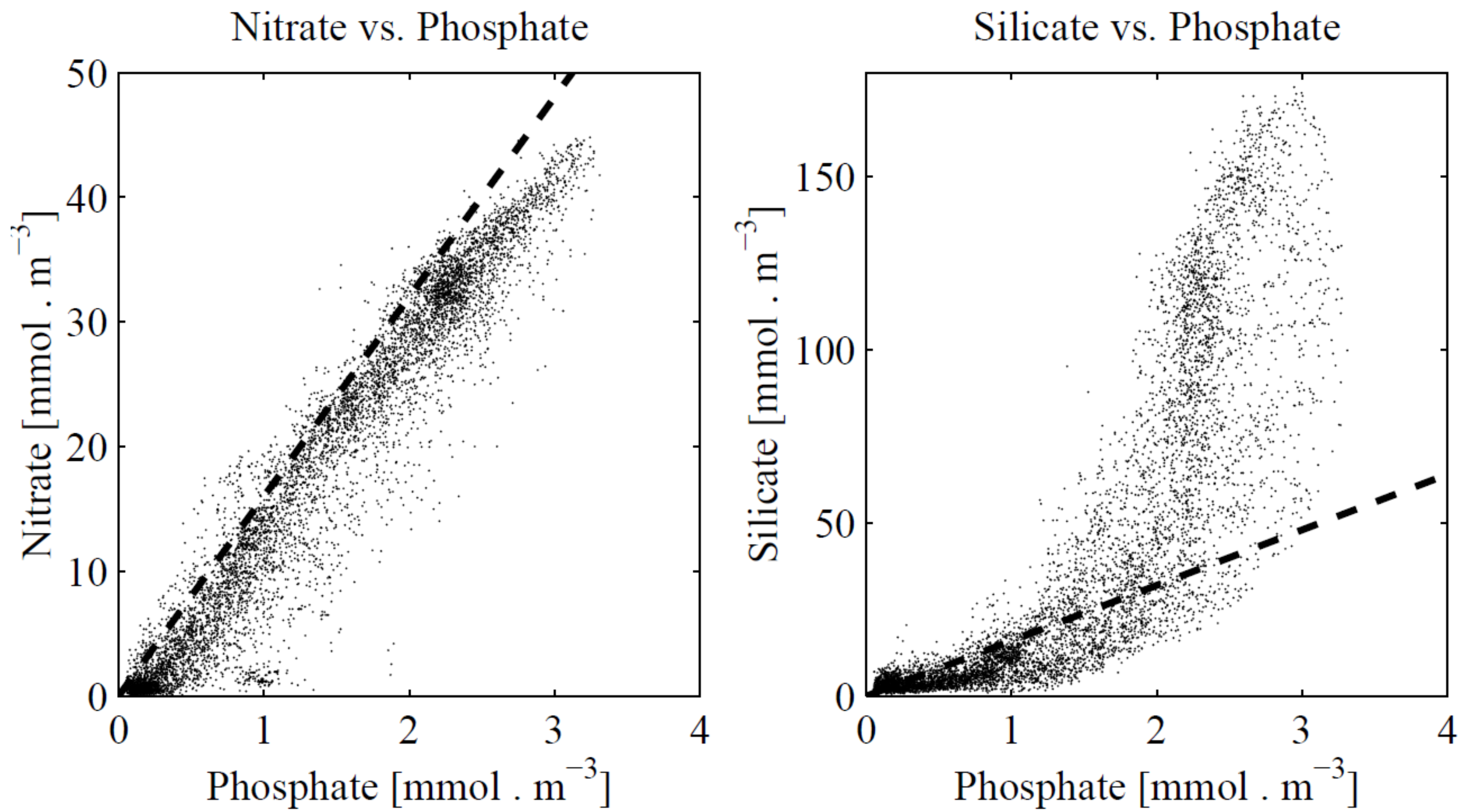


Figure 2: Plots of nitrate versus phosphate and silicate versus phosphate from the Levitus global climatologies. Data range from the surface to the seafloor. The dashed lines represent N:P = 16:1 and Si:P = 16:1, standard Redfield

Tyrrell, Nature, 1999

Redfieldian biological pump



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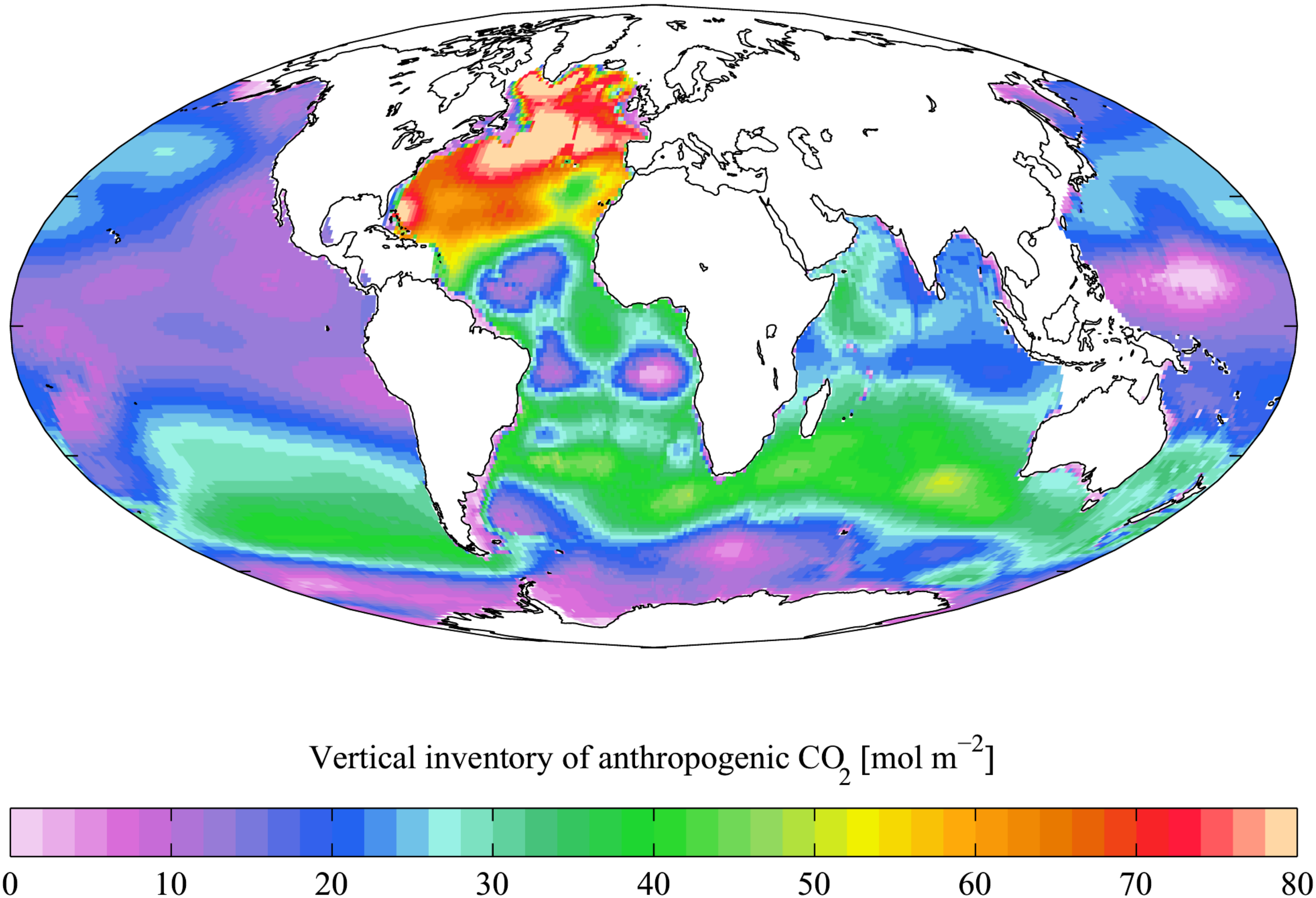
Tyrrell, Nature, 1999

ΔC*

- The most well-known of these is the ΔC* method of Gruber et al. (1996)
- This uses DIC, alkalinity, oxygen, T, S
- It additionally requires estimation of the air-sea disequilibrium of CO2 at the surface
- This is done by tracking water parcels along isopycnals to find anthro-free conditions from which the effective disequilibrium can be calculated

Gruber et al., GBC, 1996



Key et al., GBC, 2004

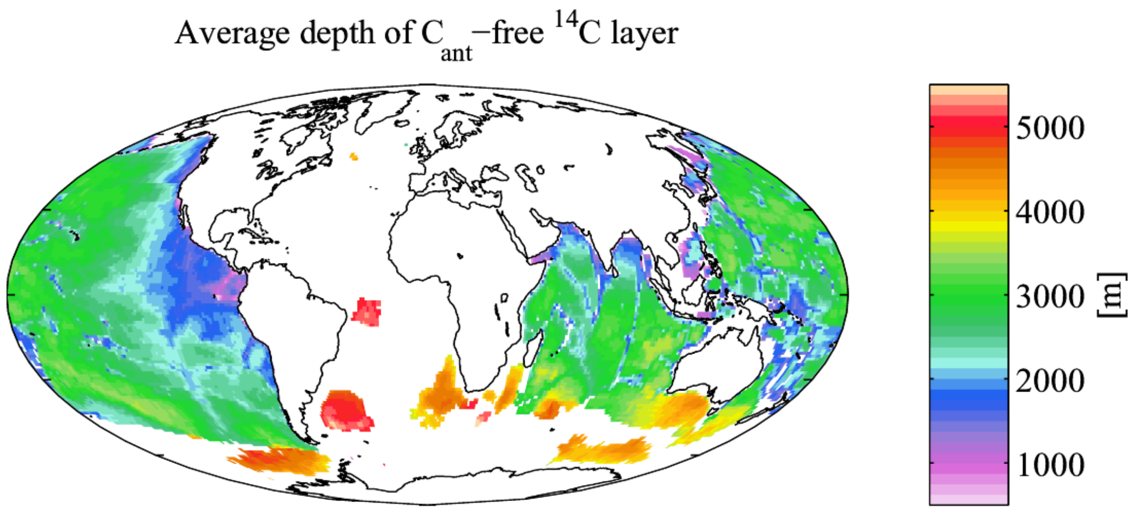
TrOCA method

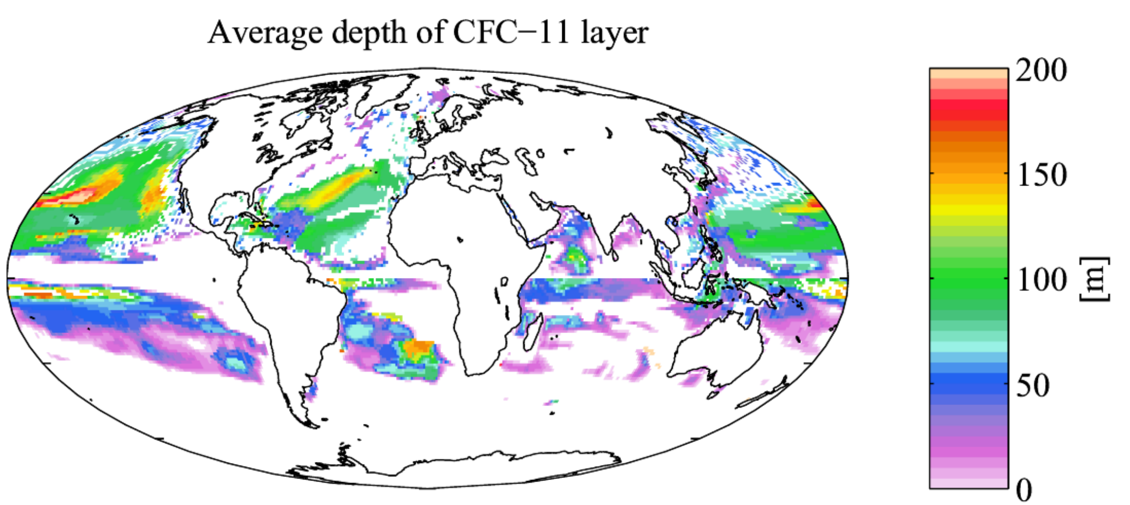
$$C_{ant}^{TrOCA} = \frac{O_2 + 1.279\left[C_T + \frac{A_T}{2}\right] - \exp\left(7.511 - (1.087 \times 10^{-2})\theta + \frac{-7.81\times10^5}{A_T^2}\right)}{1.279}$$

- Where the "constants" are the result of an optimisation procedure that uses a calibration dataset based on two pools of data:
  - C_{ant}-free water masses; ^{14}C criterion
    C_{ant} = 0 (since ^{14}C age > industrial revolution)
  - C_{ant}-contaminated water masses; CFC-11 criterion
    C_{ant} = estimated assuming saturation with a pCO_2 concentration appropriate for CFC-11 age

Touratier et al., *Tellus B*, 2007

Synthetic calibration data





Maps of average depth from which calibration data is drawn

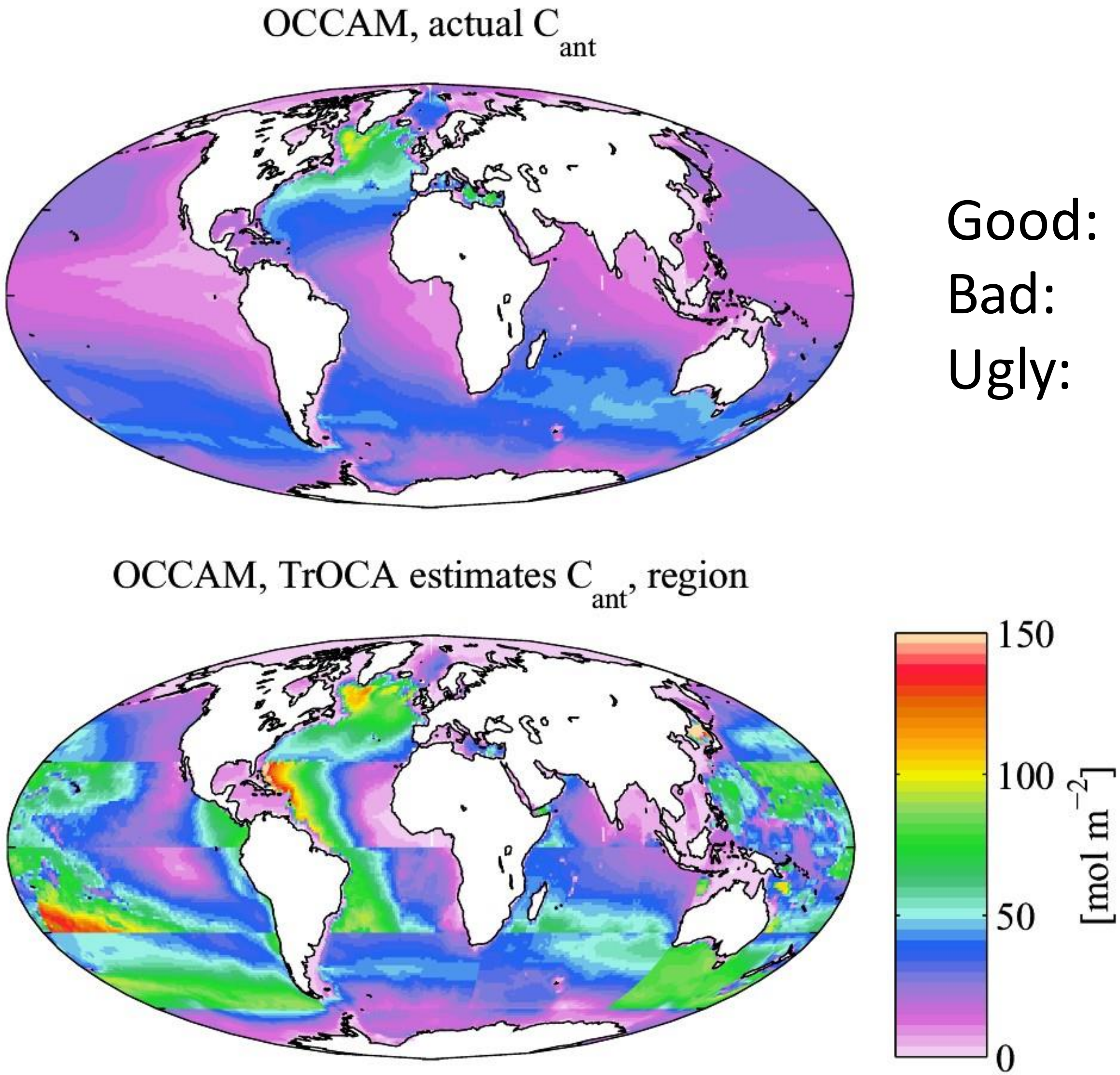
More C_{ant}-free data since large volume of ocean has not been ventilated "recently"

CFC-11 signal narrow (1992-1995) so only a relatively thin envelope of calibration data

(This doesn't seem to matter much)

Yool et al., Biogeosciences, 2010

Actual vs. regional TrOCA estimate



Good: N. Atlantic
Bad: Eq. Pacific
Ugly: Southern

Yool et al., Biogeosciences, 2010

MLRs

- Based on repeated surveys between which CO2 has increased, plus similar independent chemical and hydrographical parameters
- Regression of these variables to predict DIC
- Residuals of regression coefficients assumed to be due to anthro CO2

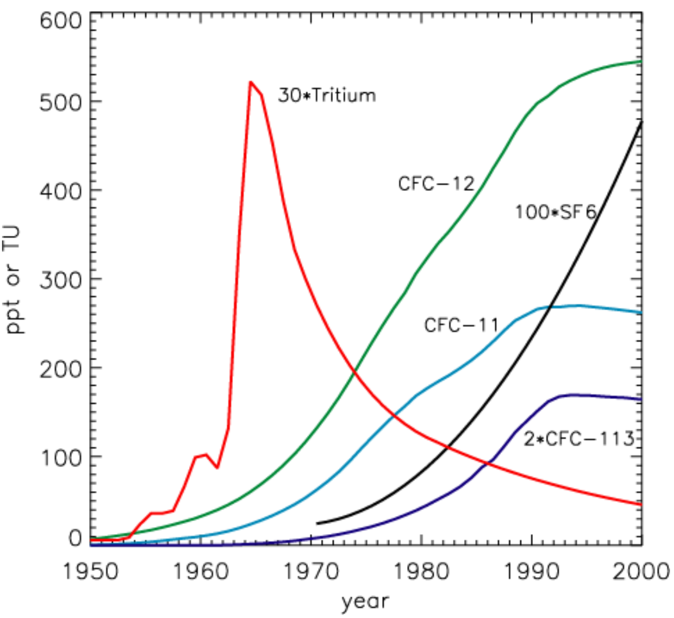
Year 1: $TIC^{pred} = a_0^{Yr\,1} + a_1^{Yr\,1}\boldsymbol{\theta} + a_2^{Yr\,2}\mathbf{S} + a_3^{Yr\,2}\mathbf{O_2} + a_4^{Yr\,2}\mathbf{Alk} + a_5^{Yr\,2}\mathbf{Nit}$

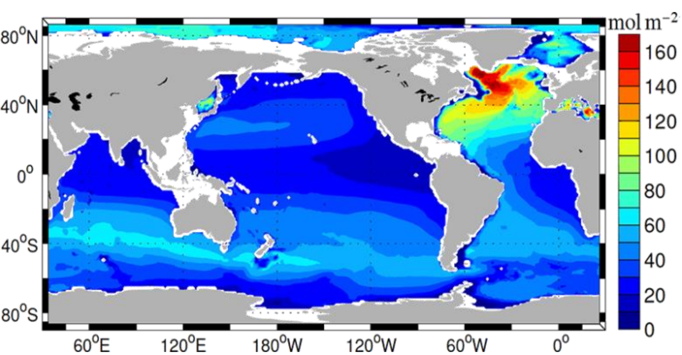
Year 2: $TIC^{pred} = a_0^{Yr\,2} + a_1^{Yr\,2}\boldsymbol{\theta} + a_2^{Yr\,2}\mathbf{S} + a_3^{Yr\,2}\mathbf{O_2} + a_4^{Yr\,2}\mathbf{Alk} + a_5^{Yr\,2}\mathbf{Nit}$

$$\mathbf{C^{anth}} = (a_0^{Yr\,2}-a_0^{Yr1}) + (a_1^{Yr\,2}-a_1^{Yr1})\boldsymbol{\theta} + (a_2^{Yr\,2}-a_2^{Yr1})\mathbf{S} + (a_3^{Yr\,2}-a_3^{Yr1})\mathbf{O2} + (a_4^{Yr\,2}-a_4^{Yr1})\mathbf{Alk} + (a_5^{Yr\,2}-a_5^{Yr1})\mathbf{Nit}$$

e.g. Brown et al., JGR, 2010

Transit time distribution

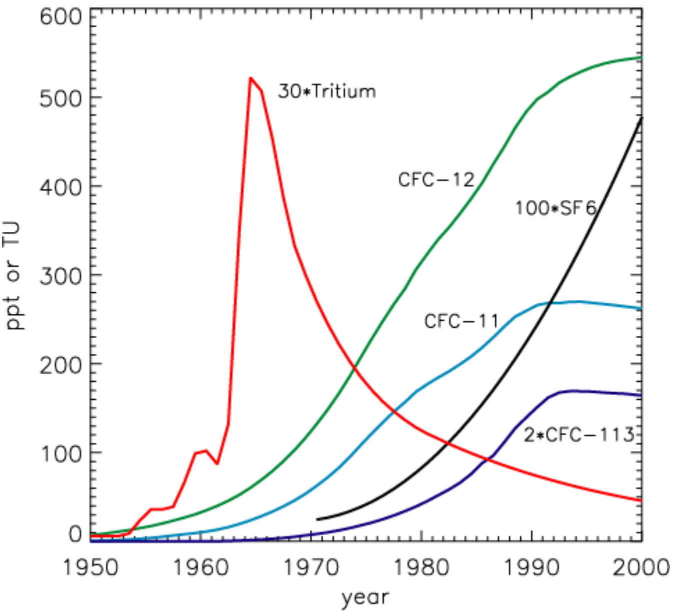


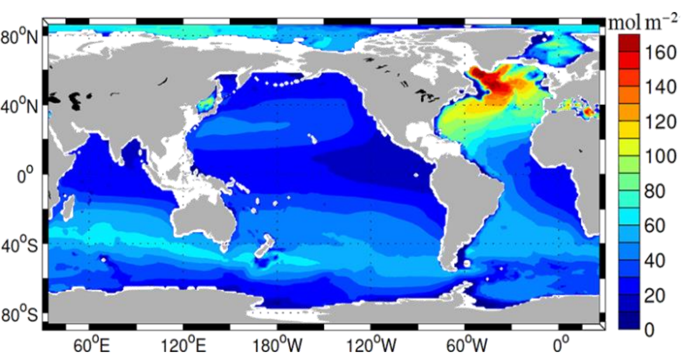


- Spatial differences in oceanic CO2 are, in part, due to its atmospheric history
- One approach for identifying anthro CO2 is to use this in conjunction with the time history of other tracers such as CFCs, ^3H-^3He

Waugh et al., JGR, 2003
Khatiwala et al., Nature, 2009

Transit time distribution





- Information from these different tracers can be used to define a "contact time" with the atmosphere
- In its simplest form, this can be combined with the time history of atmospheric pCO2 to determine anthro CO2 within the ocean (but it's a lot more complicated than that!)

Waugh et al., JGR, 2003

Khatiwala et al., Nature, 2009

Summary

- For budgeting (now and the future), important to determine ocean anthro CO_2
- However, it’s not possible to discern anthro CO_2 chemically
- A range of methods exist, but these have (often important) assumptions and limitations
- However, with repeat surveys, deconvoluting from one-time survey data is becoming less important

Ocean acidification

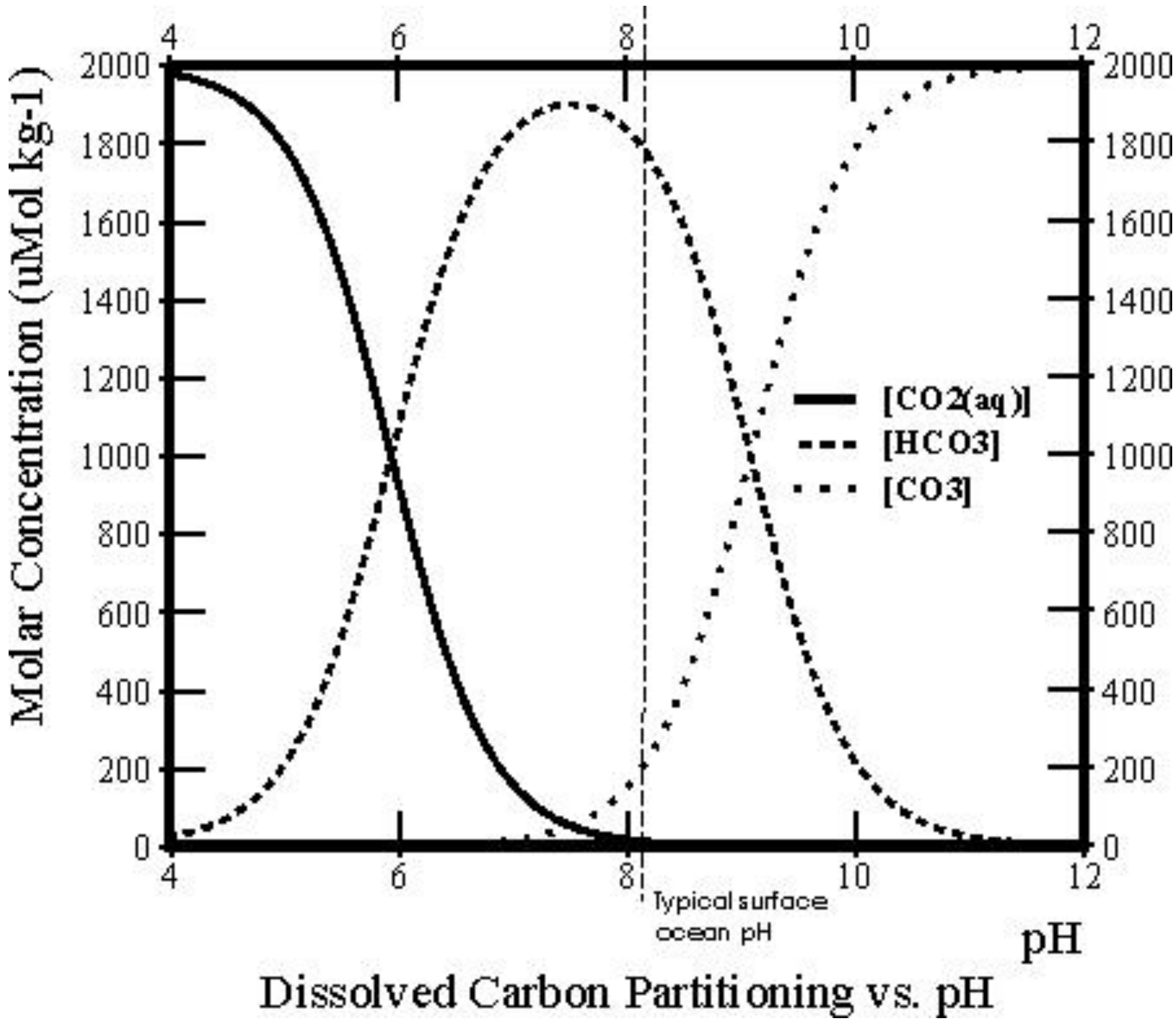
Anthro CO2 does not come alone …

- As atmospheric CO2 rises, ocean CO2 rises as surface waters equilibriate
- CO2 entering seawater does not remain as "free CO2" but instead reacts with seawater

$$CO_2 + H_2O \text{ «=» } H^+ + HCO_3^- \text{ «=» } CO_3^{2-} + 2H^+$$

- Increasing dissolution alters this balance in favour of bicarbonate and dissolved CO2, and with consequences for pH

Carbon species depend on / dictate pH



pH from multiple Time-Series sites

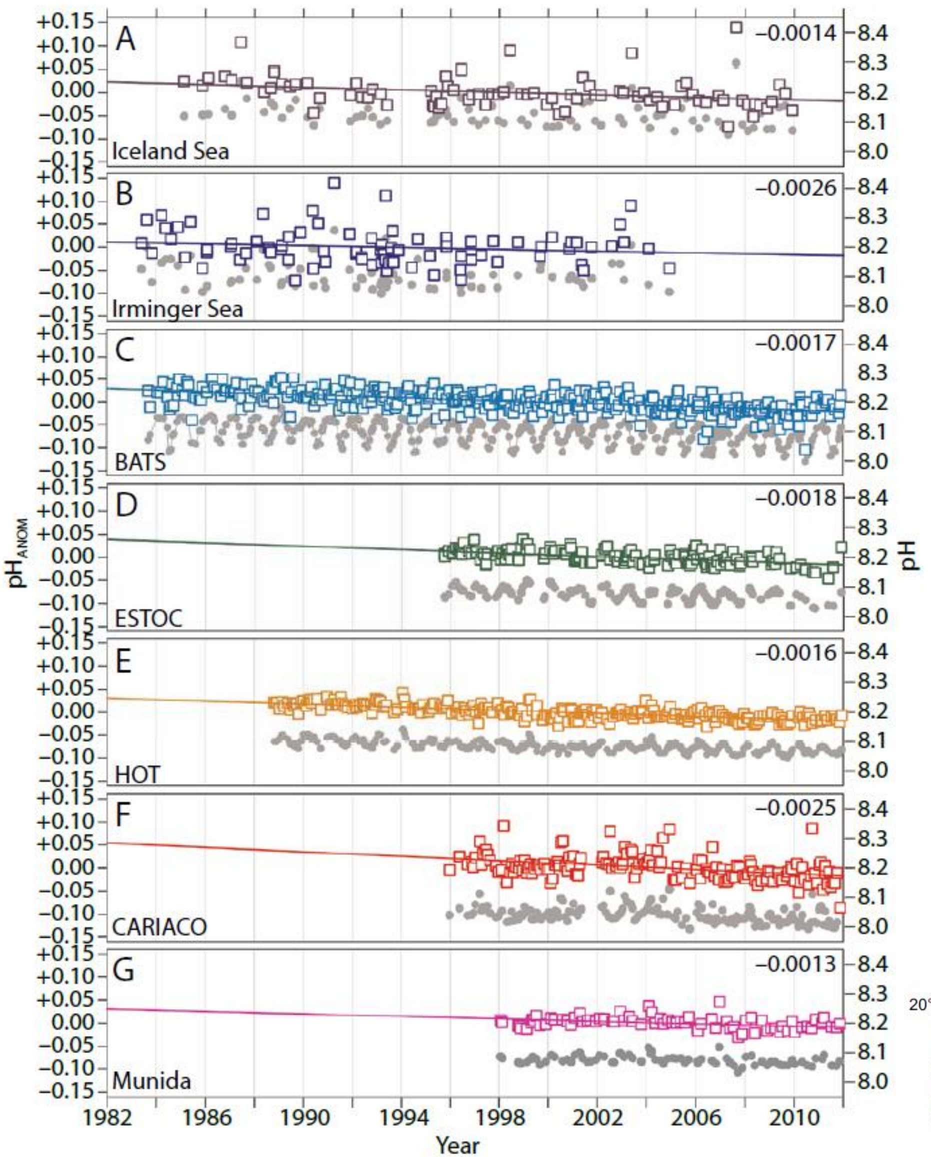
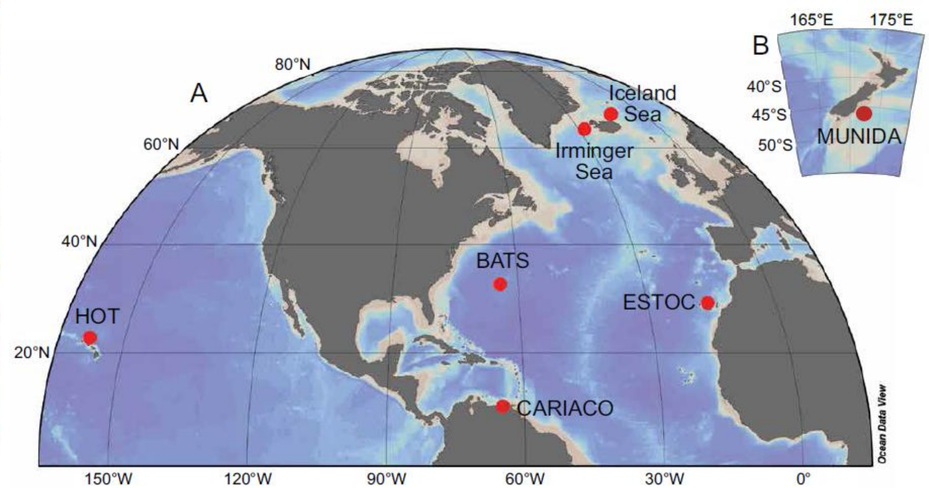
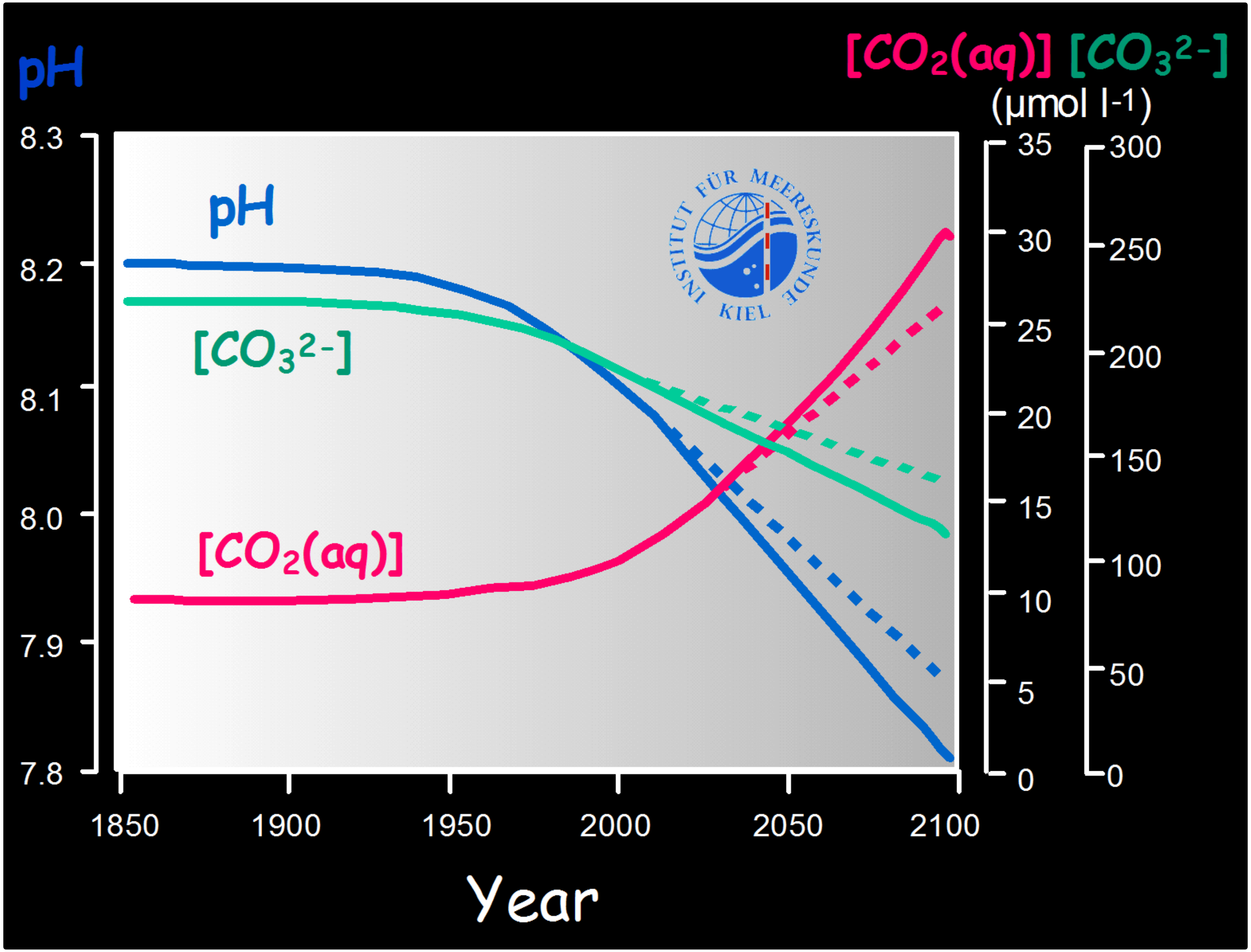


Figure 7. Time series of surface seawater anomalies of pH (colored symbols) and observed pH (gray symbols; no units), with trends (yr^{-1}) reported in Table 2 shown in top right-hand corner of each panel. Seawater CO_2-carbonate chemistry parameters were calculated from observed DIC and total alkalinity (see Box 1 for details). The time-series data are shown relative to latitude with the first panel illustrating the most northerly ocean time-series site.



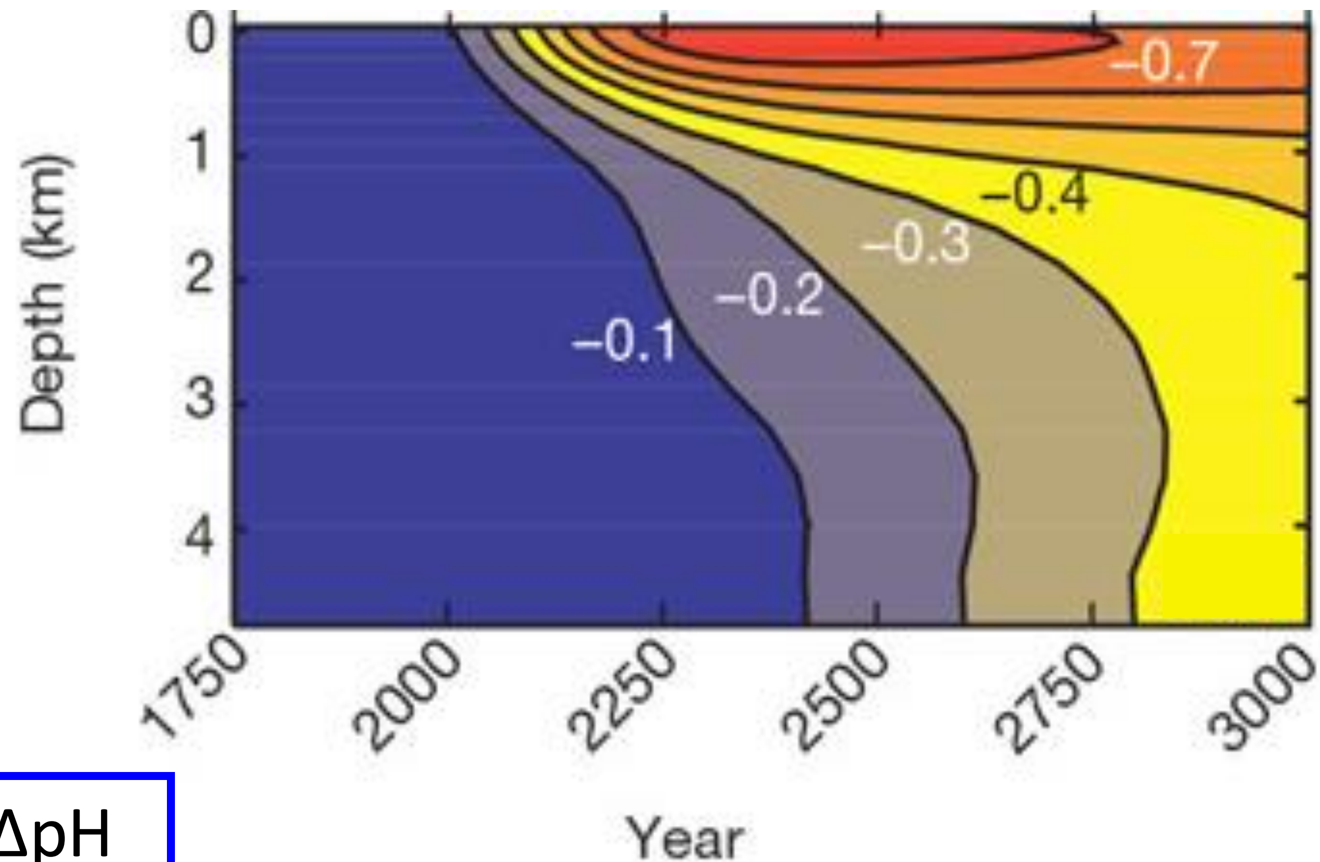
Bates et al. (2014)

Surface Ocean Effects



Wolf-Gladrow et al., Tellus B, 1999

Ocean interior pH

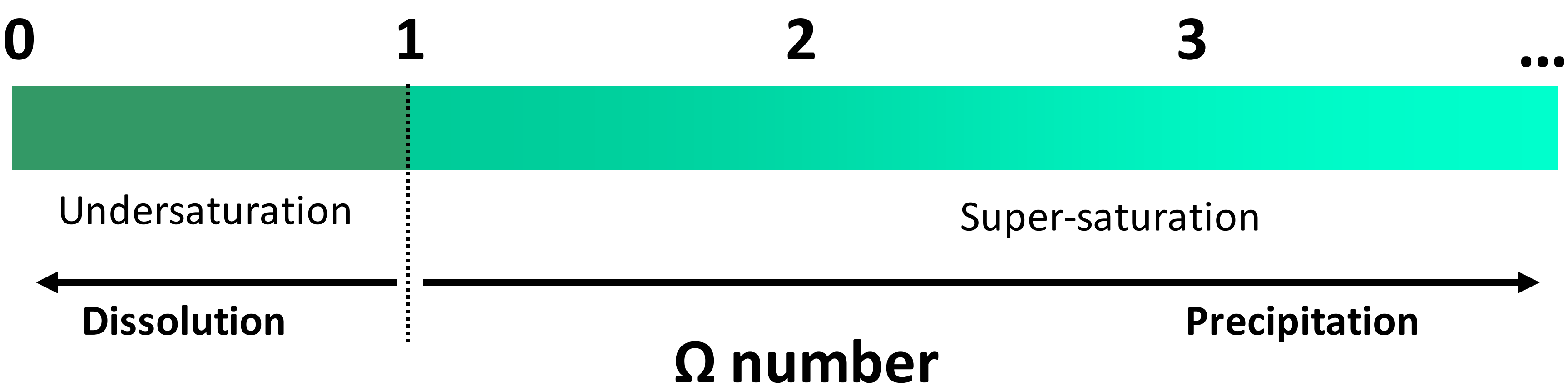


ΔpH

Caldeira & Wickett (2003)

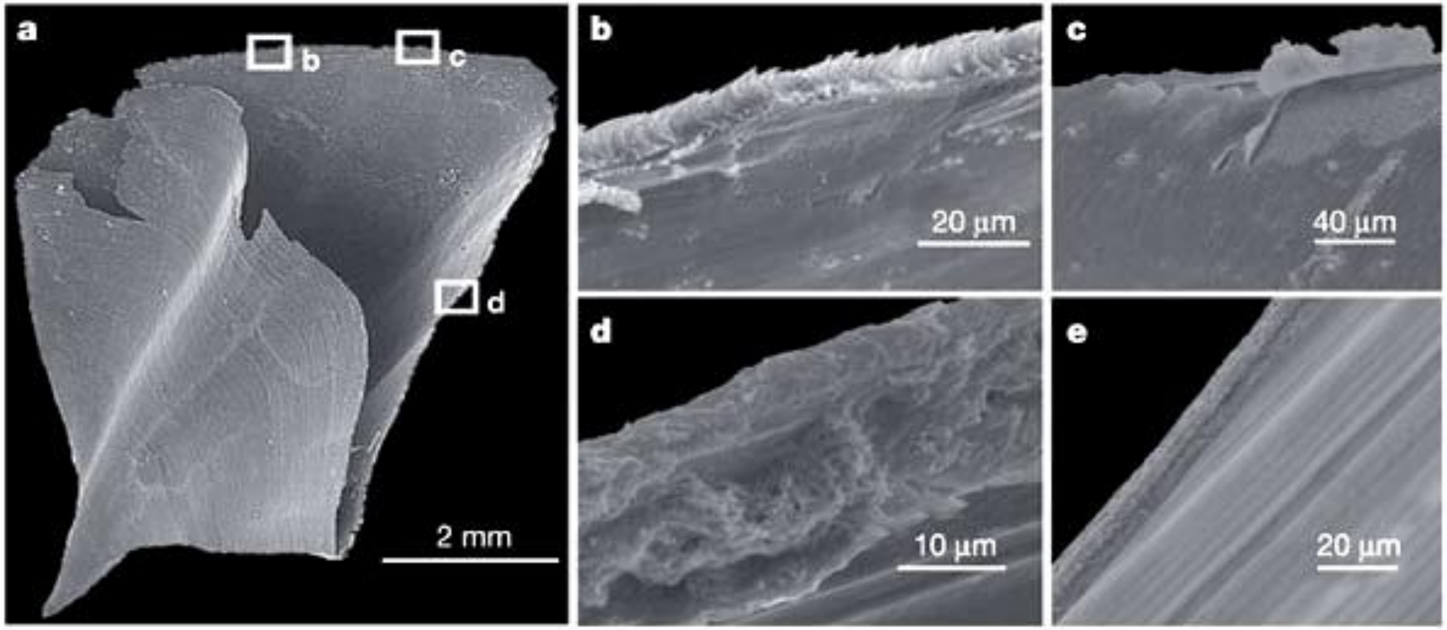
Inorganic calcification is dependent on saturation state

$$W = \frac{[CO_3^{2-}]*[Ca^{2+}]}{K'_{sp}}$$



Some important ocean calcifiers

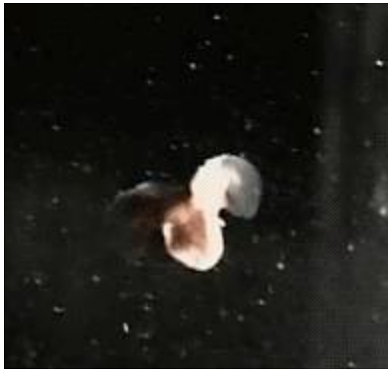
Pteropod shell dissolution at high CO_2



Orr et al., Nature, 2005

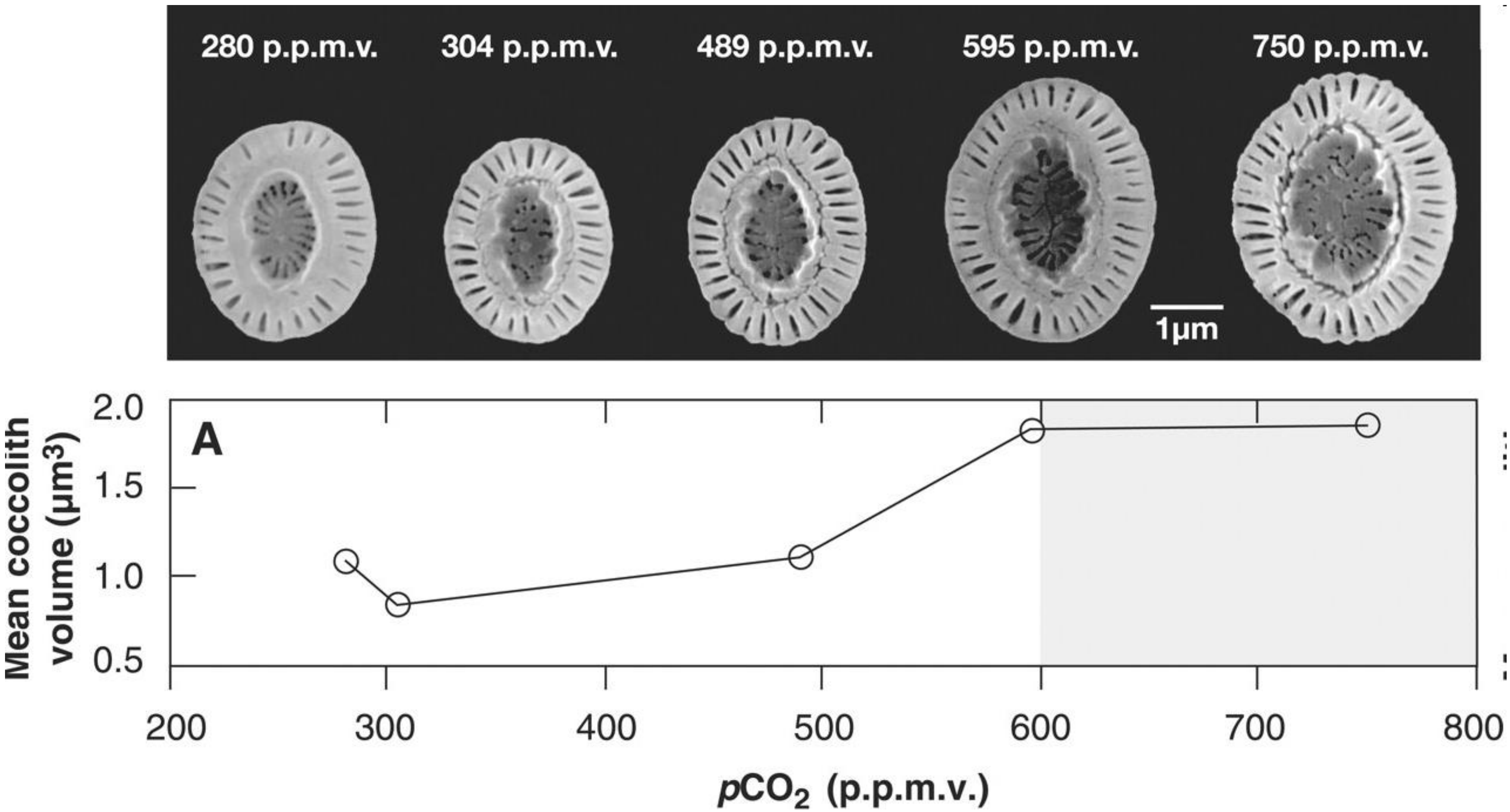
Limacina helicina

C. pyramidata



Rick Feely

However … larger Coccoliths at high CO2



Iglesias-Rodriguez et al. (2008)

Uncertainty remains

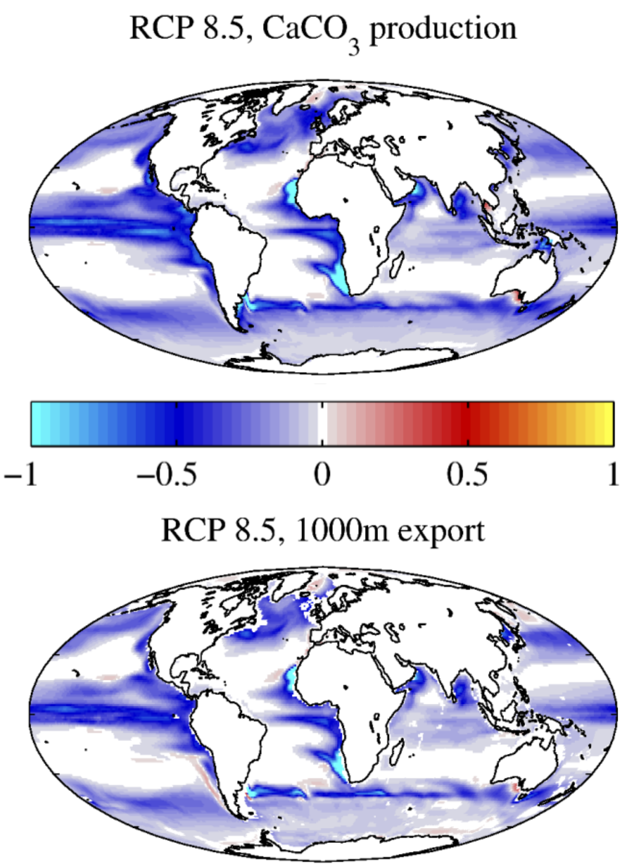
Taxa	Response	Mean Effect
Calcifying algae	Survival	
	Calcification	
	Growth	
	Photosynthesis	−28%
	Abundance	−80%
Corals	Survival	
	Calcification	−32%
	Growth	
	Photosynthesis	
	Abundance	−47%
Coccolithophores	Survival	
	Calcification	−23%
	Growth	
	Photosynthesis	
	Abundance	
Mollusks	Survival	−34%
	Calcification	−40%
	Growth	−17%
	Development	−25%
	Abundance	
Echinoderms	Survival	
	Calcification	
	Growth	−10%
	Development	−11%
	Abundance	
Crustaceans	Survival	
	Calcification	
	Growth	
	Development	
	Abundance	
Fish	Survival	
	Calcification	
	Growth	
	Development	
	Abundance	
Fleshy algae	Survival	
	Calcification	
	Growth	+22%
	Photosynthesis	
	Abundance	
Seagrasses	Survival	
	Calcification	
	Growth	
	Photosynthesis	
	Abundance	
Diatoms	Survival	
	Calcification	
	Growth	+17%
	Photosynthesis	+12%
	Abundance	

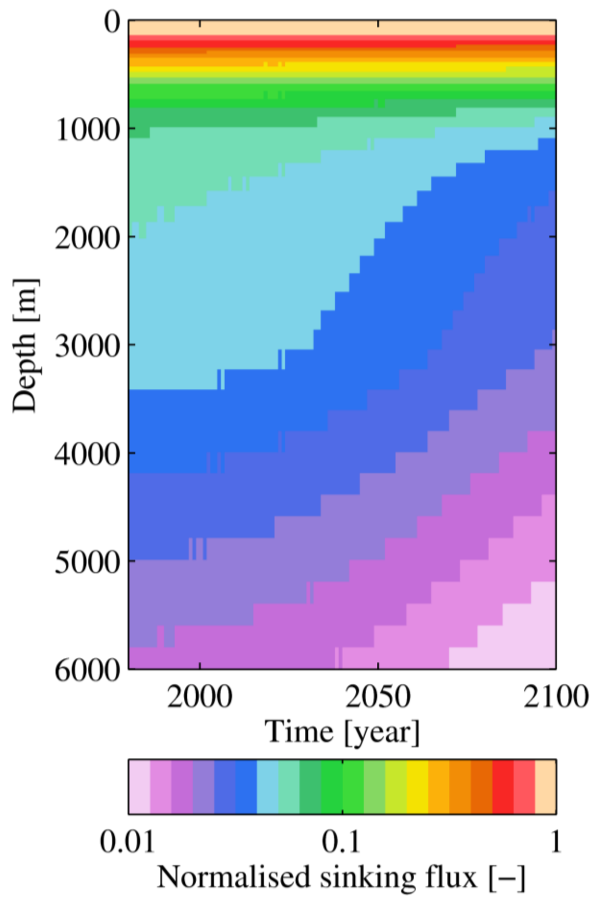
Not tested or too few studies
Enhanced <25%
95% CI overlaps 0
Reduced <25%
Reduced >25%

- Calcifying organisms show consistent reductions across indicators with OA
- Some organisms do better under OA
- There remain many unknowns (e.g. neurological effects in fish, etc.)

Kroeker et al., GCB, 2013

Ballasting breakdown





- Minor changes to BGC tracers
- BGC fluxes generally similar but with some exceptions
- Calcification: -56% → -17%
- Export, 1000m: -41% → -18%
- Deep sea communities may be impacted disproportionally by OA-driven change

Yool et al., Biogeosciences, 2013

Summary

- Acidification accompanies anthro CO2
- It has already been extensively observed and quantified
- There are a number of known impacts, of which calcification is well studied
- However, considerable uncertainty remains and the field remains an active research area

Geoengineering

Geoengineering

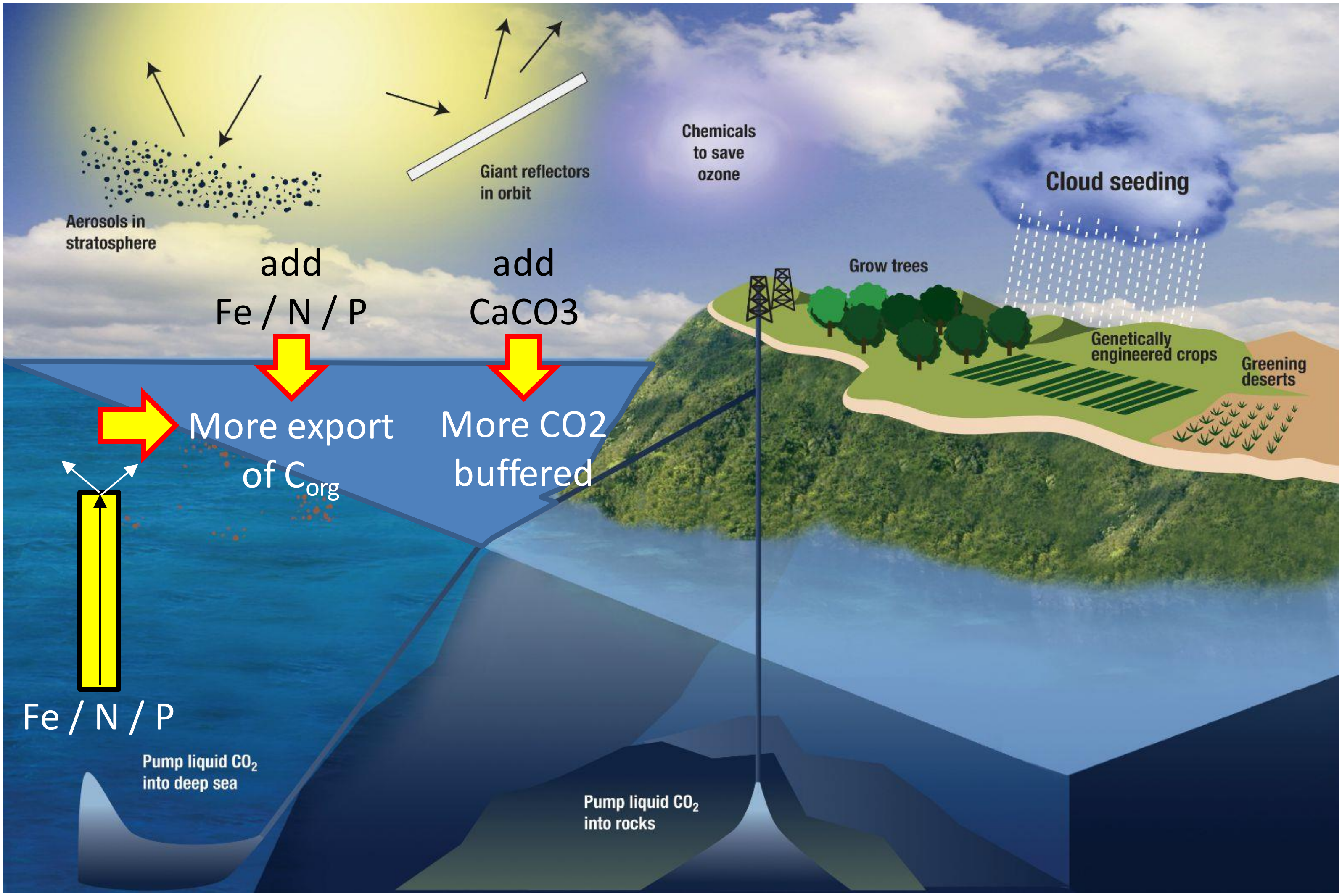
- As defined in the September 2009 report by the Royal Society, geoengineering is ...

“**The deliberate large-scale manipulation of the planetary environment to counteract anthropogenic climate change**”

- Geoengineering schemes include those that aim to directly affect incident radiation on the Earth’s surface (e.g. “space mirrors”, sulphate aerosols), and those that aim to reduce atmospheric pCO_2 (e.g. carbon capture and storage)
- Some schemes propose using the marine biota as a means to remove CO_2 from the atmosphere at a faster rate

Shepherd et al., 2010

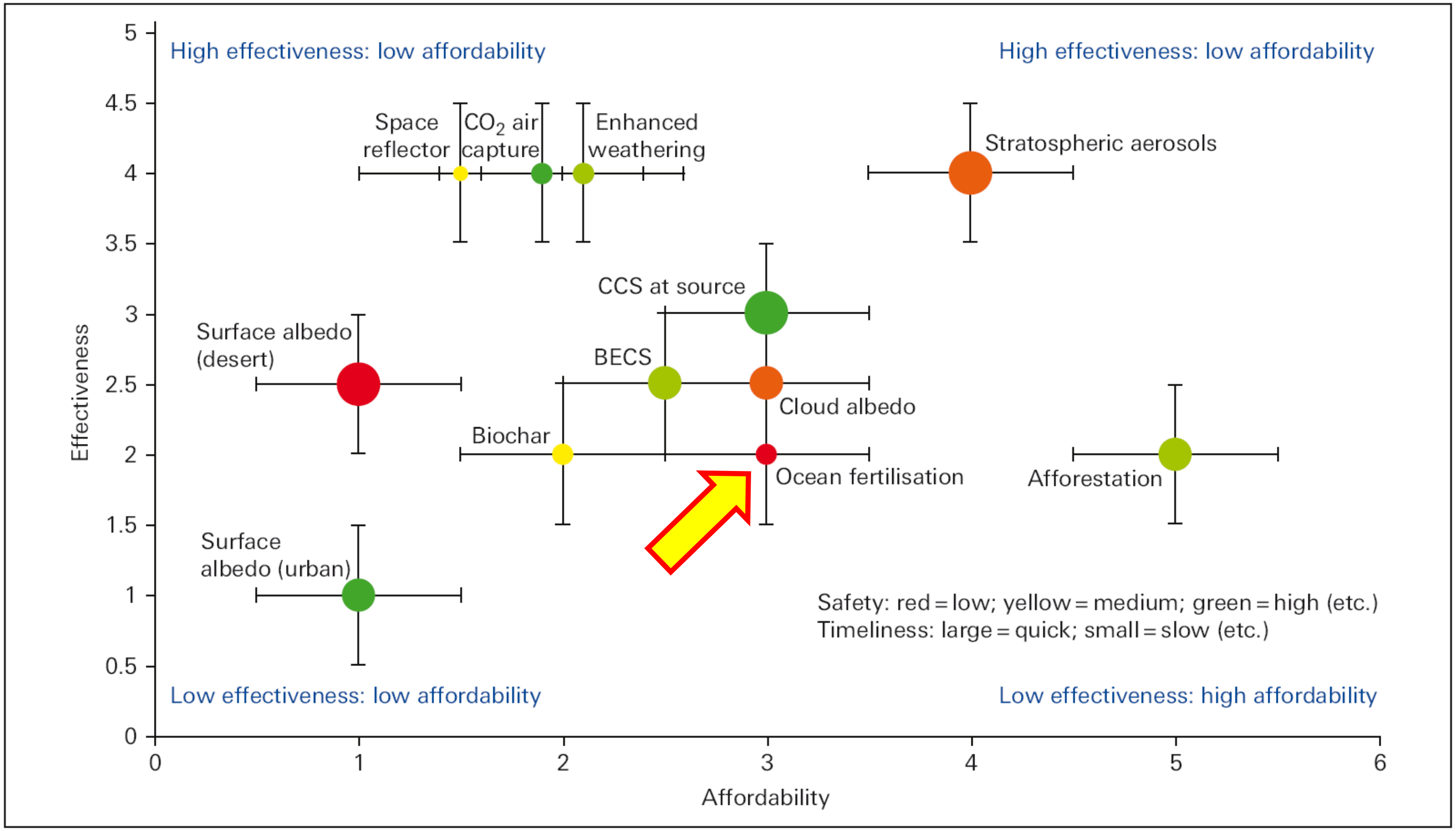
Schemes and dreams



Geoengineering via the ocean

- Principally through CO2-removal (CDR)
- Several distinct schemes have been proposed:
  - Iron fertilisation of marine productivity
  - Macronutrient fertilisation of marine productivity
  - Enhanced mixing to increase marine productivity
  - Alkalinity addition to increase chemical uptake

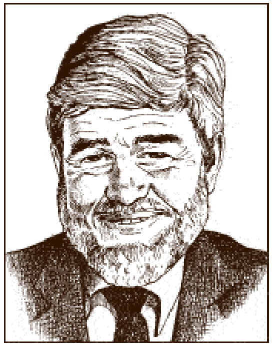
Bangs for bucks



Shepherd et al., 2010

“Give me a half tanker of iron …”

- Much of the ocean is limited by macronutrients, but in some locations these are plentiful but production by plankton is still low
- This apparent paradox was investigated during the 1980s and ultimately (after a lot of kicking and screaming) the micronutrient iron was implicated in why these macronutrients went unused
- John Martin (1935-1993) suggested that with an appropriate amount of iron, an ice age could be triggered



4 IRON CLAD REASONS
TO BUY SHARES OF PLANKTOS CORP. NOW!

1) The Discovery Channel, ABC News, FORBES Magazine, The New York Times, USA TODAY and The LA Times have all recently done exclusives on Planktos Corp. They're anxiously awaiting results. Once the Weatherbird II pulls back into port these news outlets will do ALL OF THE SELLING FOR THEM. Setting shares ablaze. You can't pay for that kind of exposure!

2) The Global Warming frenzy is reaching a fever pitch. Short of the Iraq War it's the #1 issue of the day. Even the most insignificant green companies today will return investors profits as "a rising tide lifts all boats..." At $1.25 a share you'd be crazy not to invest in Planktos.

3) The U.S. Supreme Court has just ruled the carbon dioxide (CO2) is a pollutant and as such falls under the jurisdiction of the EPA to regulate it. That means corporations will be forced to cut emissions – or find ways to offset them. That's remarkable news for Planktos Corp.

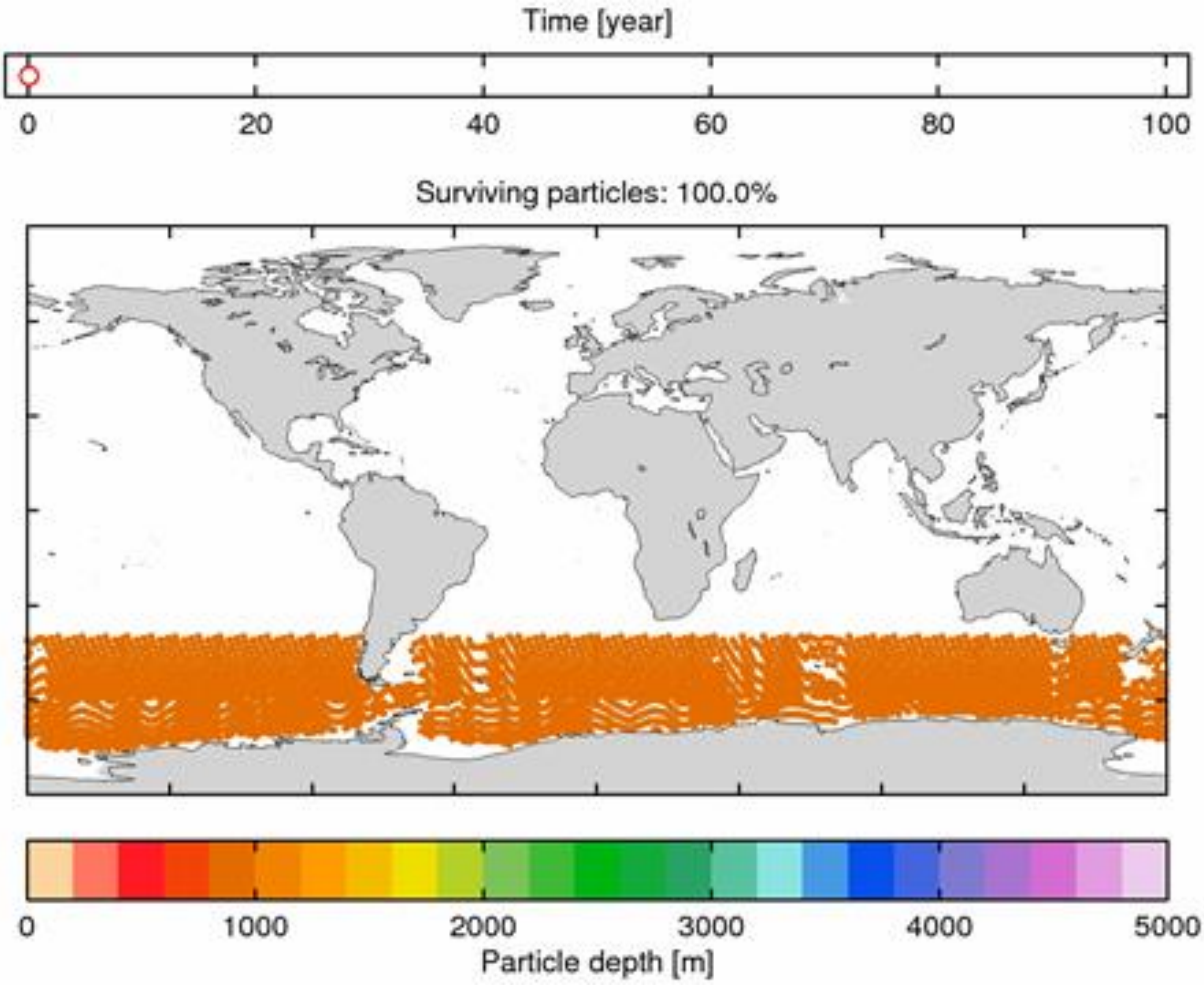
4) A $500 investment can transform into $12,000.. $20,000 or even more. At just $1.25 a share Planktos Corp. is truly a once-in-a-lifetime opportunity.

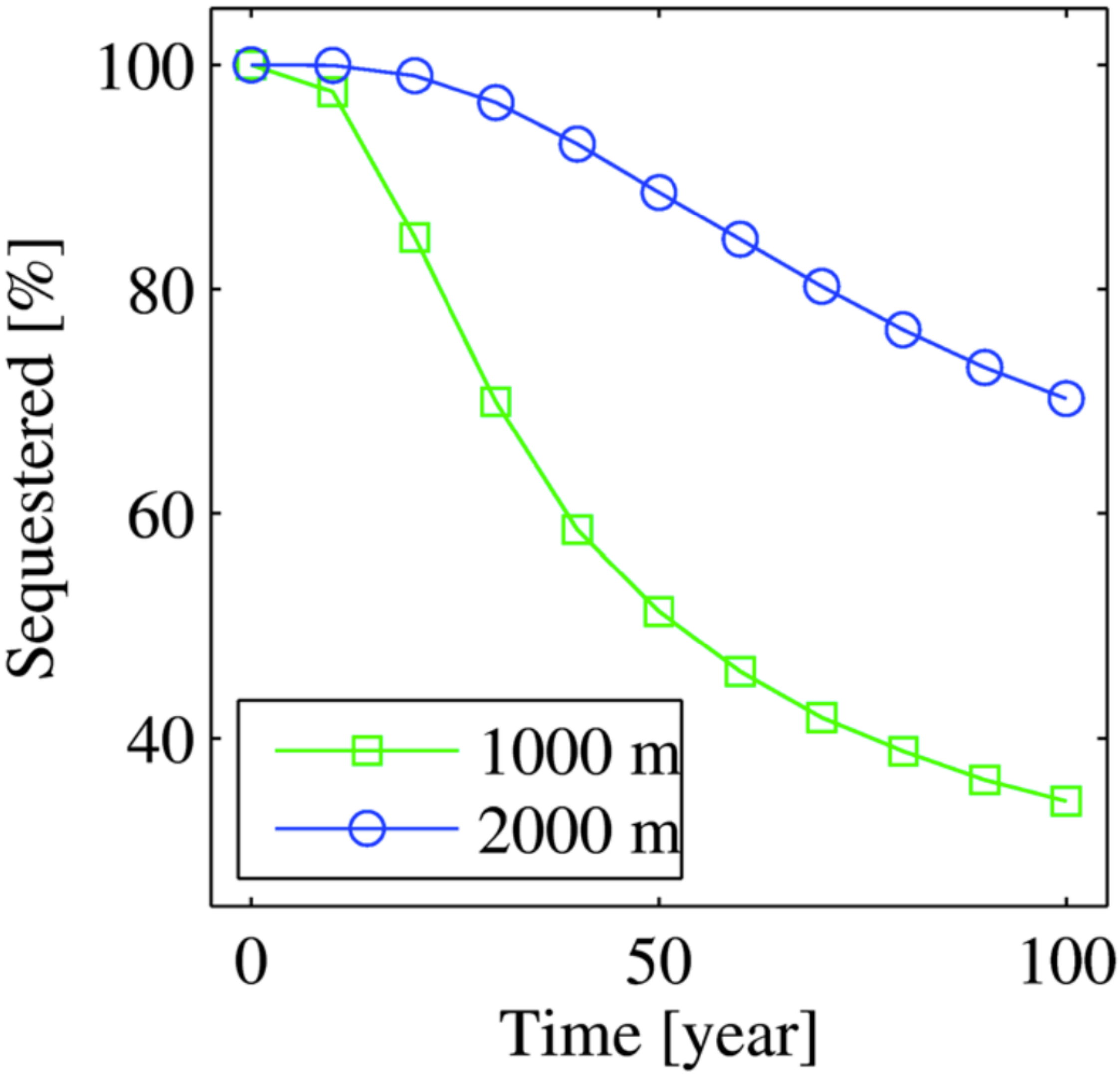
Planktos Corporation

What goes down …

- But even if production can be increased, does it always lead to more oceanic carbon storage?
- We investigated this by seeding the Southern Ocean of a model with carbon that has already reached 1000m to see how long it would stay down
- Our simulation used Lagrangian "particles" that could be transported in 3D and tracked to check on interactions with the ocean's surface

Robinson et al., *GRL*, 2014


Time [year]
0
20
40
60
80
100
Surviving particles: 100.0%
0
1000
2000
3000
4000
5000
Particle depth [m]

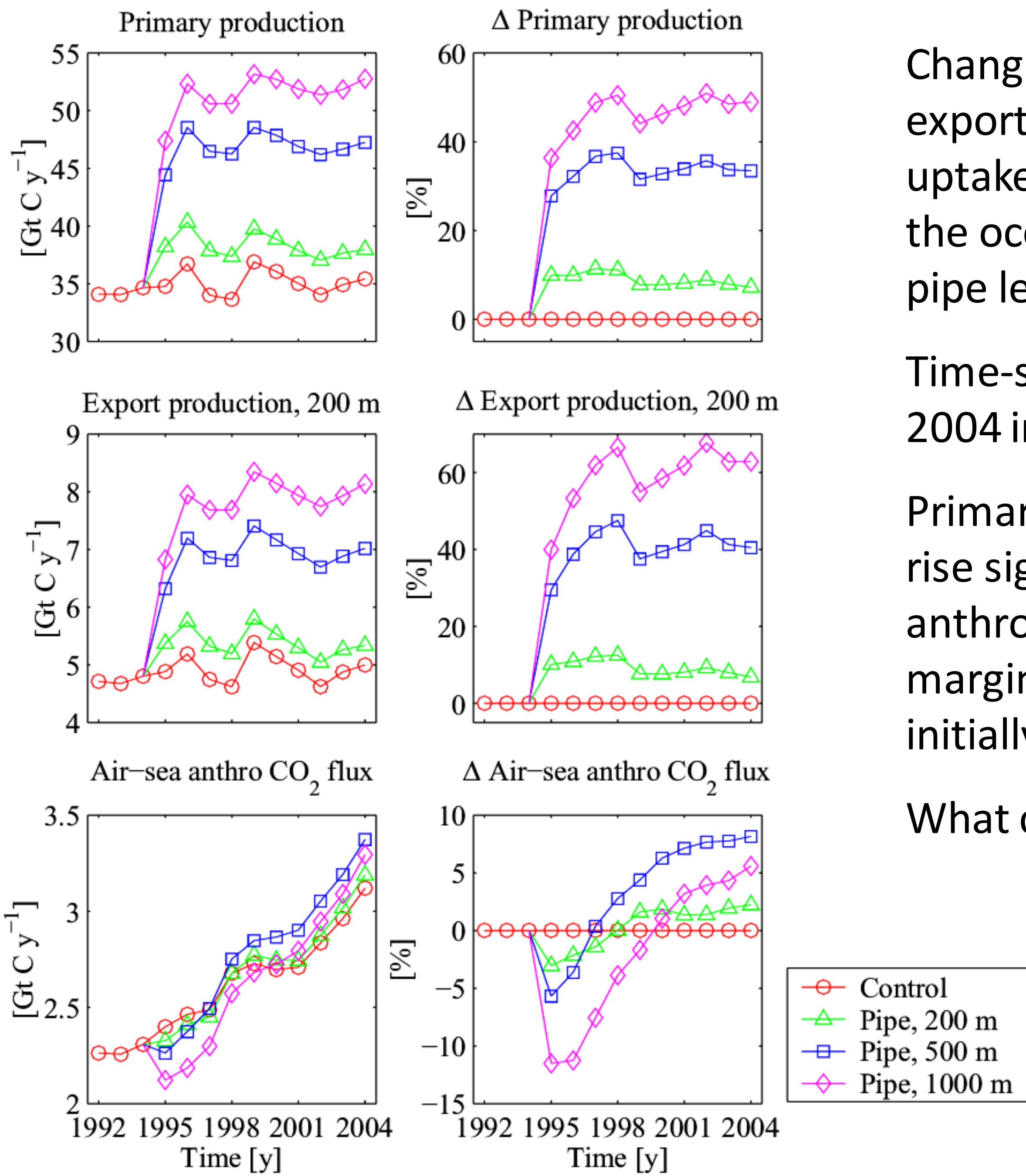


Although 1000m depth and the Southern Ocean are generally viewed as a good mix for successful geoengineering, within 100 years about 66% of the carbon put into the ocean had returned (mean lifetime of 37.8 years)

2000m improved things, but only to the tune of 29% return to the surface

Robinson et al., *GRL*, 2014

Atmocean Corporation



Changes in primary production, export production and the uptake of anthropogenic CO_2 by the ocean in response to three pipe lengths

Time-scale is recent past (1995-2004 inclusive)

Primary and export production rise significantly, but uptake of anthropogenic CO_2 only marginally increased (pipes initially *decrease* uptake)

What causes CO_2 response?

Yool et al., *JGR*, 2009

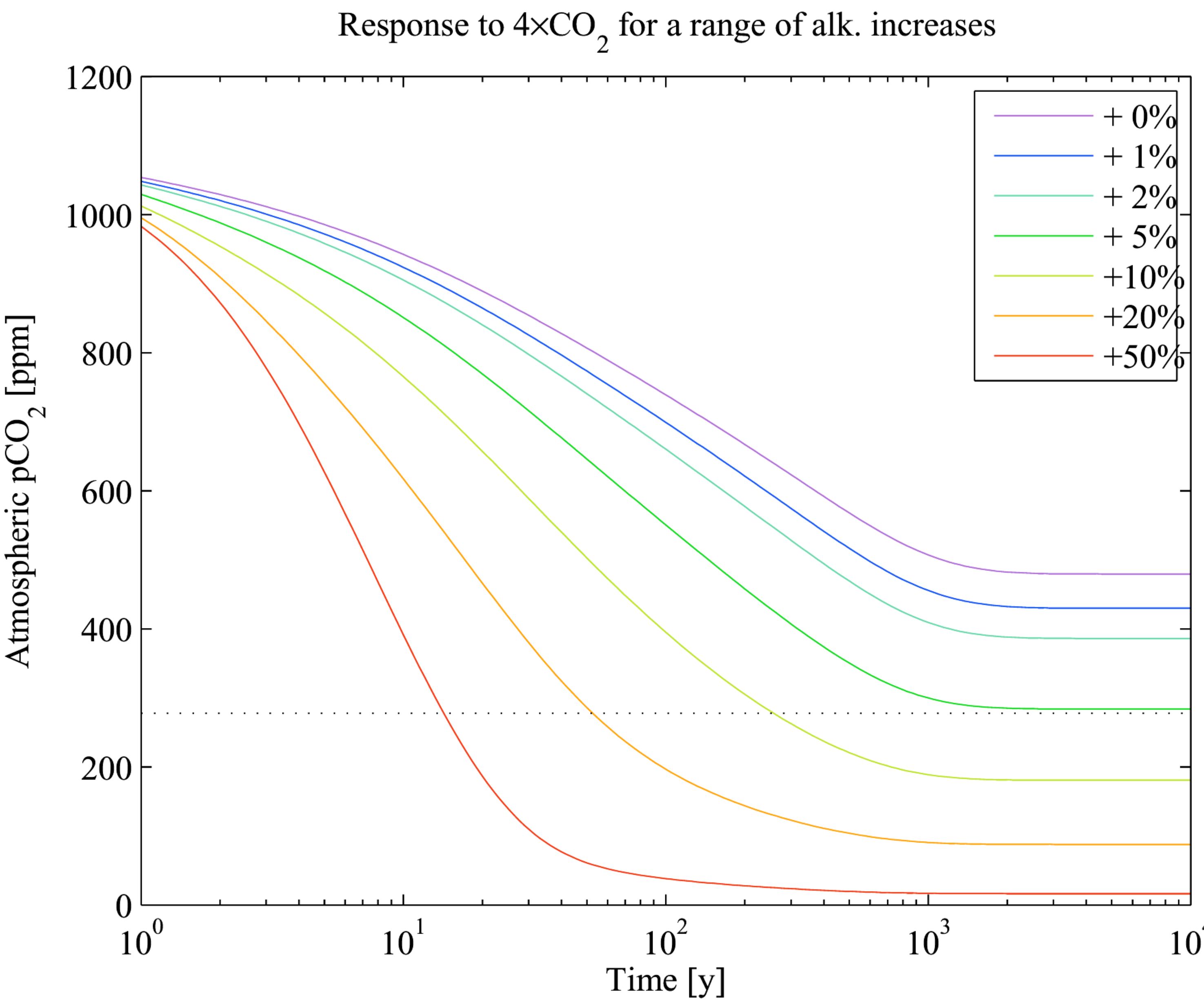
Present-day ocean uptake of anthropogenic CO_2 is approximately 2-3 Gt C y^{-1}. Given the simulated efficiency of the ocean pipes in the Tropics (where things work best), how many would be needed to increase this by 1 Gt C y^{-1}?

Area of tropics (30°S to 30°N)	= 173×10^6 km^2
Water pumped by 2 cm d^{-1} ocean pipes	= 3.46×10^{12} m^3 d^{-1}
Anthropogenic CO_2 uptake in tropics	= 0.343 Gt C y^{-1}
	= 0.939×10^{12} g C d^{-1}
Uptake per m^3 of pumped water	= 0.271 g C m^{-3}
Pumped water requirement for 1 Gt C y^{-1}	= 3.68×10^{15} m^3 y^{-1}
	= 1.01×10^{13} m^3 d^{-1}
Single ocean pipe pump rate	= 13×10^3 m^3 d^{-1}
Pipes required for 1 Gt C y^{-1}	= **776×10^6**
	= 609 km^2
	= a **lot** of pipes

Yool et al., *JGR*, 2009

Alkalinity addition

- Increasing ocean alkalinity would increase ocean buffering capacity for anthro CO_2
- Why not add lots of $CaCO_3$ to the ocean to draw anthro CO_2 out of the atmosphere where it's causing climate change?
- Two key considerations:
  - Time scale
  - Quantity of $CaCO_3$



5% gets back to 278 ppm

How much is 5%?

total ocean alkalinity	=	3.27×10^{18} eq
5% of this	=	1.64×10^{17} eq
(riverine input	=	4.66×10^{13} eq / y)
$CaCO_3$ required	=	8.18×10^{16} mol
		(assuming 1 mol $CaCO_3$ = 2 eq alk)
	=	8.18×10^{18} g
		(assuming 100.09 g / mol)
	=	8.18×10^{3} Pg
	=	3.02×10^{18} cm^3
		(assuming 2.71 g / cm^3)
	=	3.02×10^{3} km^3

The final number is equivalent to a 1 km wide by 1 km deep strip of land stretching from Seattle (Washington) to Houston (Texas)

Alkalinity schemes more commonly suggest "enhanced weathering" of rocks

Summary

- The ocean offers several prospects for CDR geoengineering
- Typically, these envisage enhancing the biological pump to draw down CO2 and isolate it from the atmosphere for extended period
- However, ocean sequestration is not efficient (*) both because the ocean is "leaky" and much of the extra biological productivity is recycled
- Qualitatively these work, but quantitatively they can scale poorly

Summary Summary

- The majority of the Earth system's "labile" carbon is in the ocean; it gets there through physico-chemical and biological routes
- About a third of anthro CO2 emissions enter the ocean, but detecting it is not an exact science
- Anthro CO2 is measurably acidifying the ocean, but its impacts are less clear than originally expected
- Ocean geoengineering schemes can work, but always pay attention to efficiency and scalability

Questions?

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