Foto: L. Tadday

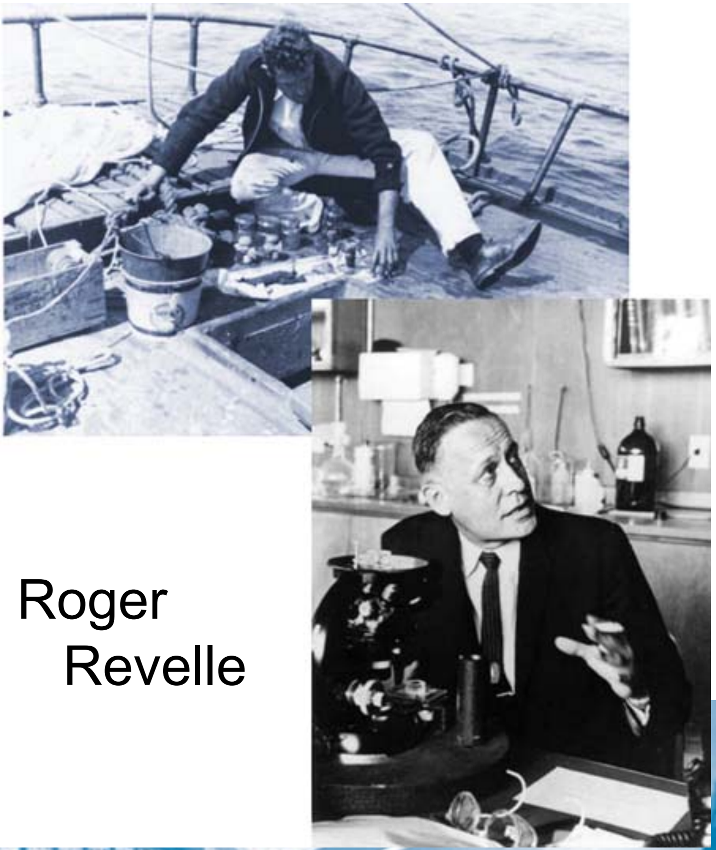
CO_2 sequestration in the ocean

Dieter Wolf-Gladrow
Alfred Wegener Institute for Polar and Marine Research
Bremerhaven, Germany

ERCA, Grenoble 3 February 2011

CO_2 emissions: A large scale geophysical experiment (Revelle & Suess, 1957)

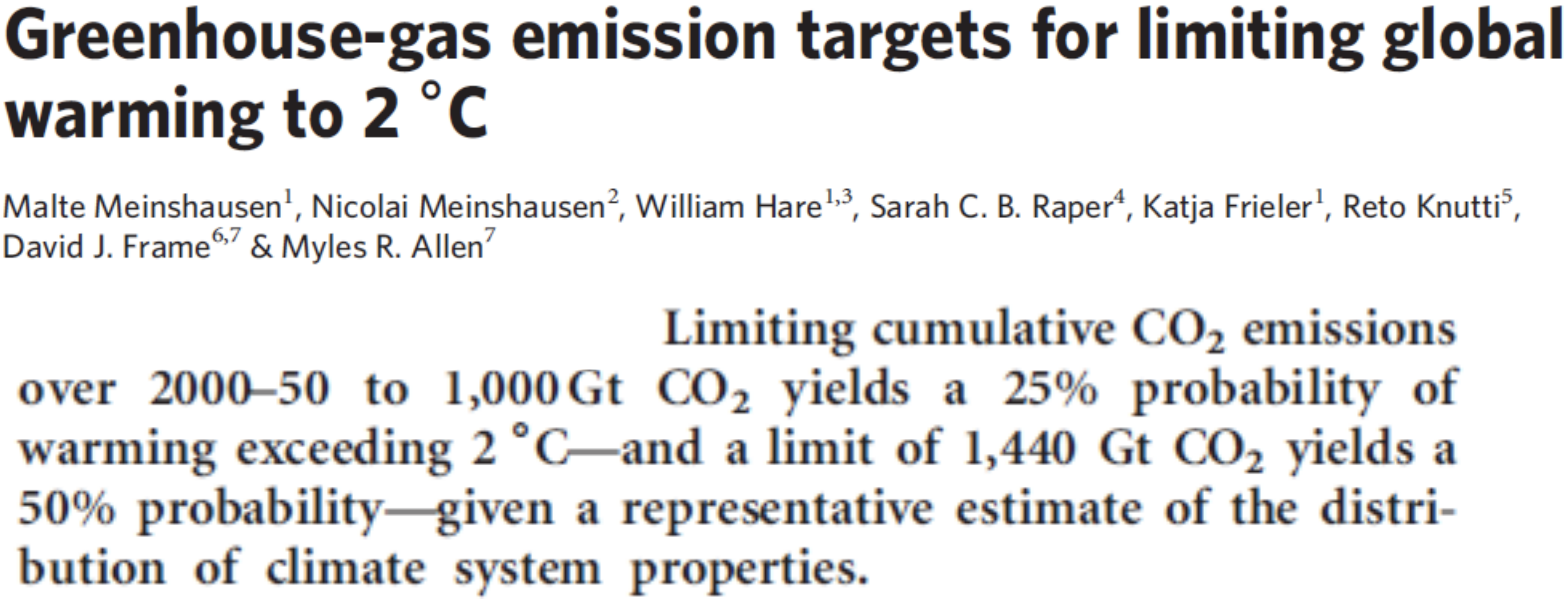
"Human beings are now carrying out a large scale geophysical experiment of a kind that could not have happened in the past nor be reproduced in the future."



Roger
Revelle

Hans Suess in 1972

The 2°C warming target
CO_2 emissions: less than 205 Gt C until 2050



Greenhouse-gas emission targets for limiting global warming to 2 °C

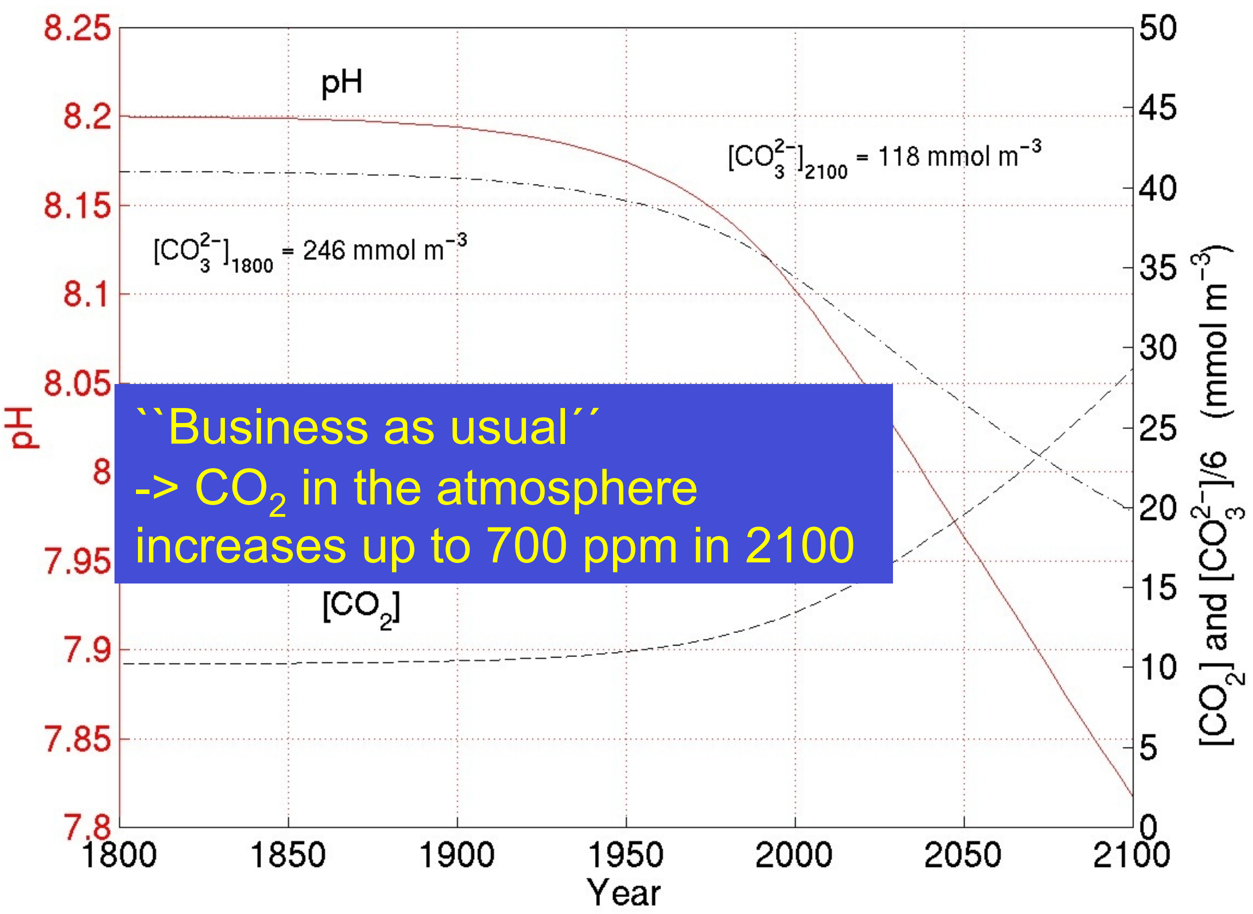
Malte Meinshausen[1], Nicolai Meinshausen[2], William Hare[1,3], Sarah C. B. Raper[4], Katja Frieler[1], Reto Knutti[5], David J. Frame[6,7] & Myles R. Allen[7]

Limiting cumulative CO_2 emissions over 2000–50 to 1,000 Gt CO_2 yields a 25% probability of warming exceeding 2 °C—and a limit of 1,440 Gt CO_2 yields a 50% probability—given a representative estimate of the distribution of climate system properties.

Between 2000 and 2050: < 1000 Gt CO_2 = 273 Gt C
Between 2010 and 2050: < 750 Gt CO_2 = 205 Gt C
Current emission: ≈ 9 Gt C yr^{-1} -> ≈ 20 years

3.67 g CO_2 = 1 g C

It‘s not just warming: Ocean acidification



``Business as usual´´
-> CO_2 in the atmosphere increases up to 700 ppm in 2100

drow et al., Tellus, B51(2), 461-476, 1999.

Advantage for algae: higher CO_2 concentration

Problems for calcifying organisms: $CaCO_3$ dissolves at low pH

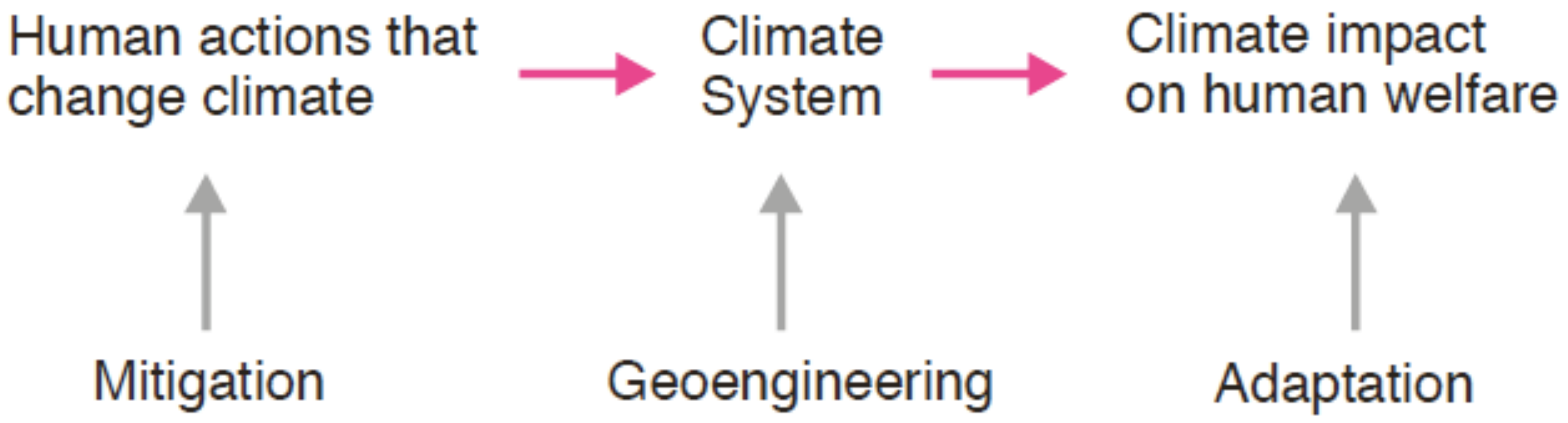
Physiology of marine organisms

Ecosystems: change in species assemblage & function

Significant decreases in ocean sound absorption -> noisier, whales

Limacina retroversa australis (pteropod, ca. 2 mm), Southern Ocean, aragonite ($CaCO_3$) (Foto: Wolf-Gladrow)

Mitigation/Geoengineering/Adaptation
Climate-engineering



Human actions that change climate → Climate System → Climate impact on human welfare

Mitigation

Geoengineering

Adaptation

Climate-engineering

(Source: David Keith)

Mitigation/Adaptation/Geoengineering

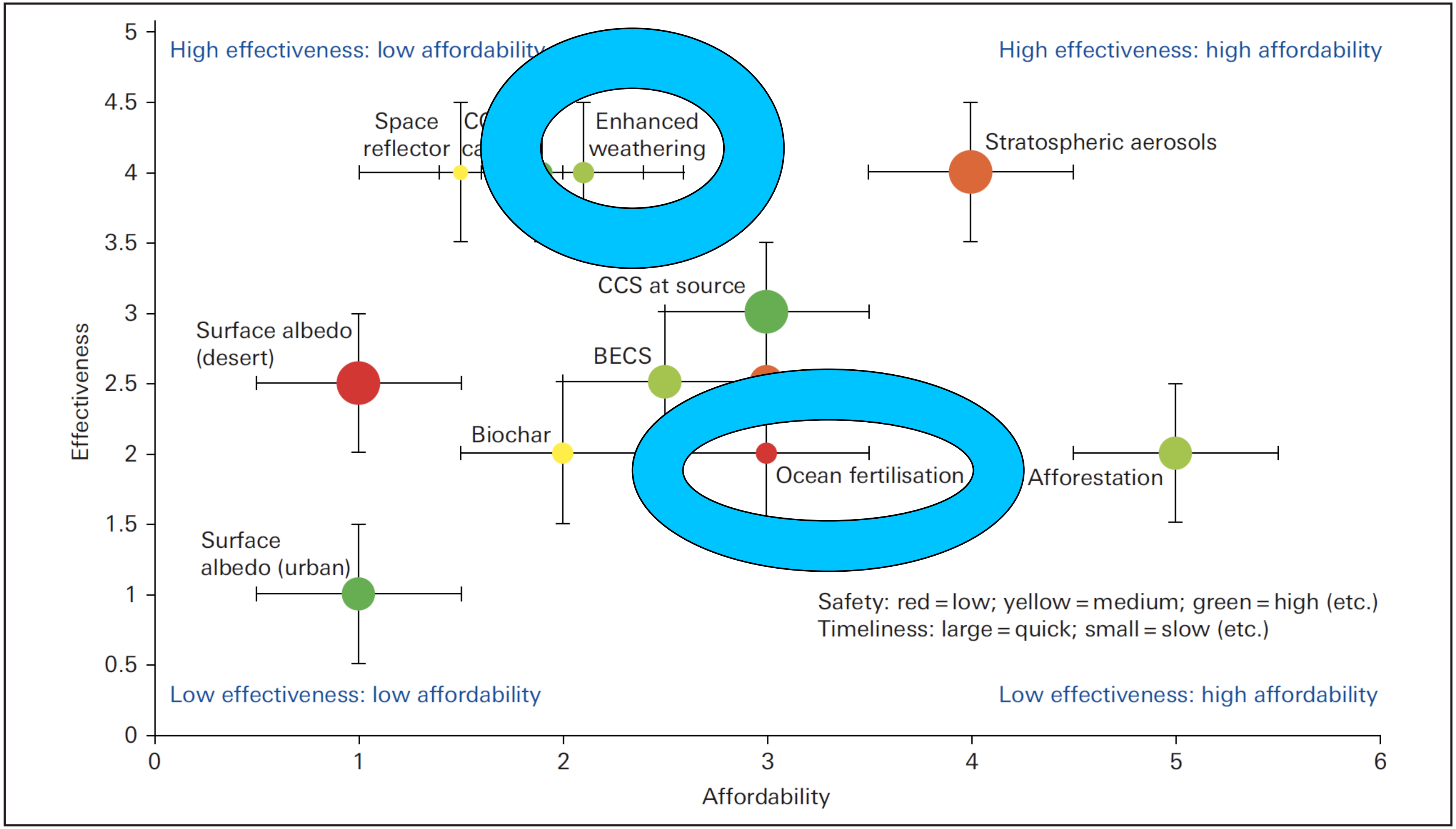
Mitigation: `activities that reduce anthropogenic emissions of greenhouse gases (particularly CO_2)´ (Lenton and Vaughan, 2009)

Adaptation: ... build a house against rain & storm ...,
... floating cities (for our Dutch neighbors) ...

Geoengineering: `large-scale engineering of our environment in order to combat or counteract the effects of changes in atmospheric chemistry´ (NAS, 1992)
+ ocean (acidification)

Effectiveness versus Affordability
Royal Society Report 2009

Figure 5.1. Preliminary overall evaluation of the geoengineering techniques considered in Chapters 2 and 3.



Outline

1. Motivation

2. The global carbon cycle & CO_2 in seawater

3. Ocean iron fertilization

   What is the potential? Will it be effective? Side effects?

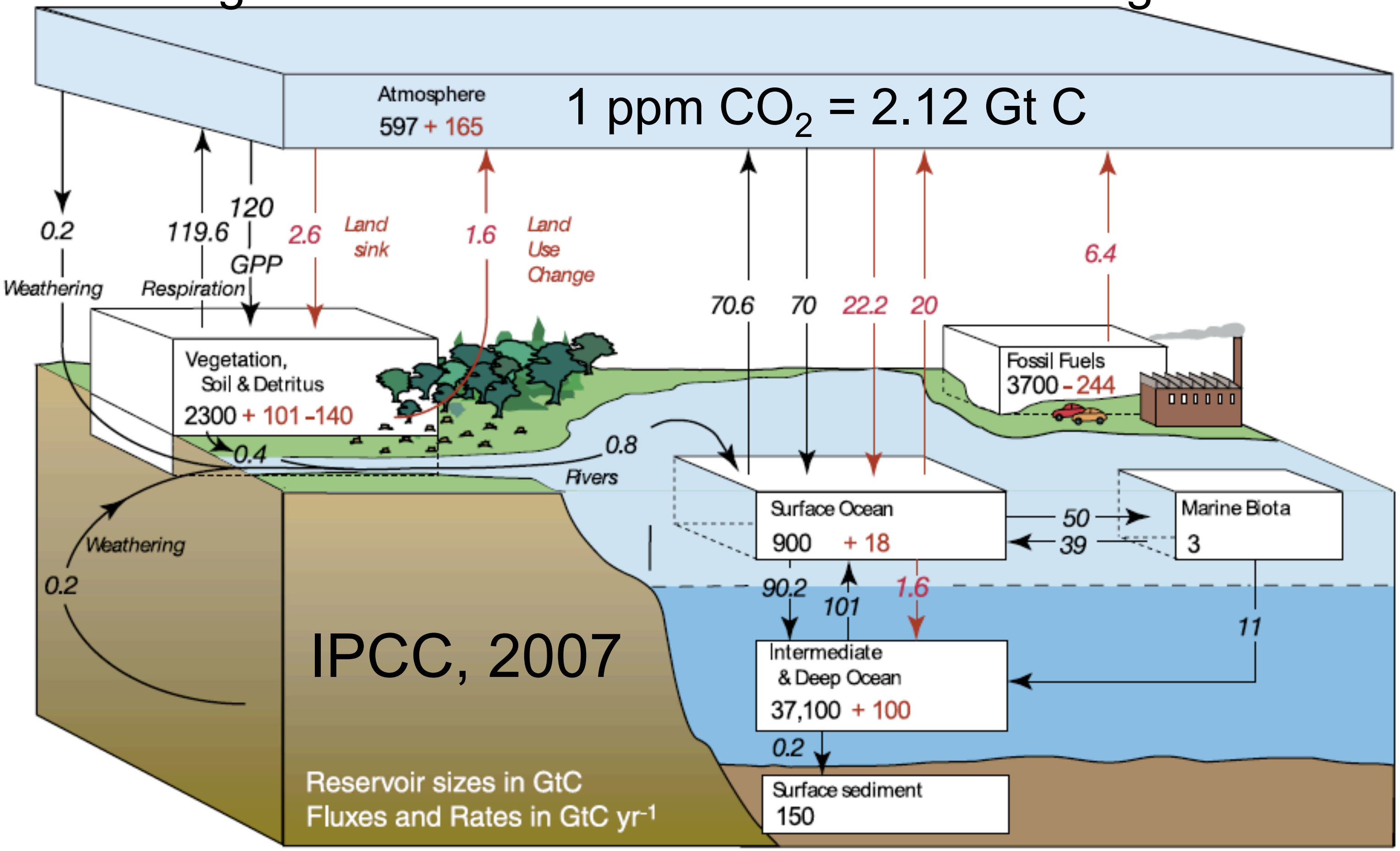
4. Enhanced weathering

   What is the potential? Will it be effective? Side effects?

5. Final remarks

The Global Carbon Cycle: Preindustrial and in the 1990s

1 Pg C = 1 Gt C = 1 000 000 000 t C = 10^{15} g C



1 ppm CO_2 = 2.12 Gt C

IPCC, 2007

3 active reservoirs: atmosphere, land biota & soils, ocean (= largest reservoir)

Natural fluxes are large (100 Pg C yr^{-1})

Anthropogenic CO_2 fluxes: different quality (not balanced)

3.67 g CO_2 = 1 g C

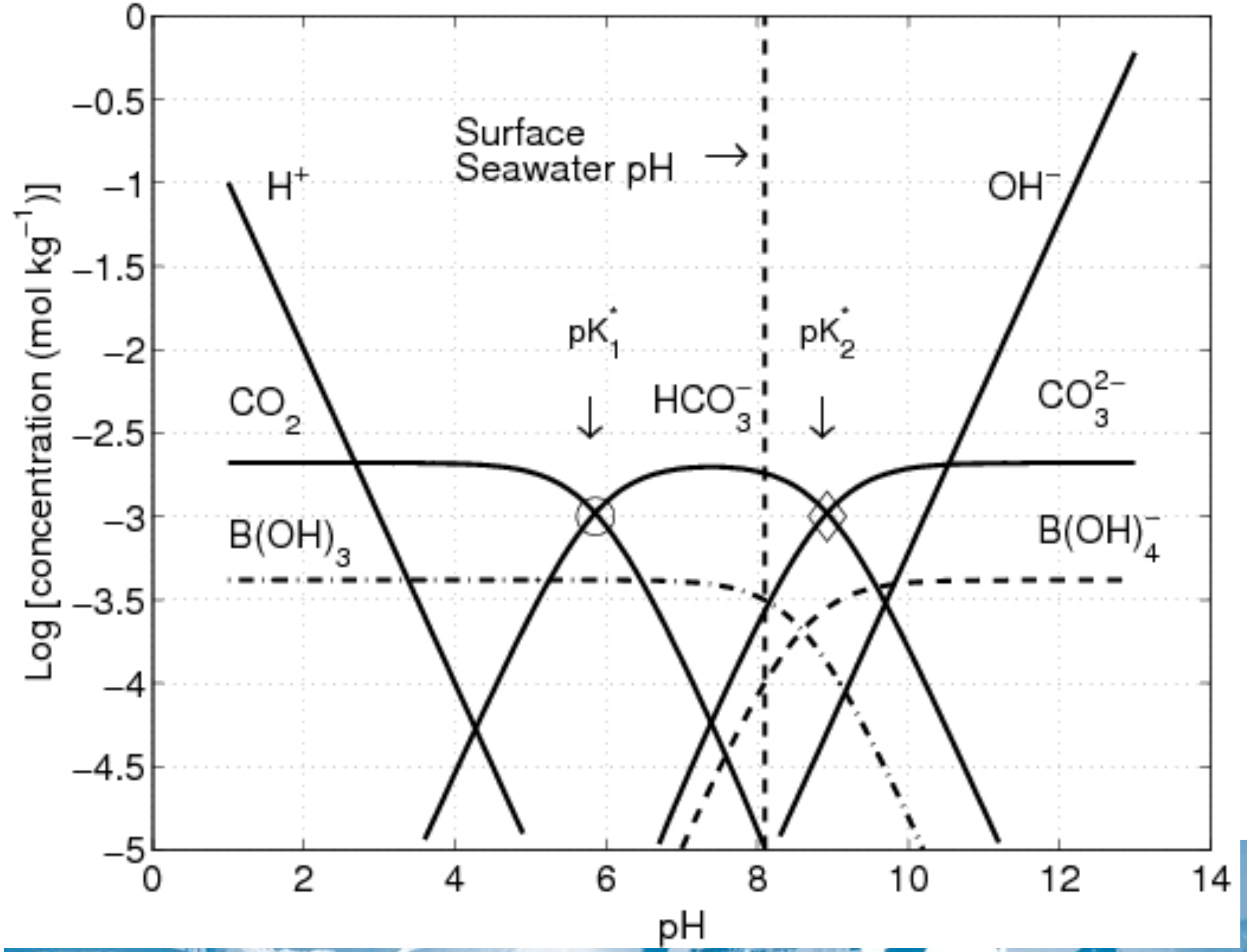
Why does CO_2 in the atmosphere-ocean system behave so much differently from O_2 or N_2?

In contrast to N_2 and O_2 most C of the combined atmosphere-ocean system is dissolved in seawater. Why is CO_2 so different?

When CO_2 dissolves in seawater it reacts with water ($CO_2 + H_2O$) and forms H_2CO_3 (true carbonic acid) that dissociates into HCO_3^- (bicarbonate) and H^+ ('protons' in the slang of marine chemists).

-> Addition of CO_2 to the ocean leads to creation of H^+ und thus to ocean acidification ('the other CO_2 problem').

Bjerrum plot
(Zeebe & Wolf-Gladrow, 2001)



Ocean acidification: shift to the left (lower pH) -> more CO_2, more HCO_3^-, less CO_3^{2-}

C in the ocean: in which form?

DIC = dissolved inorganic carbon = $[CO_2] + [HCO_3^-] + [CO_3^{2-}]$

= 98% of all C in the ocean

CO_2	dissolved gas, $CO_2(aq)$	1% of DIC	300 Pg C
HCO_3^-	bicarbonate	90% of DIC	34300 Pg C
CO_3^{2-}	carbonate ions	9% of DIC	2700 Pg C

DOC = dissolved organic carbon	700 Pg C
C in marine biota	3 Pg C

DIC distribution in the ocean

Takahashi, T. 1989. The carbon dioxide puzzle. Oceanus, 32: 22-29.

DIC

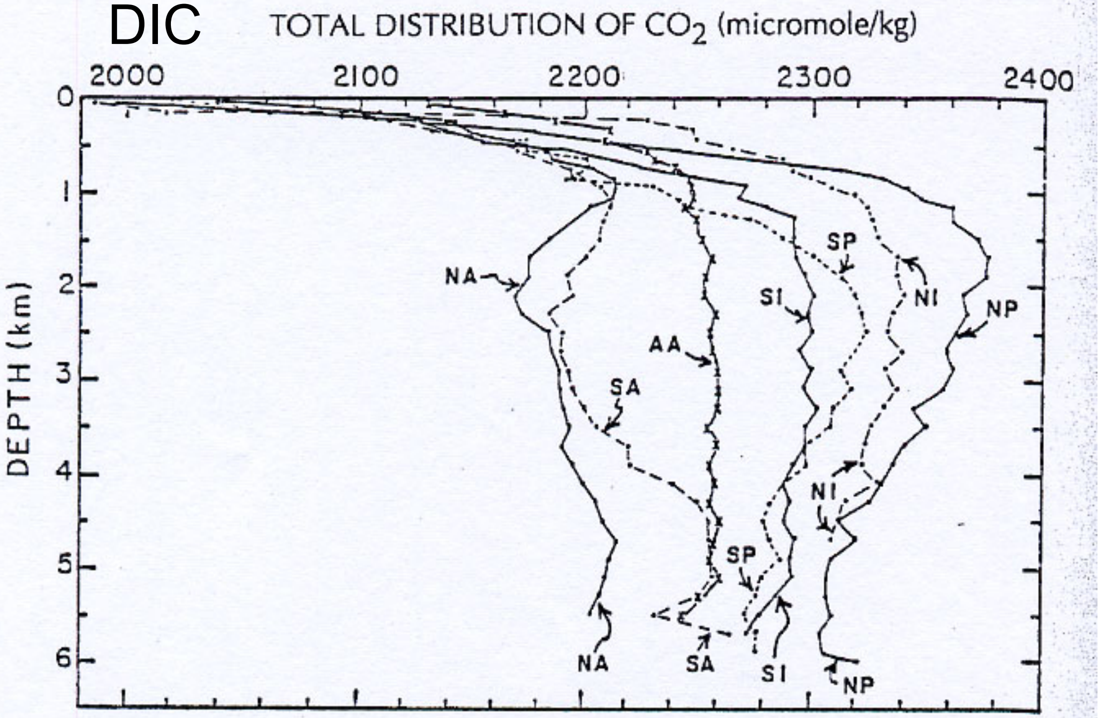


Figure 1. Depth distribution of the total CO_2 concentration in the global oceans. NA & SA = North & South Atlantic; NP and SP = North and South Pacific; NI and SI = North and South Indian Oceans; and AA = Antarctic ocean.

Inhomogeneous distribution: from < 2000 μmol kg^{-1} up to almost 2400 μmol kg^{-1} , i.e. 20% variation

1. Low concentrations in surface ocean.
2. Maxima at intermediate depths.
3. Increase from North Atlantic to Southern Ocean to North Pacific.

How to explain this distribution?

Which processes create inhomogeneous DIC distribution? I. Physical or solubility pump

Mixing in the ocean (up to 1000 years) is much slower than in the atmosphere (1 year between hemispheres)

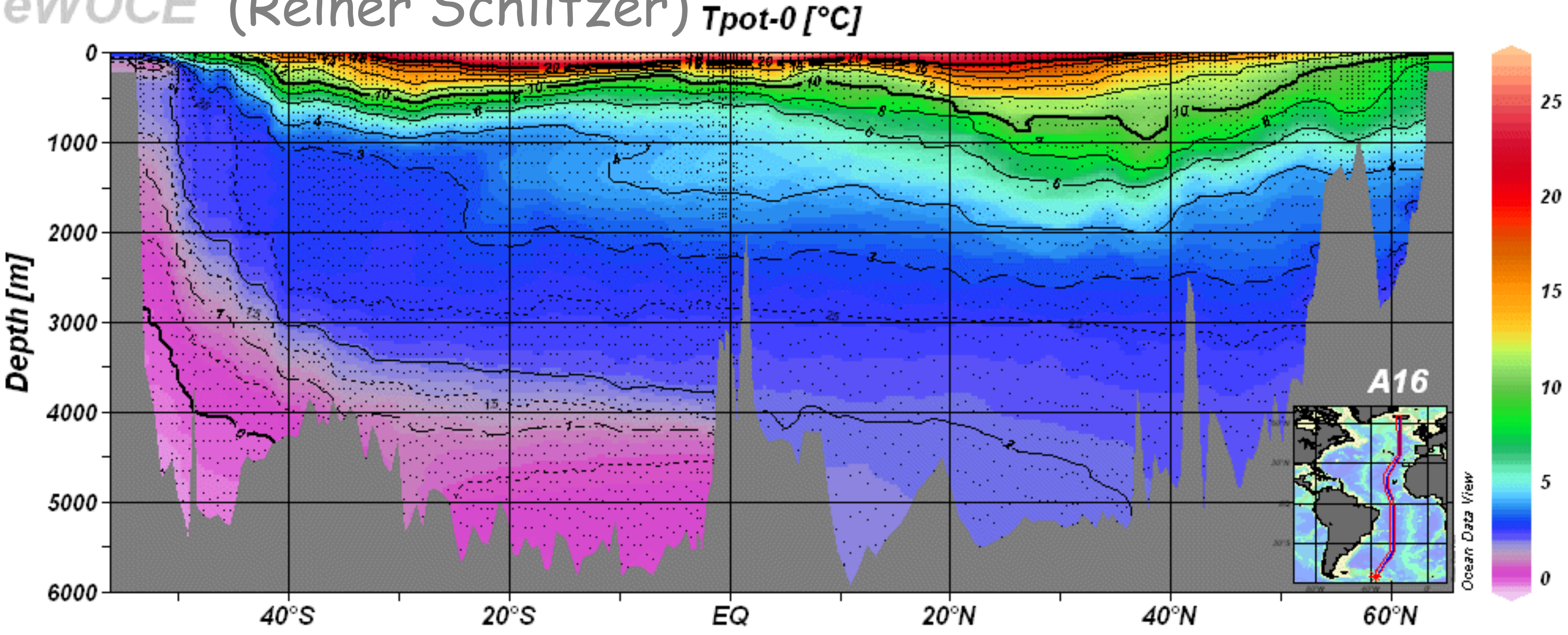
Pump: transport against the concentration gradient, i.e. from surface ocean to intermediate and deep layers.

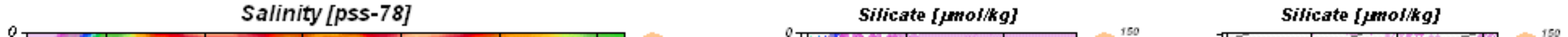
1: Physical or solubility carbon pump:
The solubility of CO_2 is higher in cold than in warm water
-> more CO_2 and DIC in cold water
+ circulation: deep water formation in cold regions, deep ocean is cold and rich in DIC

Most of the ocean is cold

The warm water sphere is restricted to a thin surface layer.
... most of the ocean is cold (< 5°C) and rich in DIC

eWOCE (Reiner Schlitzer)





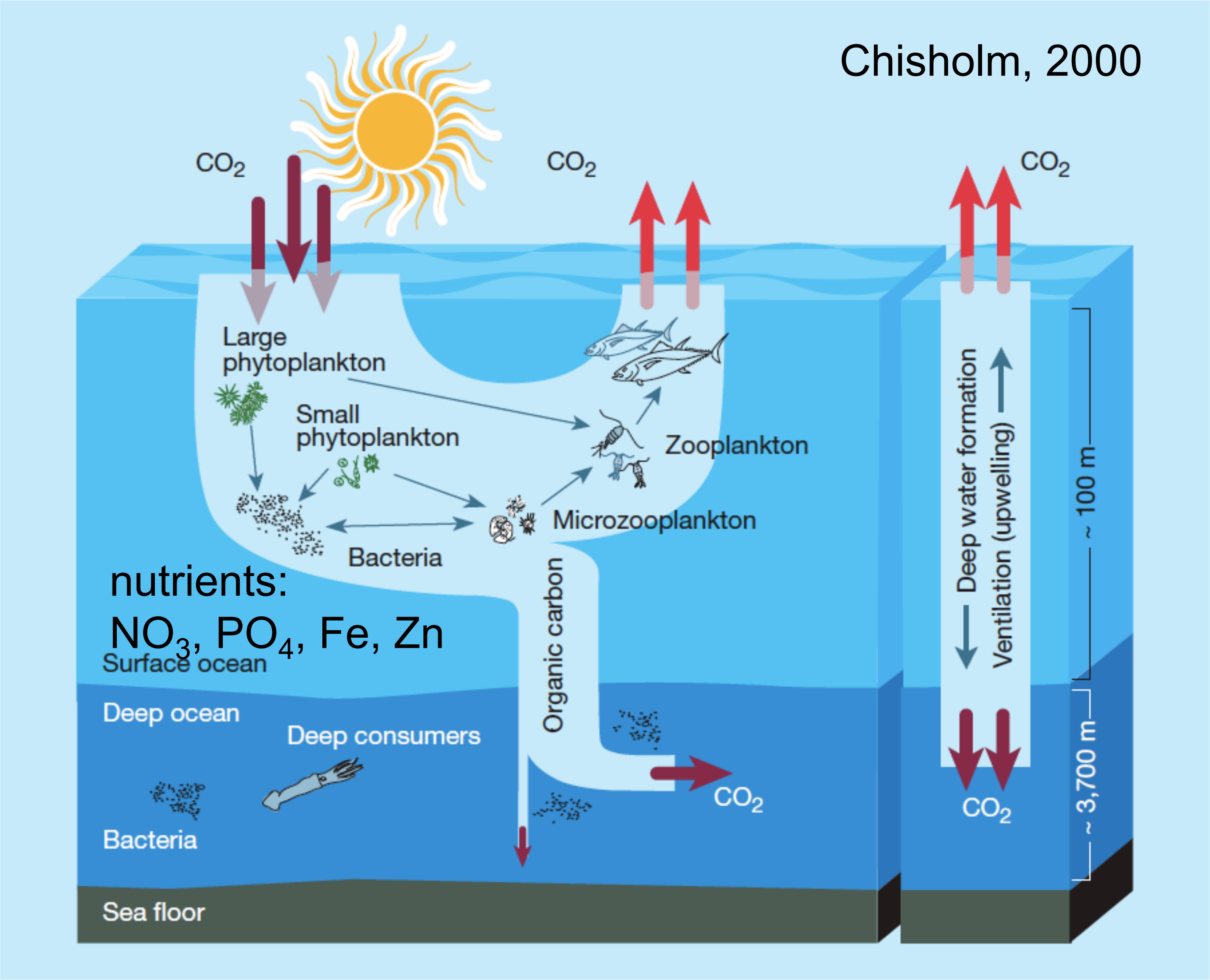
Which processes create inhomogeneous DIC distribution? II. Biological C pumps

1. Soft tissue pump: production of organic material in the surface ocean by phytoplankton (microalgae, size 2-50 μm), transport (export) to deeper layers in the form of algal aggregates or faecal pellets and remineralisation (oxidation, release of CO_2) at depth by zooplankton and bacteria.

2. **Calcium carbonate ($CaCO_3$) pump**: production of $CaCO_3$ by coccolithophores (calcifiying microalgae), foraminifera (protozoa), pteropods (marine snails, ‘butterflies of the sea’), export and dissolution at depth (release of DIC) or accumulation in sediments.

The biological pumps are complex and difficult to describe quantitatively (geochemists would be happy if one could ignore ‘biology’). However, 75% of the vertical DIC gradient is due to the biological pumps.

The carbon pumps



Chisholm, 2000

nutrients:
NO_3, PO_4, Fe, Zn

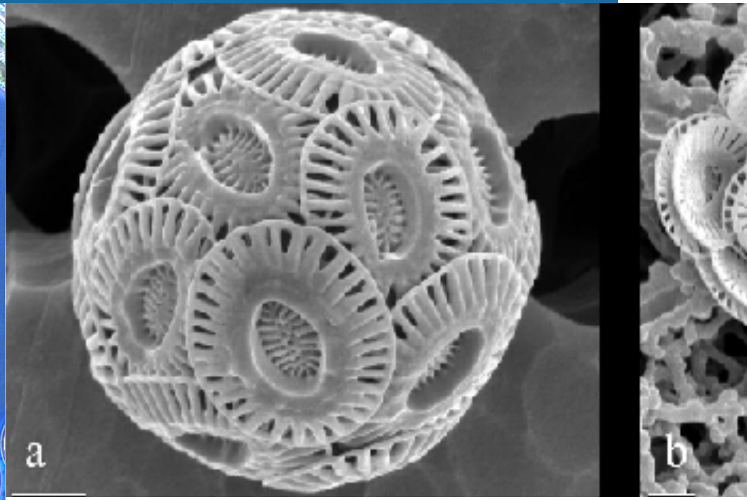
Biological C pumps: some of the key players!

Coscinodiscus oculus-iridis (diatom)

foraminifera

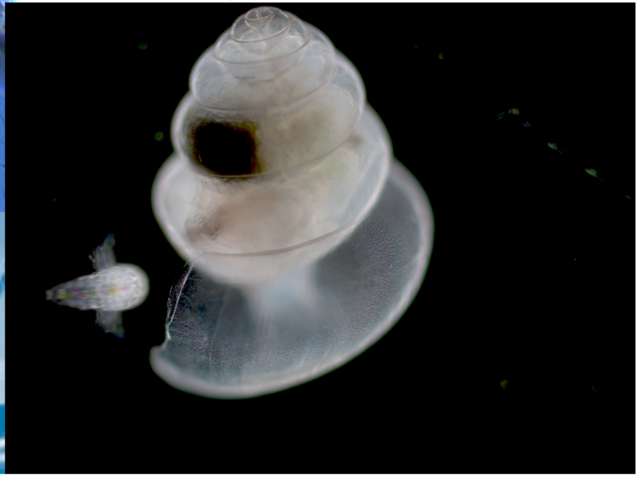
Fragilariopsis kerguelensis (diatom)

Emiliania huxleyi (coccolithophore)

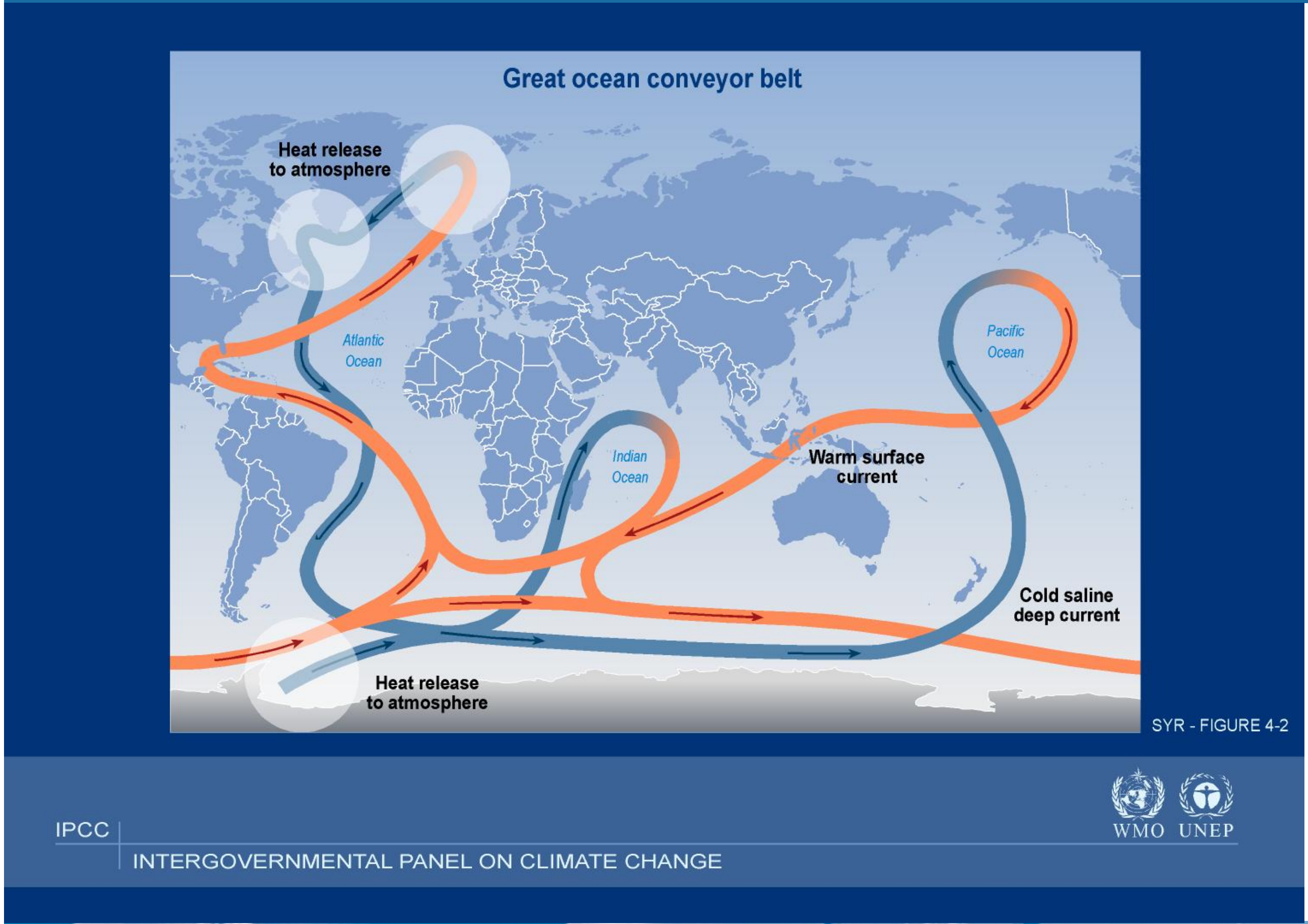


... and many more

Limacina retroversa australis (pteropod, ca. 2 mm),



Which processes create inhomogeneous DIC distribution? Great ocean conveyor belt*



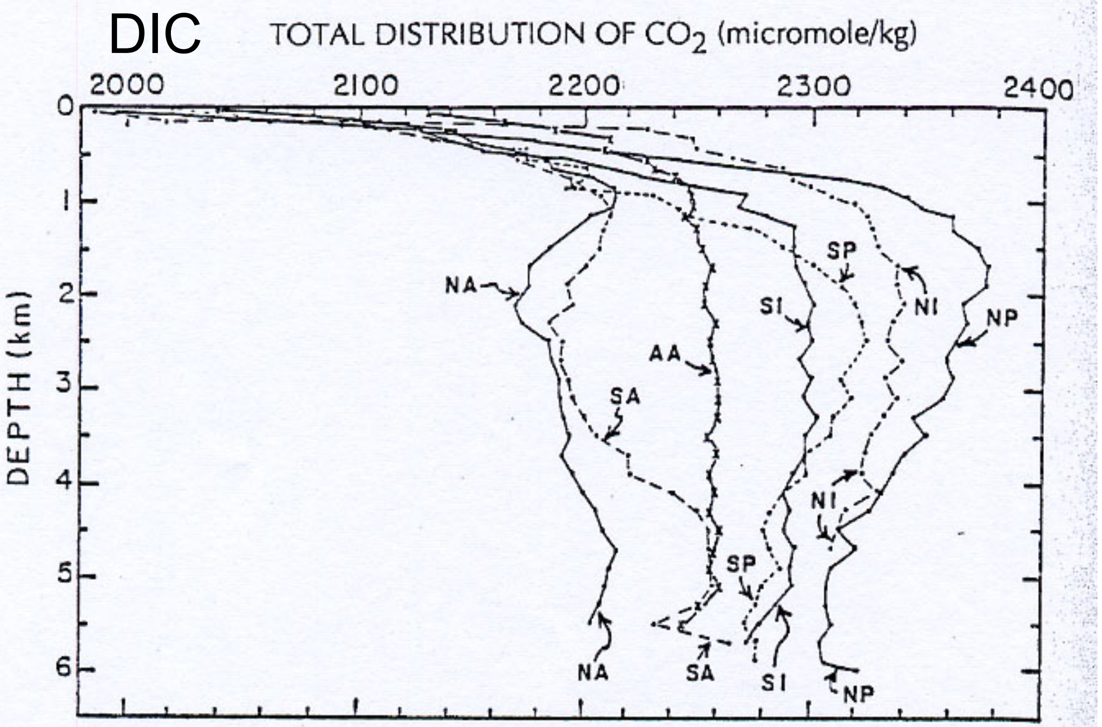
Biological
C pumps
⇒
DIC at depth
increases
along the
conveyor belt
from the
Atlantic
to the
Pacific

---

*For a critical view of the ‘conveyor belt’ see, for example,
Wunsch, C., Towards understanding the Paleocean, Quaternary Science Reviews, 29, 1960-1967, 2010.
Lozier, M.S., Deconstructing the Conveyor Belt, Science, 328, 1507-1511, 2010.

DIC distribution in the ocean

Takahashi, T. 1989. The carbon dioxide puzzle. Oceanus, 32: 22-29.



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CO_2 in seawater: take-home message

3 chemical species: CO_2, HCO_3^-, CO_3^{2-}

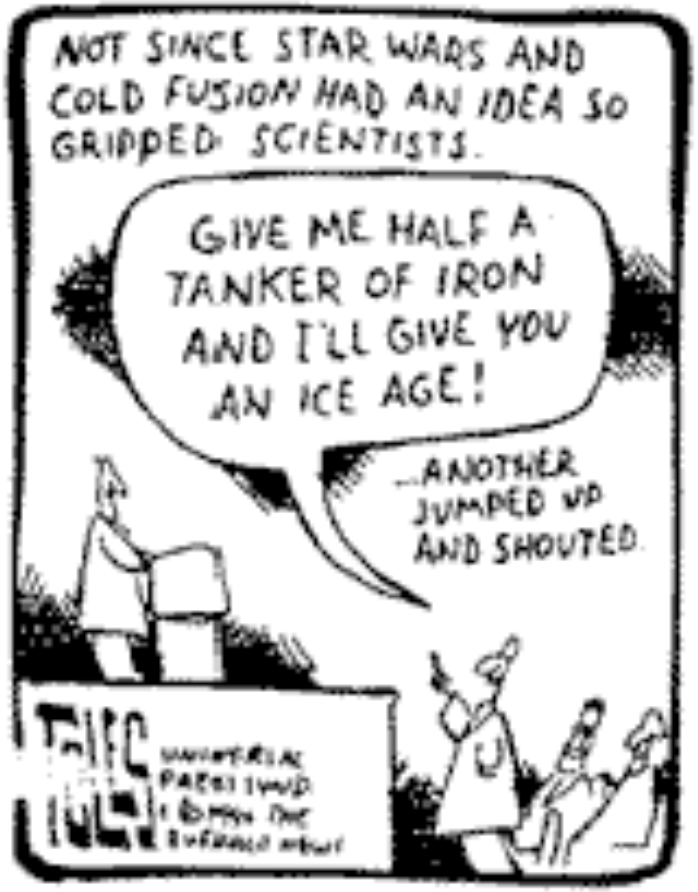
DIC, TA

C-pumps:
1. physical (CO_2 solubility varies with temperature & ocean circulation)
2. biological (soft-tissue, $CaCO_3$)

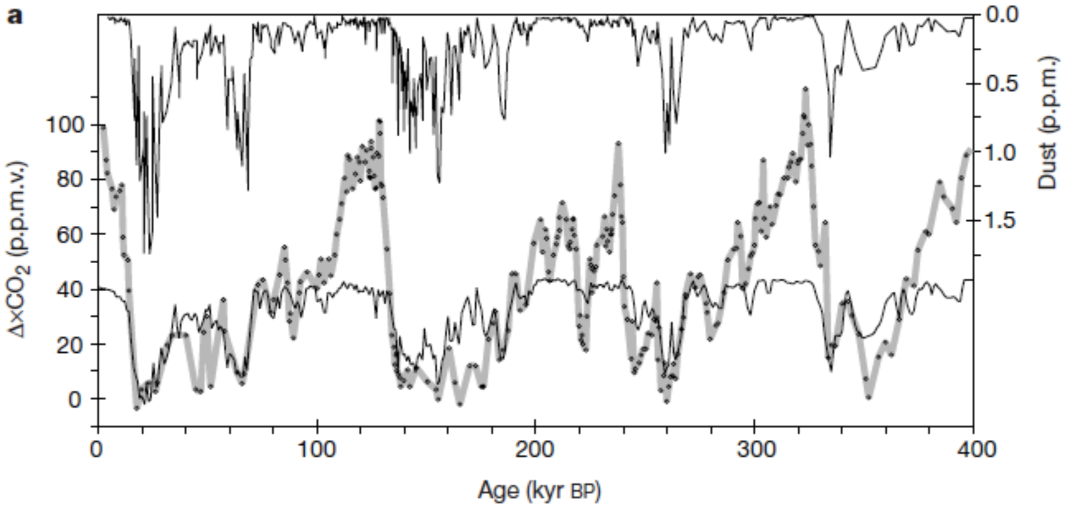
More CO_2 uptake by ocean:
1. Decrease DIC (biol. C-pump; OIF)
2. Increase TA (enhanced weathering)

Ocean Iron Fertilization

CO_2 sequestration in the ocean: Ocean Iron Fertilization (OIF)



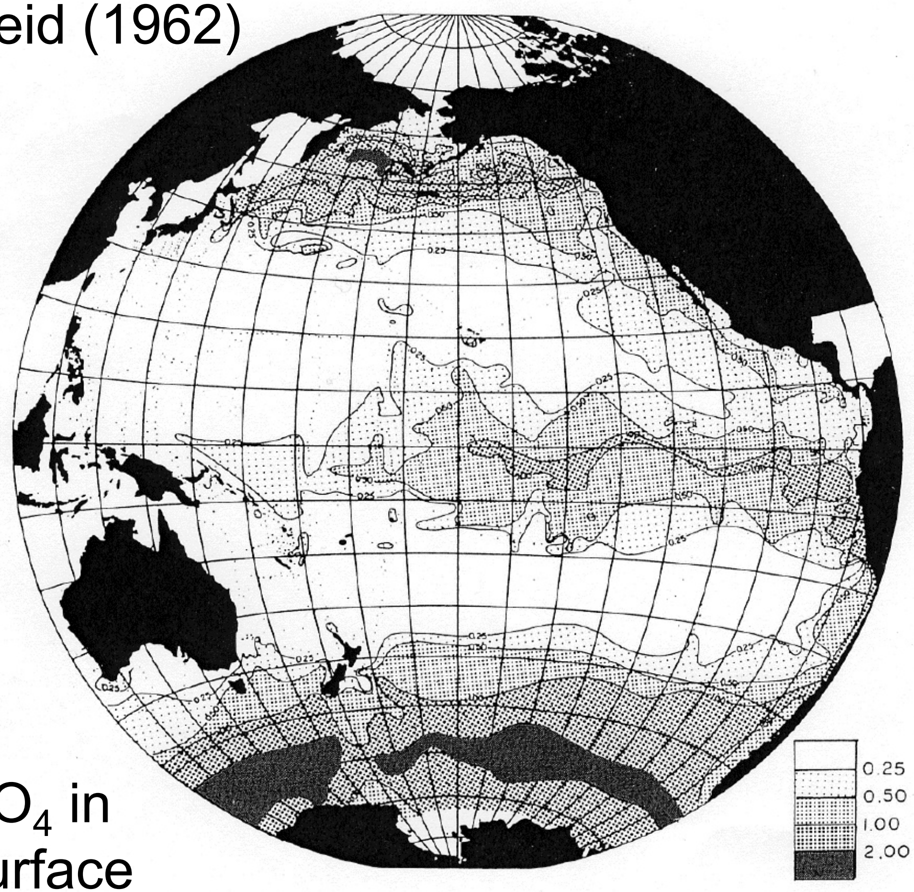
John Martin



Petit et al., 1999
Watson et al. 2000

High Nutrient (NO_3, PO_4) Low Chlorophyll (HNLC) regions

Reid (1962)



μmol L^{-1}

PO_4 in surface ocean

Northern North Pacific

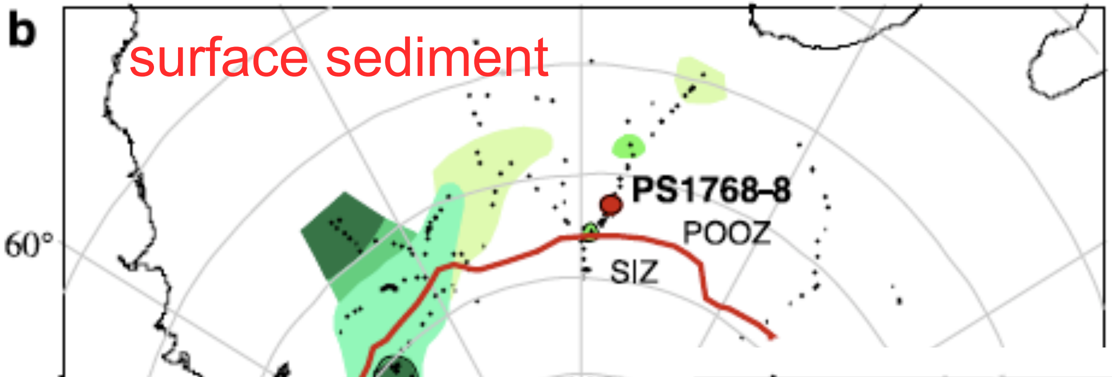
Equatorial Pacific

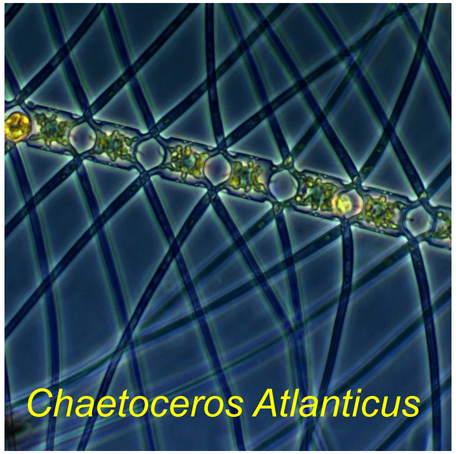
Southern Ocean

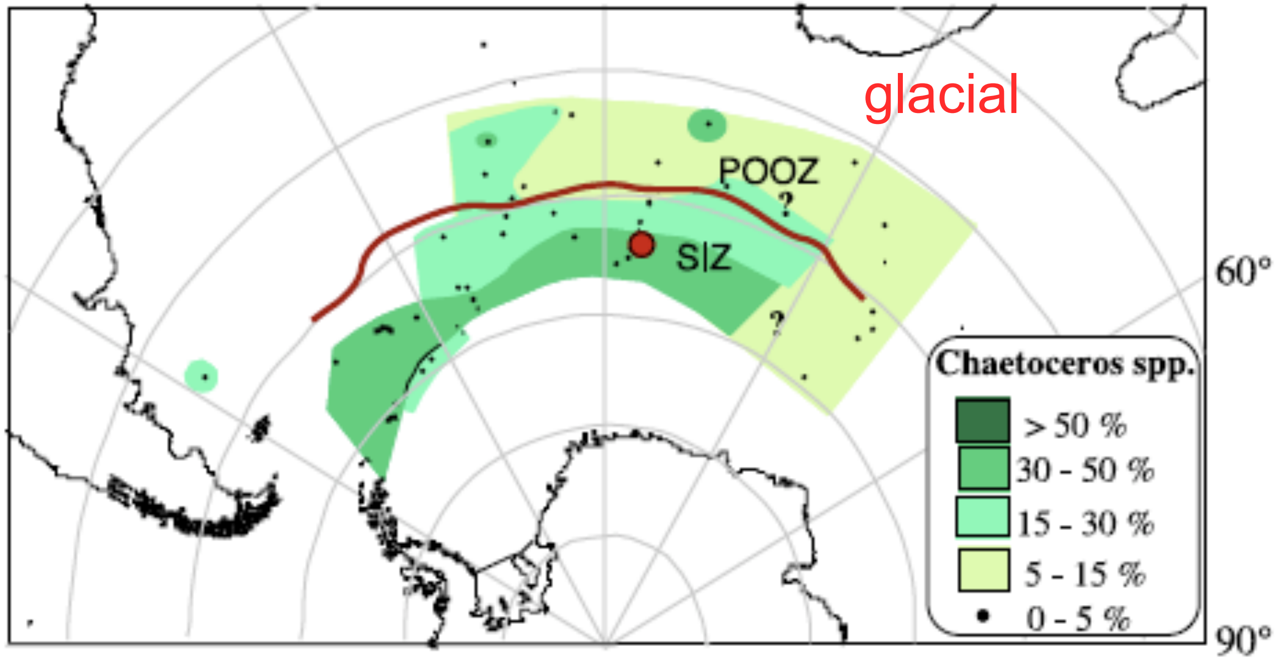
Extensive phytoplankton blooms in the Atlantic sector of the glacial Southern Ocean

Motivation

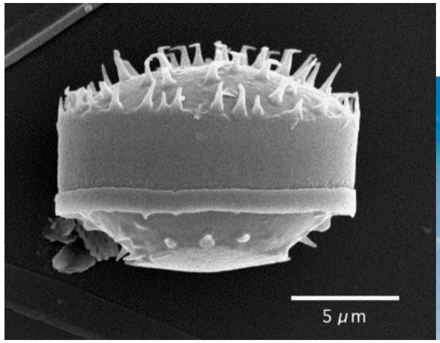
Andrea Abelmann,[1] Rainer Gersonde,[1] Giuseppe Cortese,[1] Gerhard Kuhn,[1] and Victor Smetacek[1]





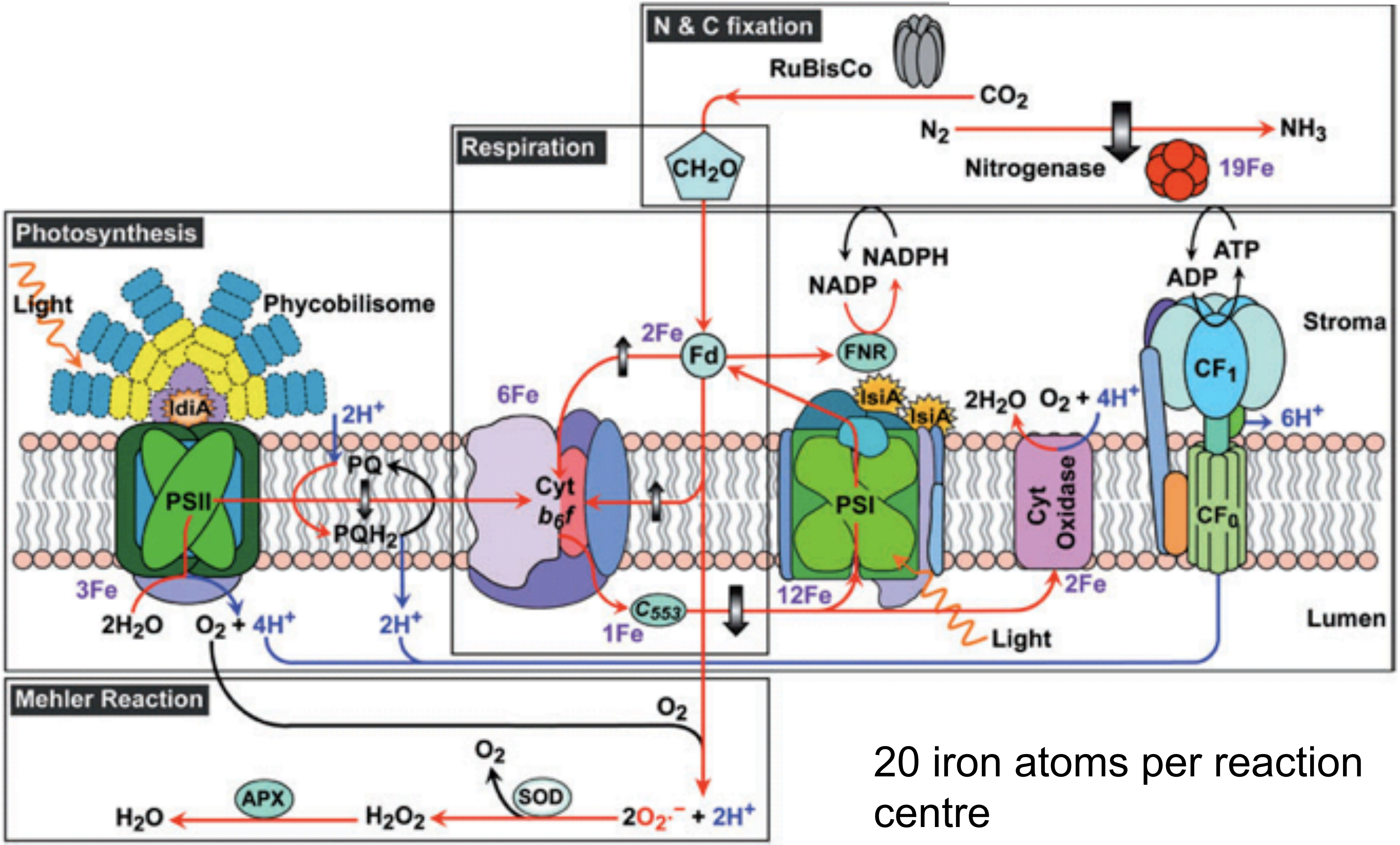


Chaetoceros spores



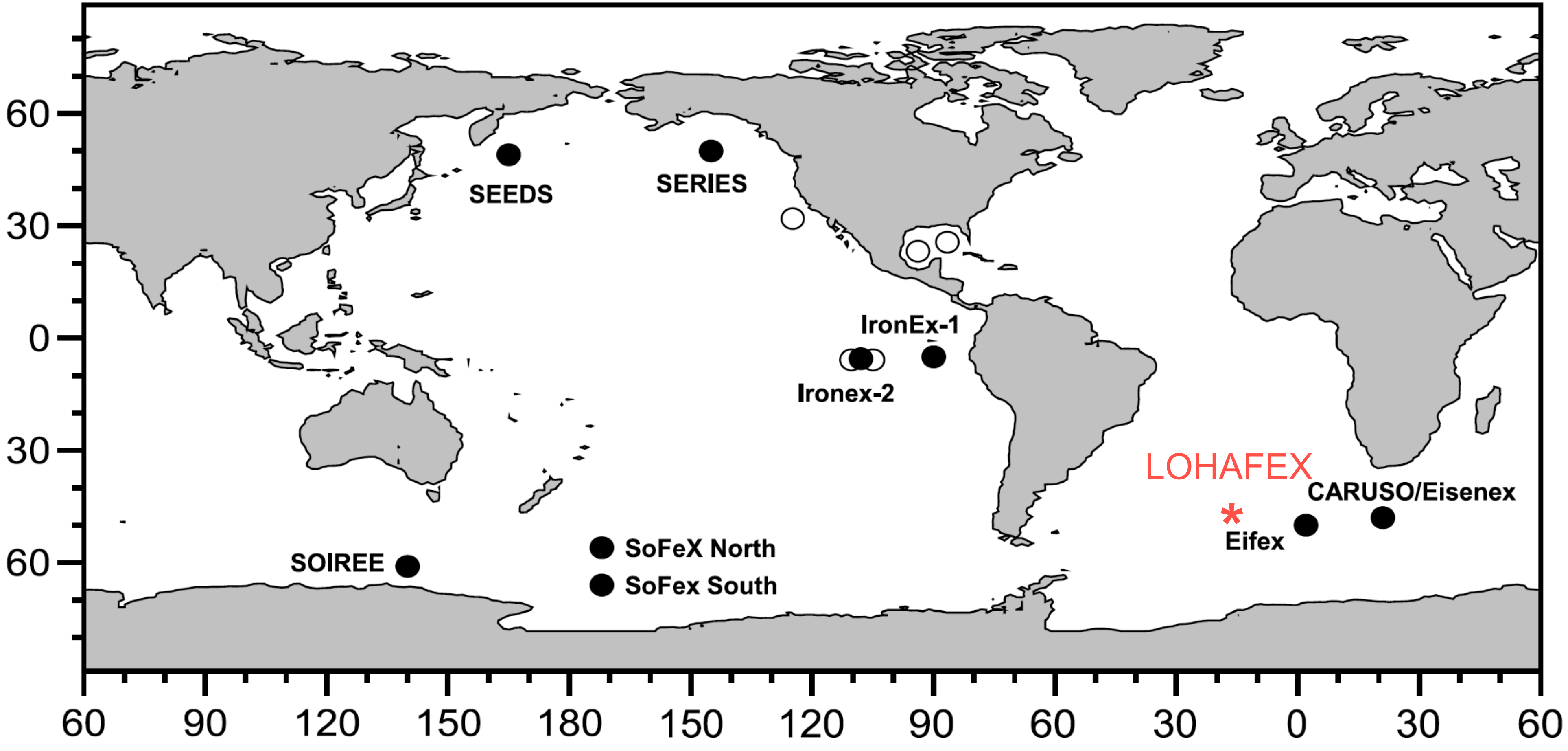
Iron in enzymes photosystem I & II

Shi et al., 2007



20 iron atoms per reaction centre

Iron fertilization experiments



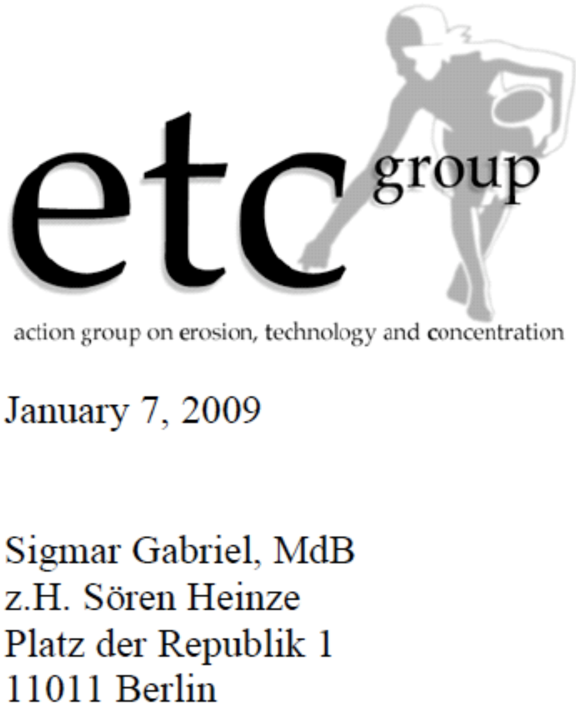
de Baar et al. 2005

LOHAFEX = LOHA (iron, Hindi) Fertilization EXperiment

7 January - 17 March 2009

Political storm

GREENPEACE



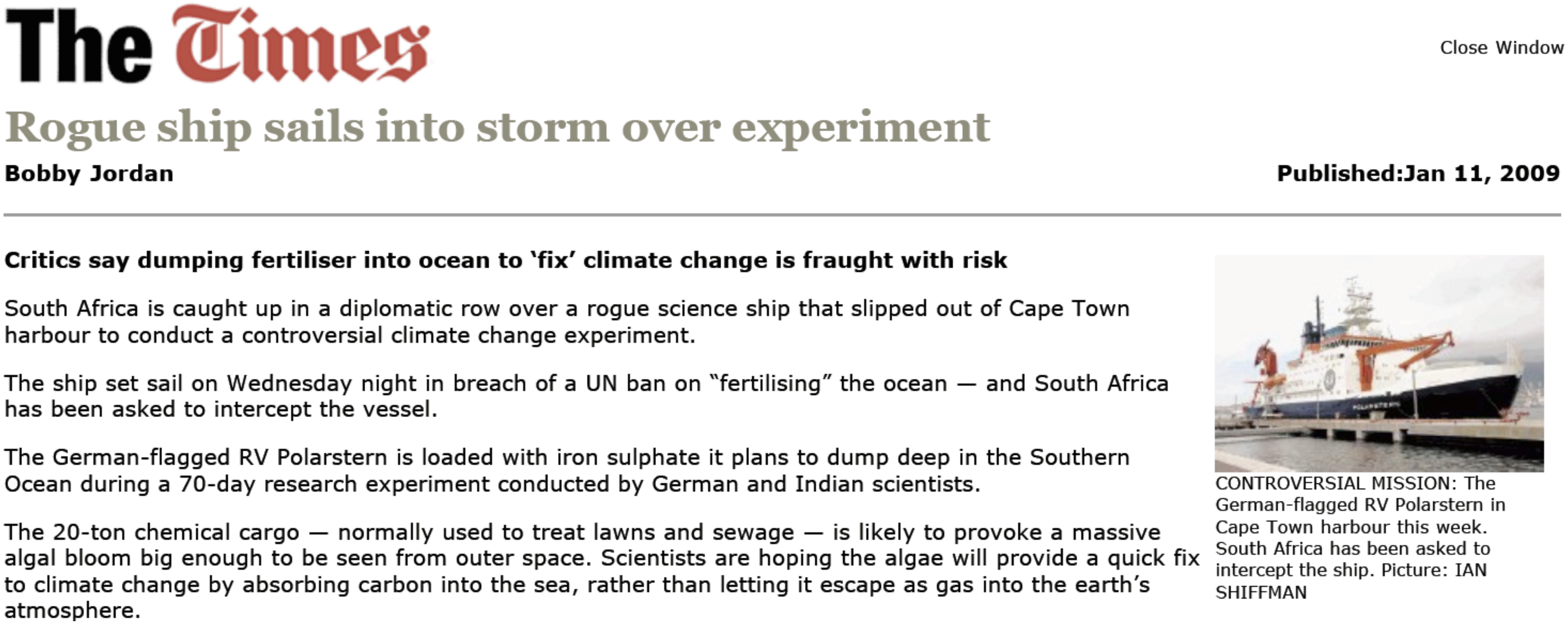
etc group

action group on erosion, technology and concentration

January 7, 2009

Sigmar Gabriel, MdB
z.H. Sören Heinze
Platz der Republik 1
11011 Berlin

-> write risk assessment
evaluated by British
Antarctic Survey,
IfM-GEOMAR Kiel
& reviews by
legal advisers



The Times

Close Window

Rogue ship sails into storm over experiment

Bobby Jordan

Published:Jan 11, 2009

Critics say dumping fertiliser into ocean to 'fix' climate change is fraught with risk

South Africa is caught up in a diplomatic row over a rogue science ship that slipped out of Cape Town harbour to conduct a controversial climate change experiment.

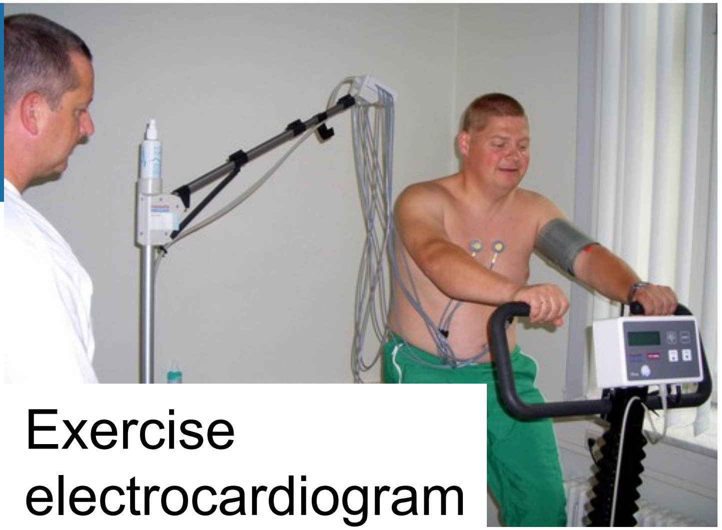
The ship set sail on Wednesday night in breach of a UN ban on "fertilising" the ocean — and South Africa has been asked to intercept the vessel.

The German-flagged RV Polarstern is loaded with iron sulphate it plans to dump deep in the Southern Ocean during a 70-day research experiment conducted by German and Indian scientists.

The 20-ton chemical cargo — normally used to treat lawns and sewage — is likely to provoke a massive algal bloom big enough to be seen from outer space. Scientists are hoping the algae will provide a quick fix to climate change by absorbing carbon into the sea, rather than letting it escape as gas into the earth's atmosphere.

CONTROVERSIAL MISSION: The German-flagged RV Polarstern in Cape Town harbour this week. South Africa has been asked to intercept the ship. Picture: IAN SHIFFMAN

Perturbation experiment


Exercise
electrocardiogram

... to investigate the structure and functioning of pelagic ecosystems

Pertubation:
Add 20 t of iron sulfate over an area of 300 km^2
≈ 4 t of iron ≈ 0.01 g Fe m^{-2}
(4000 m water column contains about ten times more Fe)

⇒ concentration in mixed layer: 2 nmol L^{-1}
(tap or mineral waters may show 100 times higher concentrations).

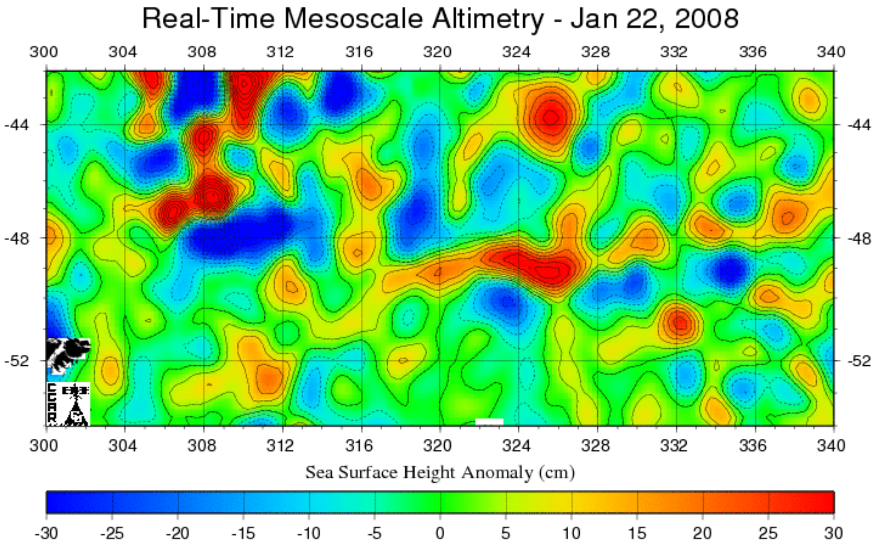
Avoid too much spreading/dilution of patch (initial radius 10 km) by fertilizing centre of a mesoscale eddy (radius 60 km)

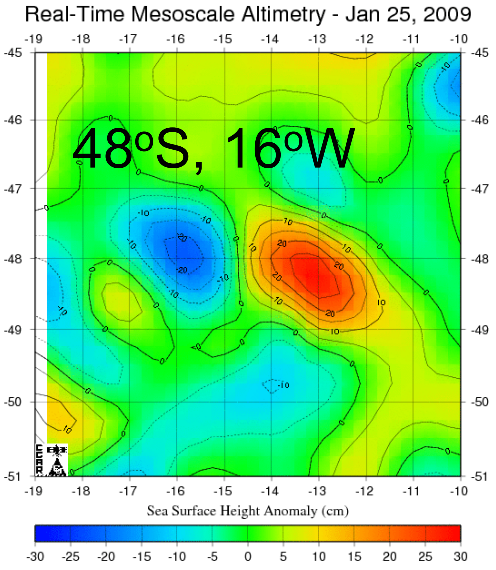
A good eddy should ...

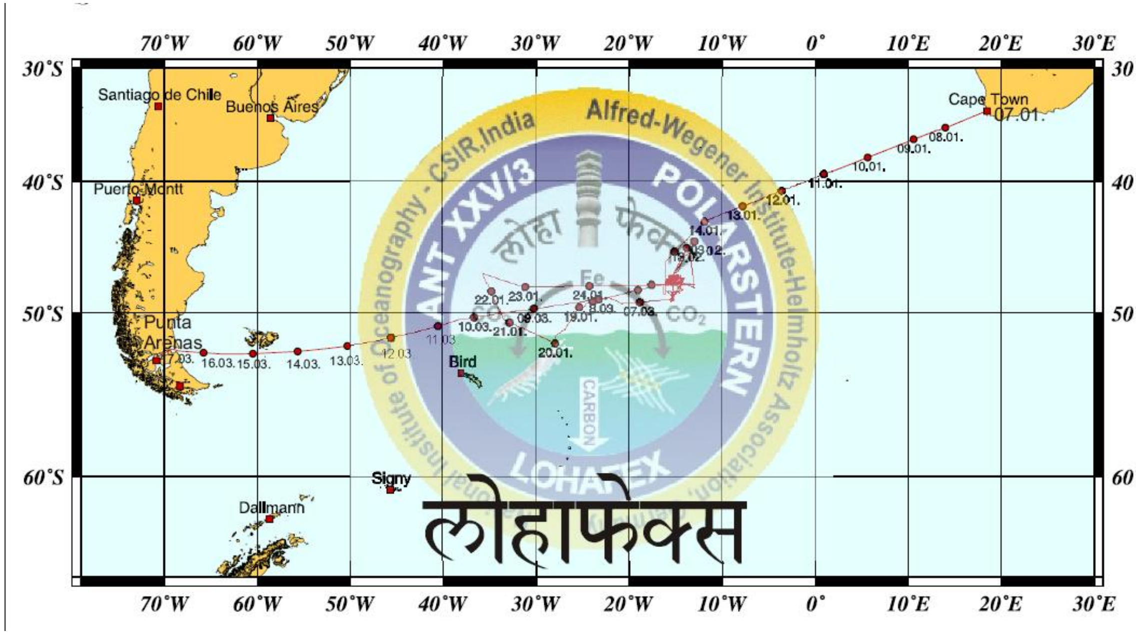
... be **stable** for at least 2 months.
(finite size Lyapounov exponents)

... contain **high nutrient concentrations** in surface layer.

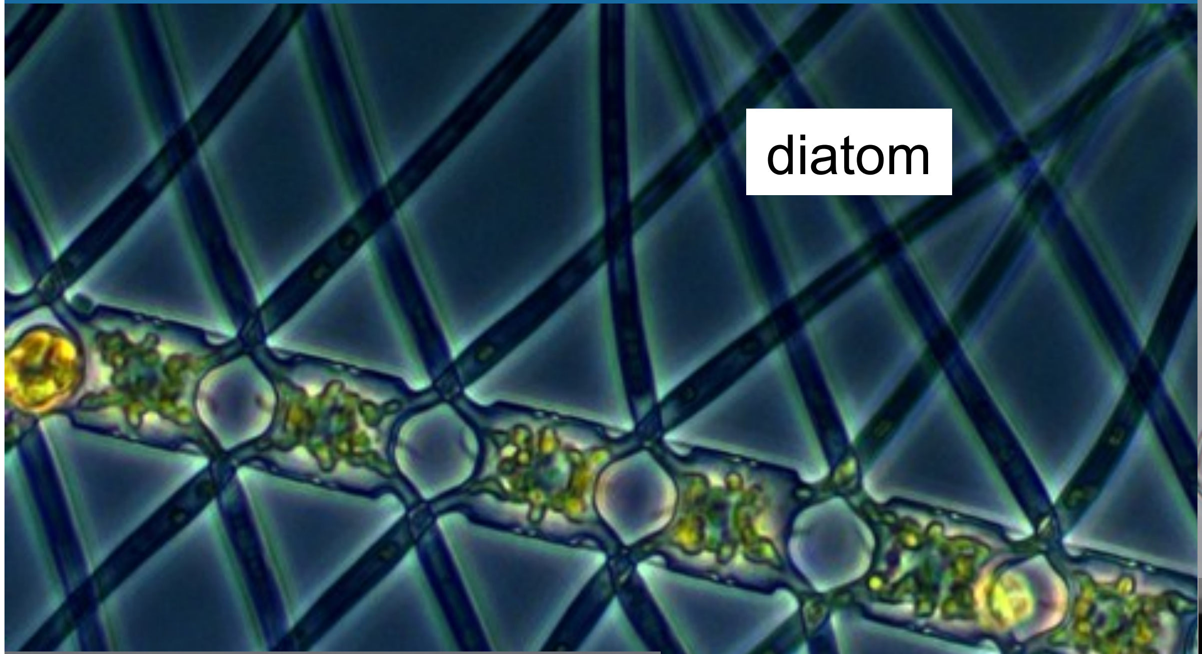
... contain a **seed population of phytoplankton** (0.5 mg chlorophyll m^{-3} is lower limit).

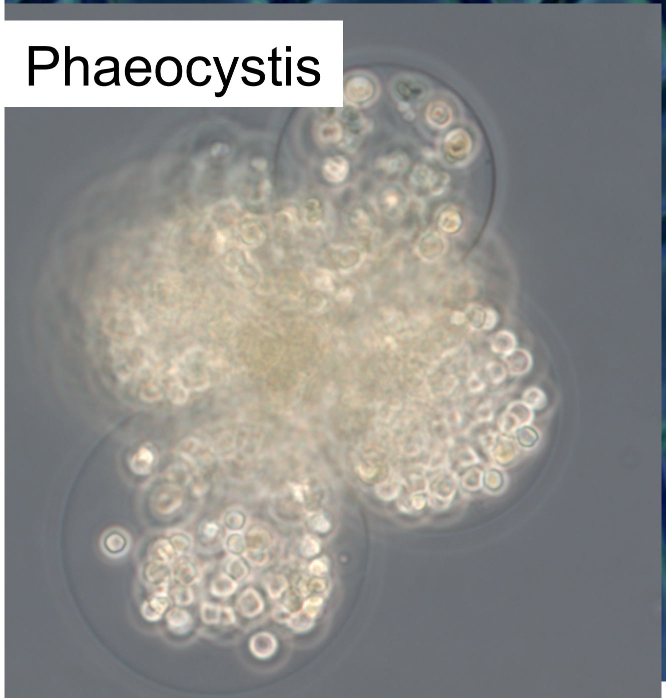


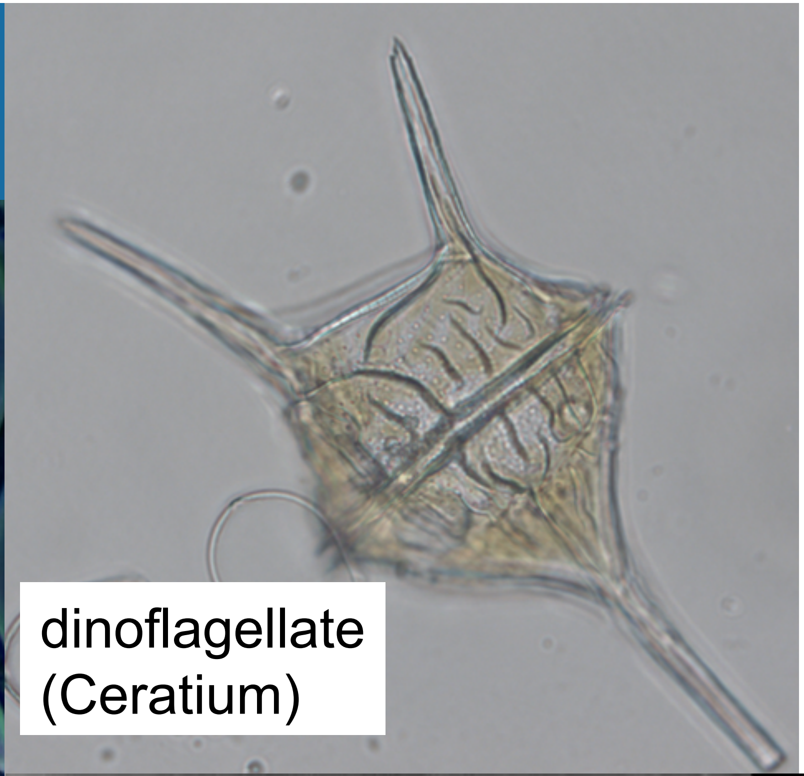


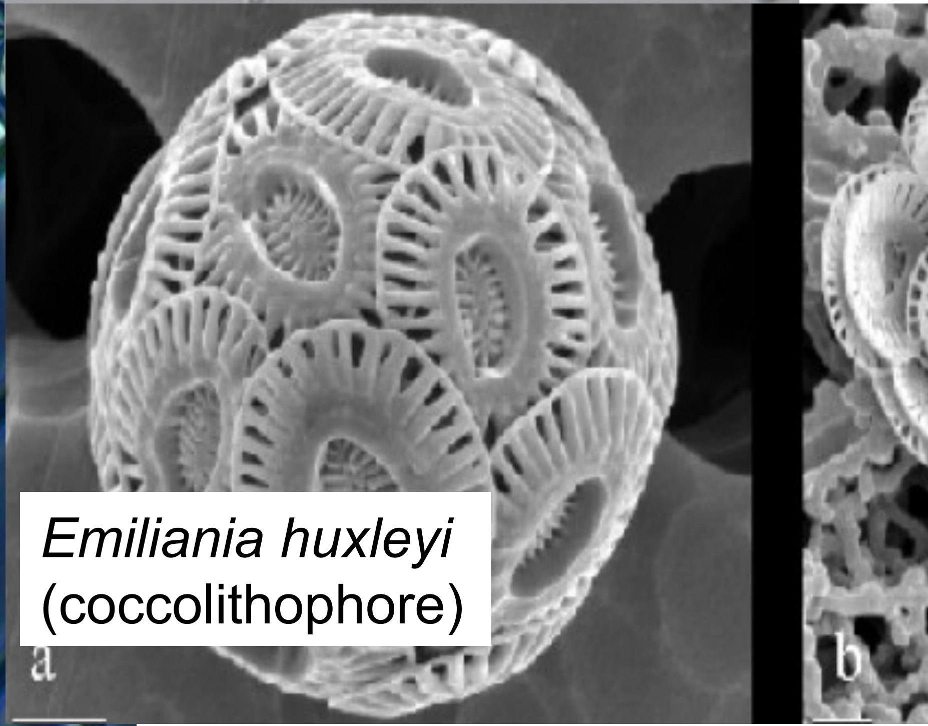


Phytoplankton: Who will win?

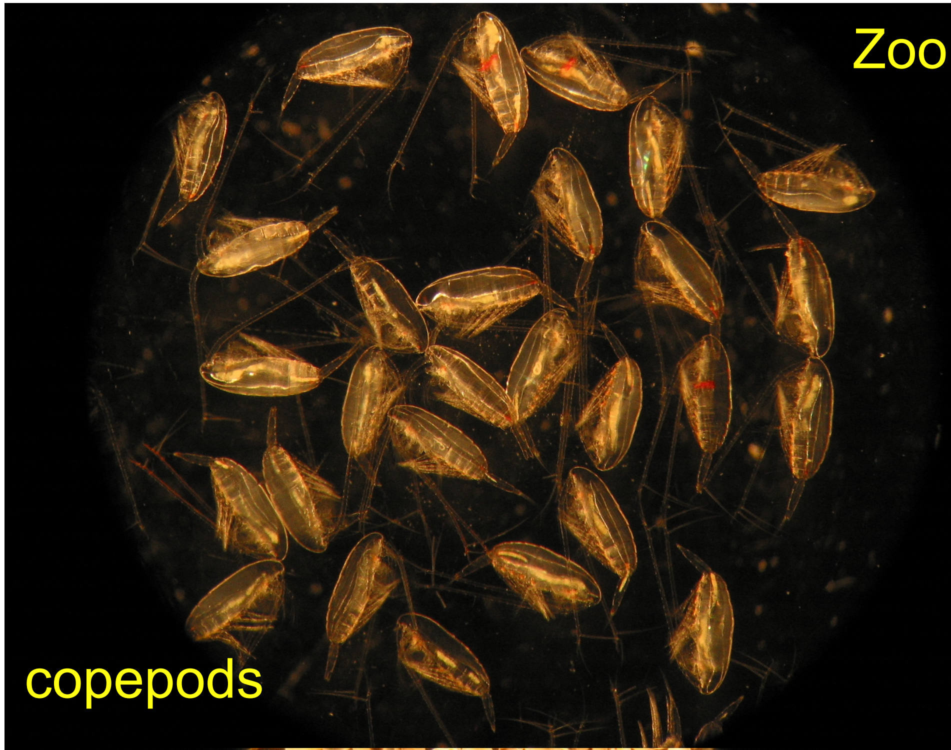

diatom


Phaeocystis

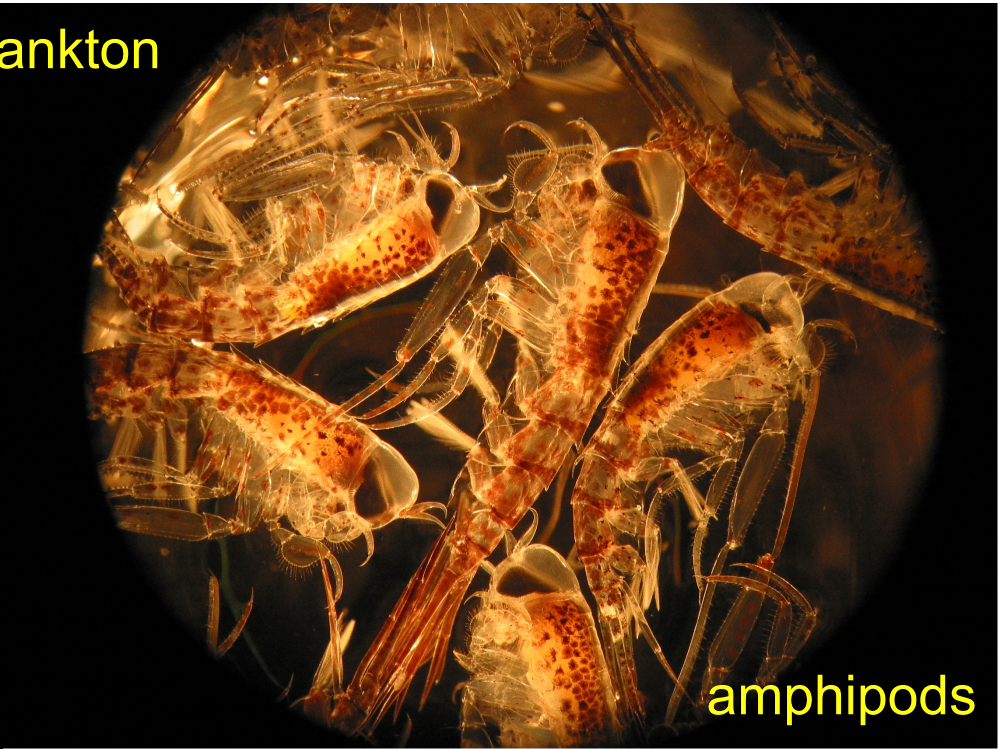

dinoflagellate
(Ceratium)


Emiliania huxleyi
(coccolithophore)

Zooplankton

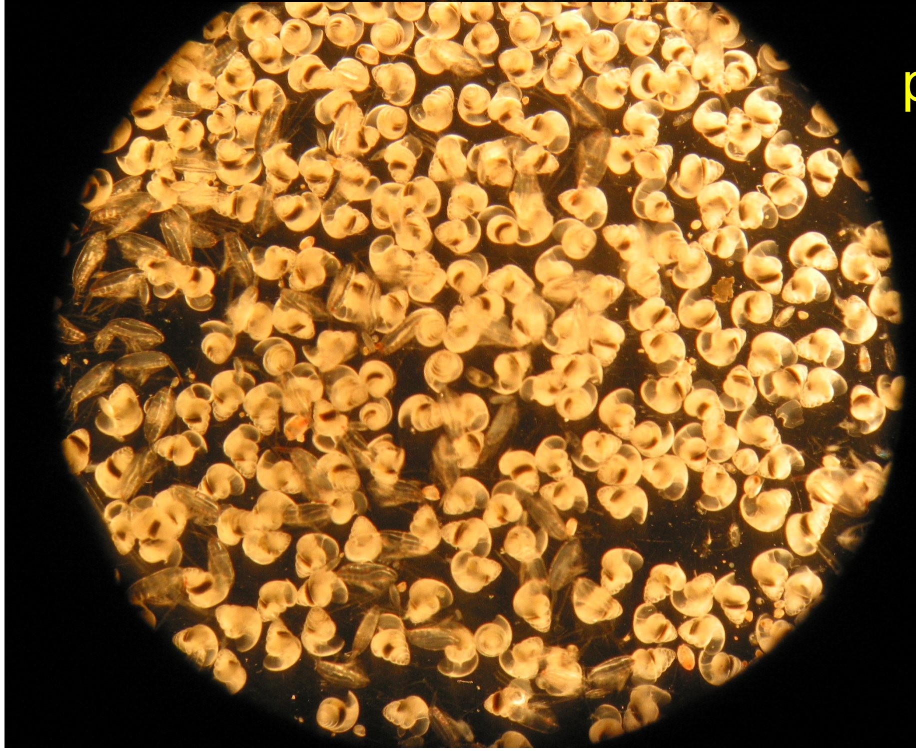


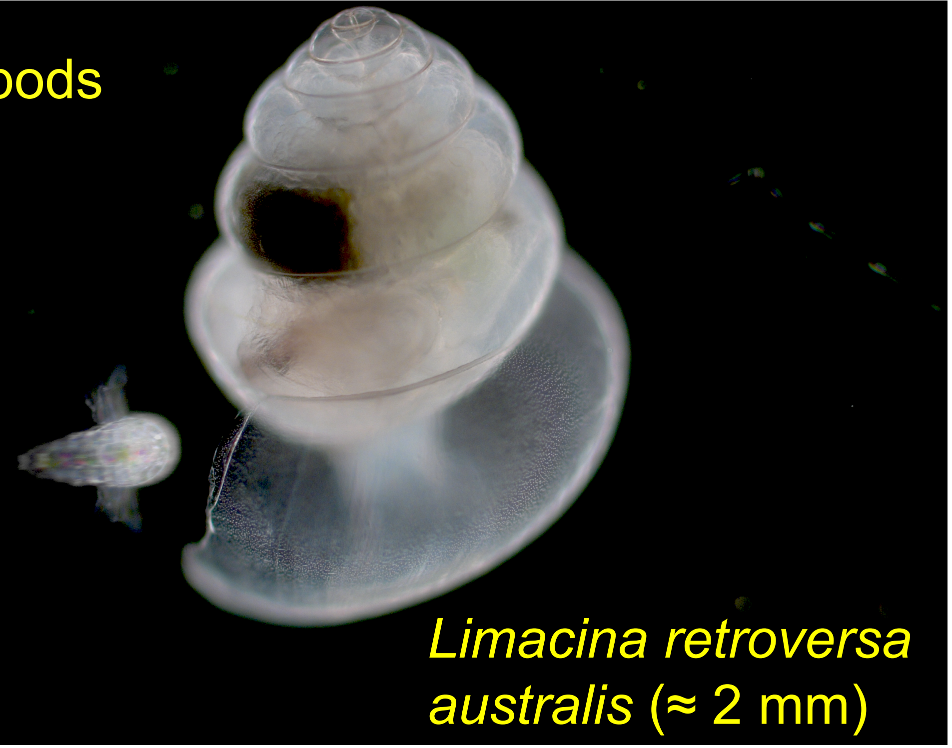
copepods



amphipods

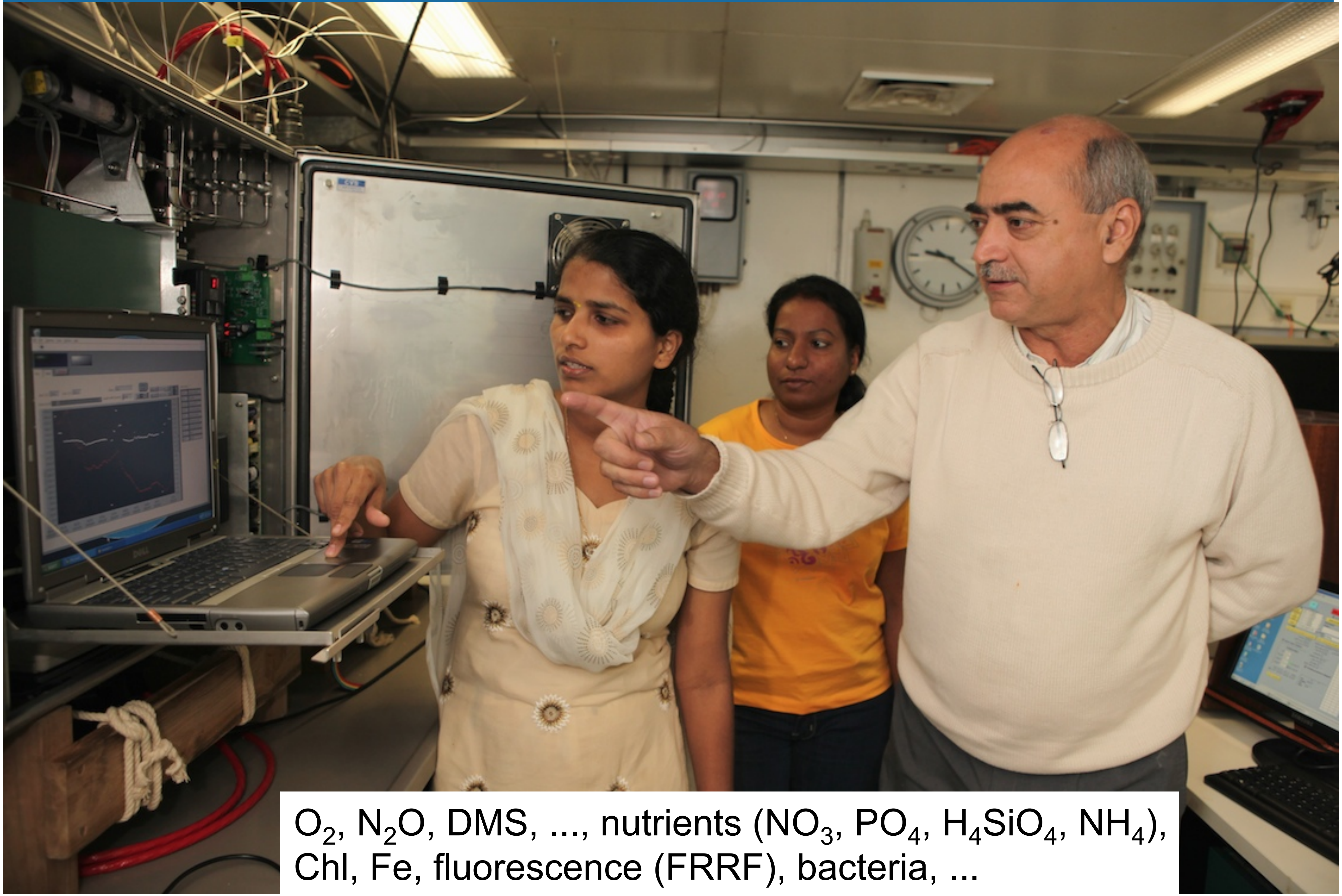
pteropods





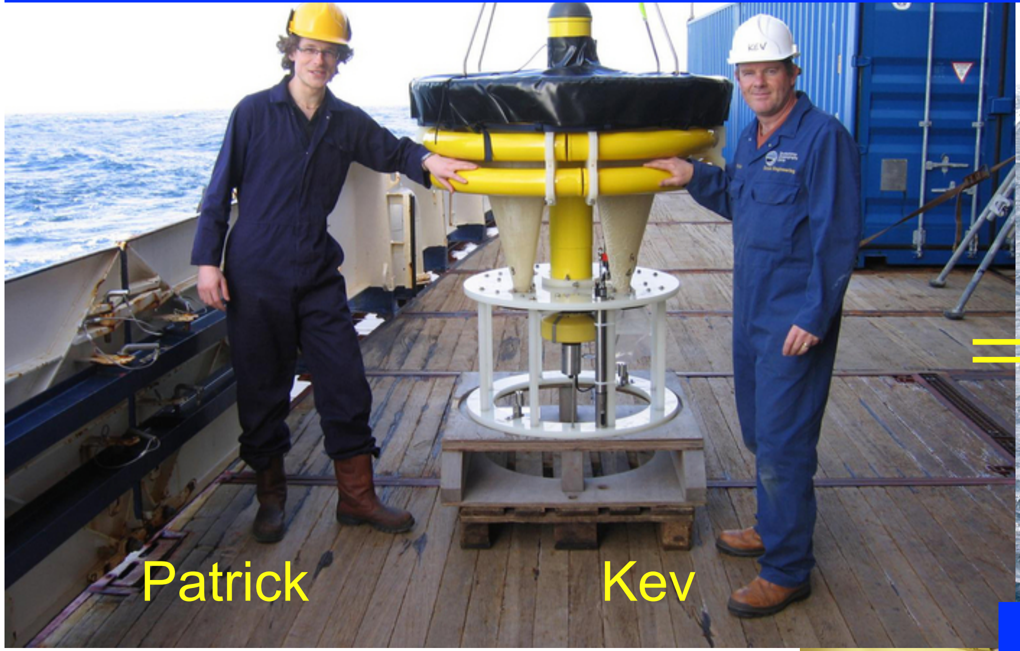
Limacina retroversa australis (≈ 2 mm)

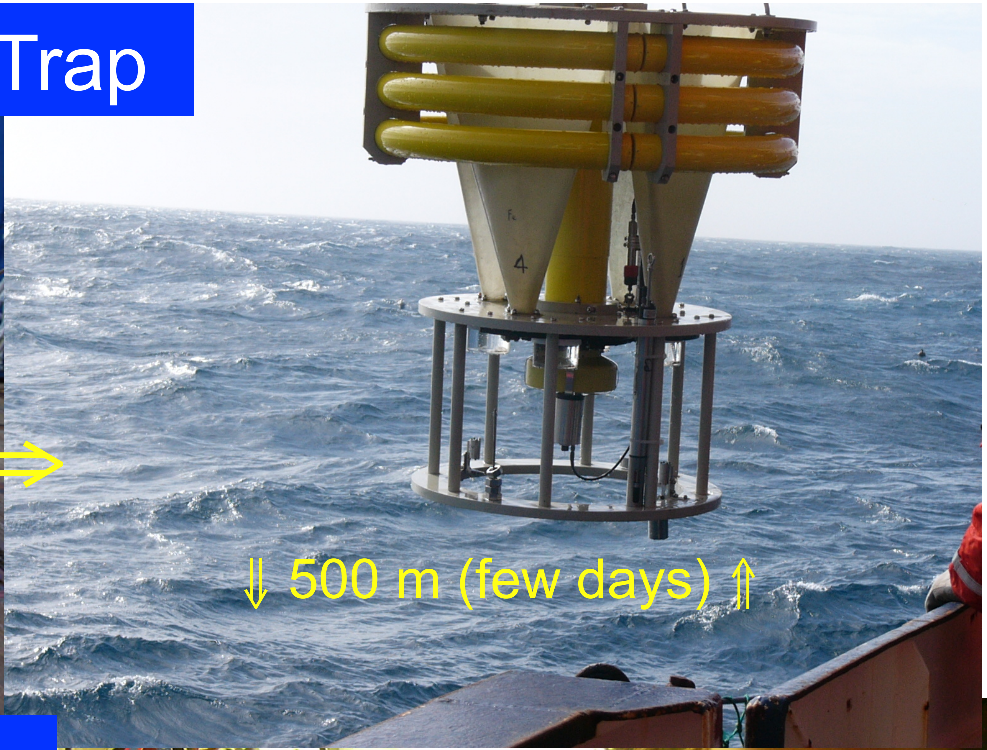
Measurements

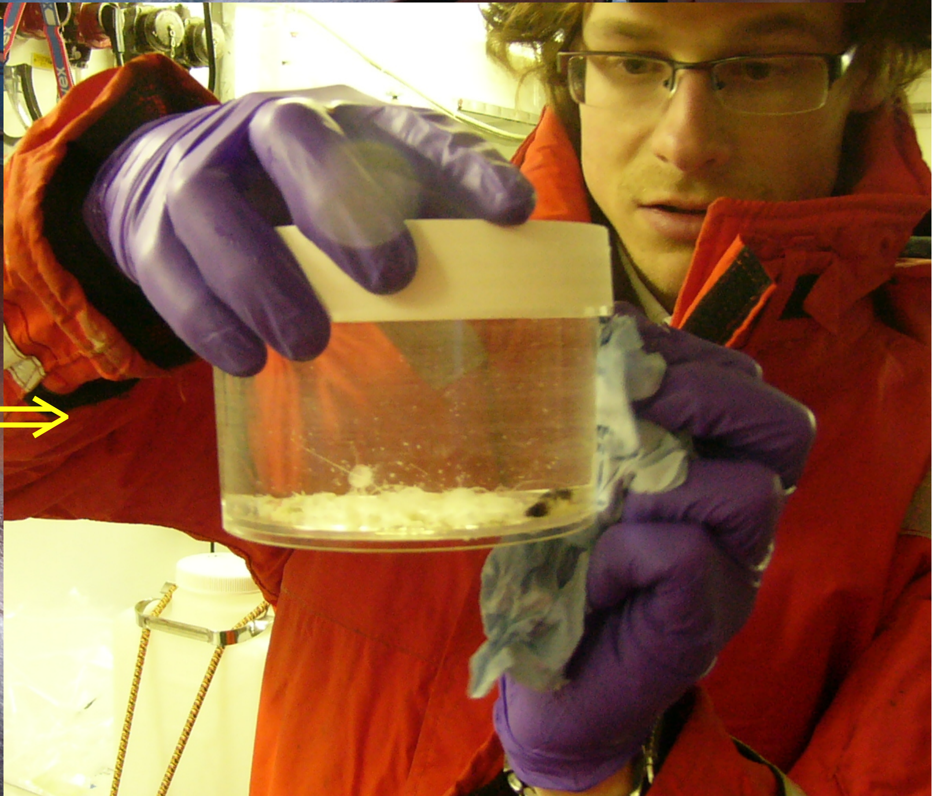


O_2, N_2O, DMS, ..., nutrients (NO_3, PO_4, H_4SiO_4, NH_4), Chl, Fe, fluorescence (FRRF), bacteria, ...

Neutrally Buoyant Sediment Trap



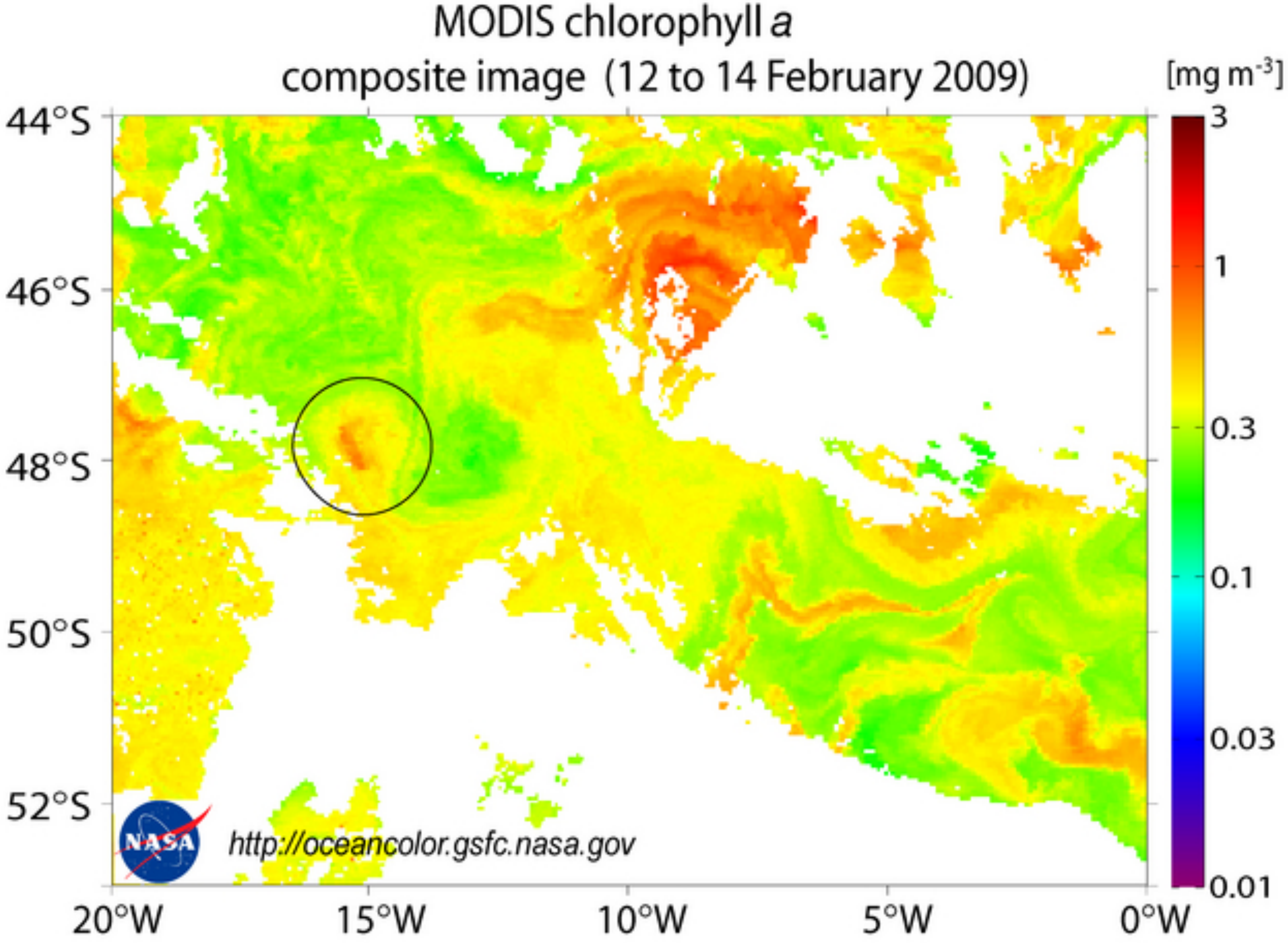




CTD rosette (Conductivity, Temperature, Depth)
Underwater Video Profiler (UVP)

1 picture s^{-1}
3000 m depth

LOHAFEX algal bloom



Carbon export? CO_2 uptake?

Chlorophyll increased by factor 2-3 (5 during EIFEX), mainly due to picophytoplankton.

Recycling system with considerable turnover.

⇒ Expectation: low carbon export.

Confirmed by sediment traps, particle recorder, ...

CO_2 uptake from atmosphere was low.

LOHAFEX: conclusions

Iron addition stimulated production. Accumulation rates of phytoplankton increased for a very short time only because of heavy grazing pressure by zooplankton. **Picophytoplankton and zooplankton profited most**. Positive effects are expected for higher trophic levels.

LOHAFEX showed that iron fertilization of nutrient-rich (NO_3,PO_4) waters does not necessarily lead to algal blooms, carbon export and thus CO_2 uptake (it‘s not just chemistry: $NO_3 + PO_4 + Fe \Rightarrow$ ...).

The state and functioning of the whole ecosystem plays an essential role; in particular: the plankton assemblage (initial conditions) and the amount of silicic acid.

⇒ Iron fertilization makes no sense here!

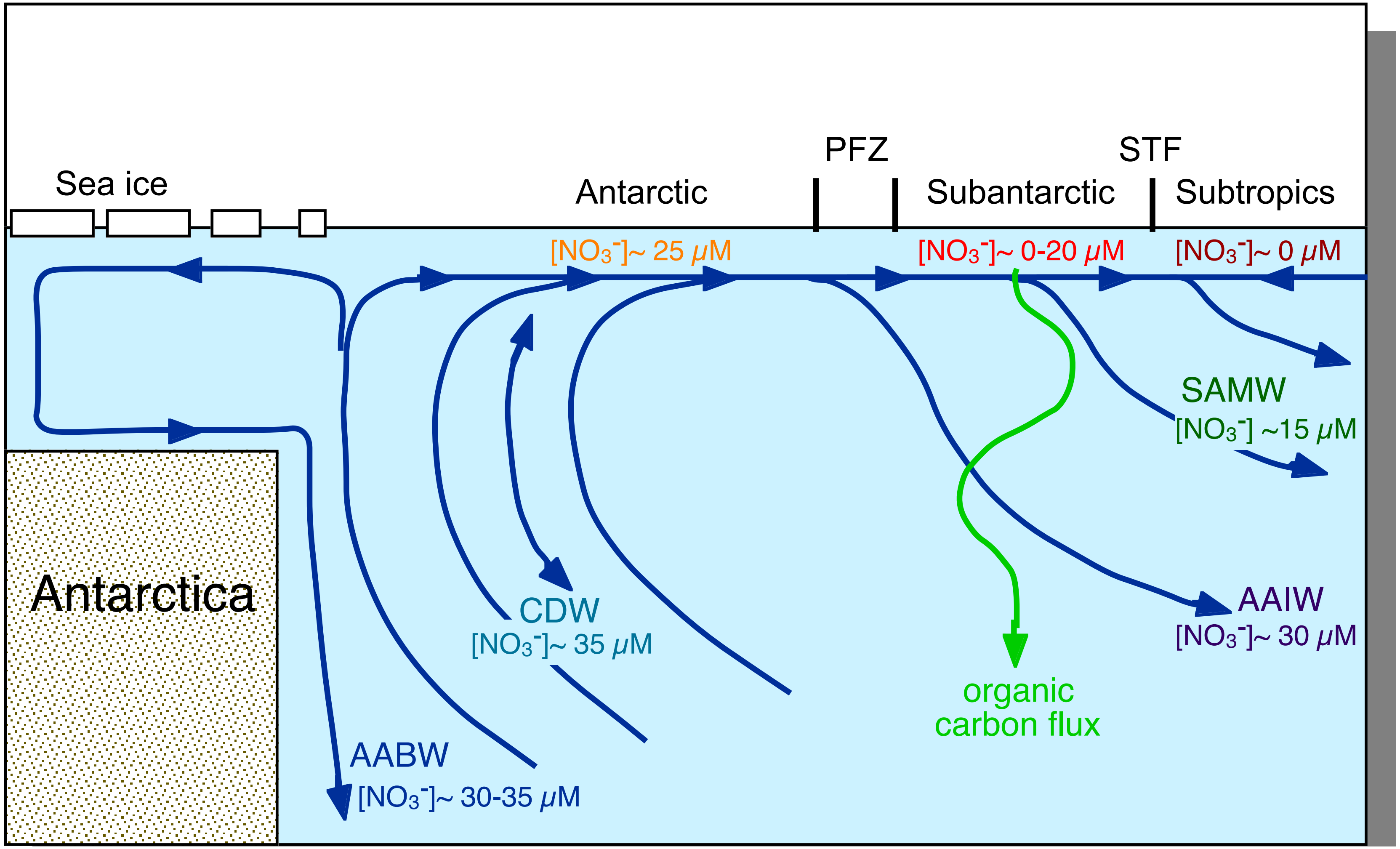
LOHAFEX: geoengineering or basic research?

Geoengineering: develop, optimize, and apply methods for the reduction of atmospheric greenhouse gases or reduction of incoming solar radiation in order to mitigate climate change. Observation of low C export is a failure.

Basic research: Investigate the structure and functioning of ecosystems under various conditions. Observation of low C export is a major result and not a failure.

When we came home from LOHAFEX we were exhausted & happy!

Potential for Fe fertilization in the Southern Ocean? Circulation & NO_3



PFZ = Polar Frontal Zone   STF = Subtropical Front

AABW = Antarctic Bottom Water   CDW = Circumpolar Deep Water

AAIW Antarctic Intermediate Water   SAMW = Subantarctic Mode Water

Potential for Fe fertilization in the Southern Ocean?

Macronutrients (NO_3, PO_4) leave the Southern Ocean via Antarctic Intermediate Water (AAIW) and mode waters without taking C along. Add Fe south of the AAIW/mode water formation regions to stimulate biological production and export of carbon from the surface layer.

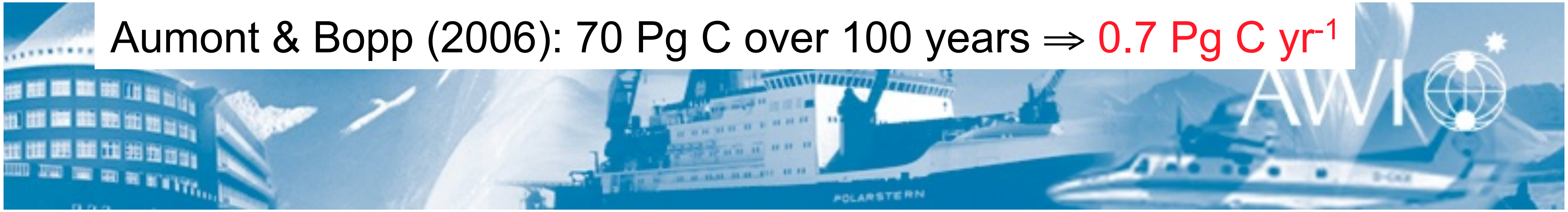
Potential = water transport ($m^3\ yr^{-1}$) x NO_3 concentration ($mol\ m^{-3}$)
x conversion to C ($mol\ C\ (mol\ N)^{-1}$)
x conversion to mass ($g\ C\ (mol\ C)^{-1}$) = **1.3 Pg C yr^{-1}**

34 Sv = 34 x $10^6\ m^3\ s^{-1}$ (Rintoul & Sloyan, 2001)

NO_3 = 15 $\mu mol\ L^{-1}$

Sarmiento & Orr (1991): Complete macronutrient depletion due to iron fertilization of HNLC regions ⇒ 98 - 181 Pg C over 100 years
⇒ 1 - 1.8 Pg C yr^{-1}

Aumont & Bopp (2006): 70 Pg C over 100 years ⇒ 0.7 Pg C yr^{-1}



EIFEX: European Iron Fertilization Experiment
2004 48°S 2°E

Smetacek et al. (submitted)

Assmy et al. (submitted)

Compared to LOHAFEX: stronger bloom, diatoms, … and export

Ocean pipes: nutrients from the deep
Lovelock & Rapley (2007)

Ocean pipes could help the Earth to cure itself

SIR — We propose a way to stimulate the Earth's capacity to cure itself, as an emergency treatment for the pathology of global warming.

Measurements of the climate system show that the Earth is fast becoming a hotter planet than anything yet experienced by humans. Processes that would normally regulate climate are being driven to amplify warming. Such feedbacks, as well as the inertia of the Earth system — and that of our response — make it doubtful that any of the well-intentioned technical or social schemes for carbon dieting will restore the status quo. What is needed is a fundamental cure.

The oceans, which cover more than 70% of the Earth's surface, are a promising place to seek a regulating influence. One approach would be to use free-floating or tethered vertical pipes to increase the mixing of nutrient-rich waters below the thermocline with the relatively barren waters at the ocean surface. (We acknowledge advice from Armand Neukermans on engineering aspects of the pipes.) Water pumped up pipes — say, 100 to 200 metres long, 10 metres in diameter and with a one-way flap valve at the lower

and with a one-way flap valve at the lower

end for pumping by wave movement — would fertilize algae in the surface waters and encourage them to bloom. This would pump down carbon dioxide and produce dimethyl sulphide, the precursor of nuclei that form sunlight-reflecting clouds.

Such an approach may fail, perhaps on engineering or economic grounds. And the impact on ocean acidification will need to be taken into account.

But the stakes are so high that we put forward the general concept of using the Earth system's own energy for amelioration. The removal of 500 gigatonnes of carbon dioxide from the air by human endeavour is beyond our current technological capability. If we can't 'heal the planet' directly, we may be able to help the planet heal itself.

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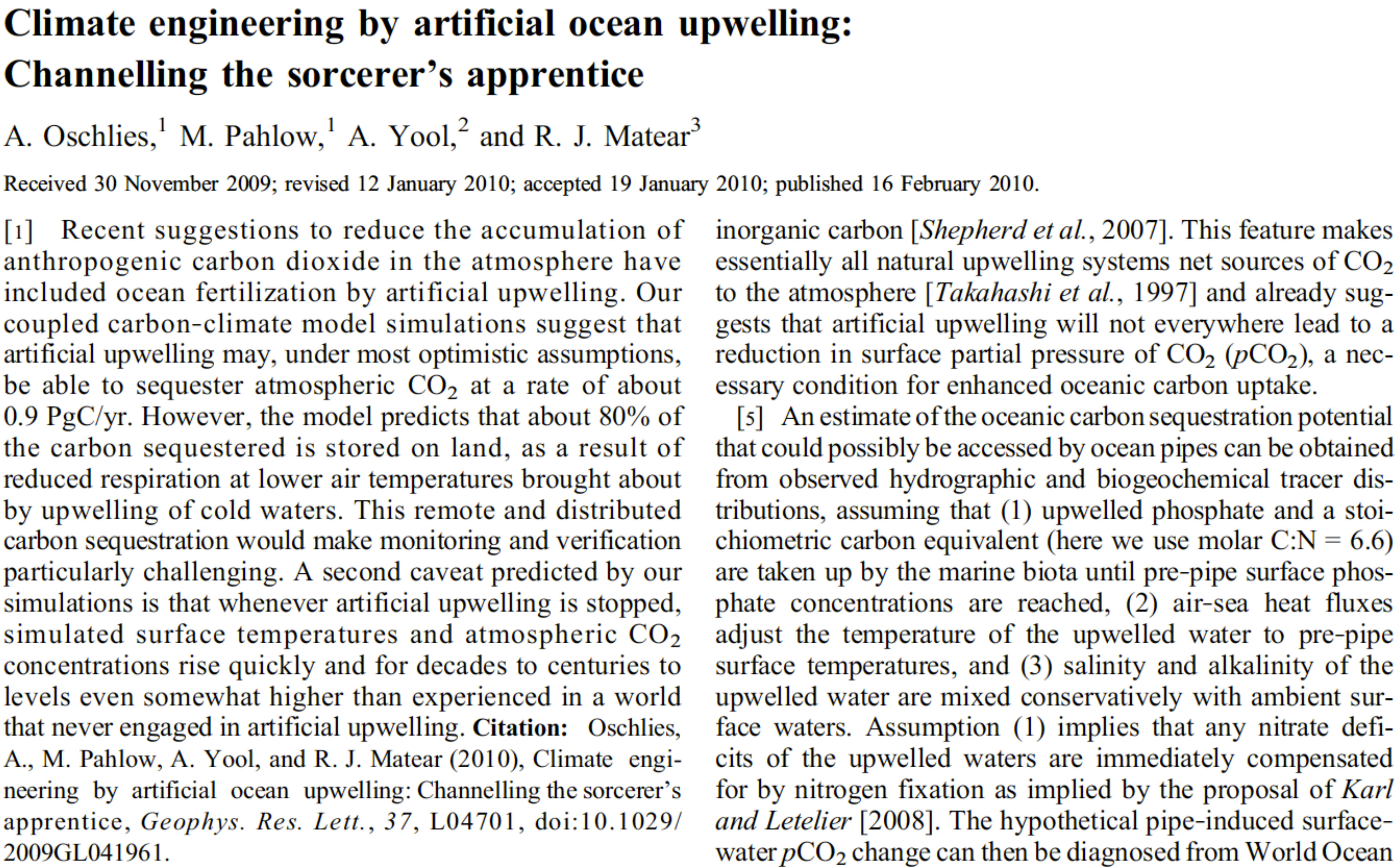
Ocean pipes: nutrients & DIC from the deep
Dutreuil, Bopp, and Tagliabue (2009)

``Unsurprisingly, we find that deploying an array of ocean pipes acts to increase atmospheric CO_2 by 1.4 ppm via a 5.1% reduction in cumulative FCO_2 [air to sea CO_2 flux], despite augmenting carbon export by 5.6%. This is contrary to the expectations of Lovelock and Rapley (2007) and results from increased mixing with sub-surface DIC-rich waters (Table 1, as noted by Shepherd et al., 2007), which overwhelms any beneficial response due to increased export and alkalinity supply. The positive anomalies in biological productivity and carbon export are maximal over the first few years of the experiment and decay by 20–30% after 20 years of deployment (Fig. 4). We further note that if we eliminate the non-local effects and mix the entire global ocean then while carbon export is over 50% greater, atmospheric CO_2 increases by over 20 ppm. Accordingly, carbon export and FCO_2 are clearly decoupled in response to changes in ocean mixing.´´

Oschlies et al. 2010



Climate engineering by artificial ocean upwelling: Channelling the sorcerer's apprentice

A. Oschlies,[1] M. Pahlow,[1] A. Yool,[2] and R. J. Matear[3]

Received 30 November 2009; revised 12 January 2010; accepted 19 January 2010; published 16 February 2010.

[1] Recent suggestions to reduce the accumulation of anthropogenic carbon dioxide in the atmosphere have included ocean fertilization by artificial upwelling. Our coupled carbon-climate model simulations suggest that artificial upwelling may, under most optimistic assumptions, be able to sequester atmospheric CO_2 at a rate of about 0.9 PgC/yr. However, the model predicts that about 80% of the carbon sequestered is stored on land, as a result of reduced respiration at lower air temperatures brought about by upwelling of cold waters. This remote and distributed carbon sequestration would make monitoring and verification particularly challenging. A second caveat predicted by our simulations is that whenever artificial upwelling is stopped, simulated surface temperatures and atmospheric CO_2 concentrations rise quickly and for decades to centuries to levels even somewhat higher than experienced in a world that never engaged in artificial upwelling. **Citation:** Oschlies, A., M. Pahlow, A. Yool, and R. J. Matear (2010), Climate engineering by artificial ocean upwelling: Channelling the sorcerer's apprentice, *Geophys. Res. Lett.*, *37*, L04701, doi:10.1029/2009GL041961.

inorganic carbon [*Shepherd et al.*, 2007]. This feature makes essentially all natural upwelling systems net sources of CO_2 to the atmosphere [*Takahashi et al.*, 1997] and already suggests that artificial upwelling will not everywhere lead to a reduction in surface partial pressure of CO_2 (pCO_2), a necessary condition for enhanced oceanic carbon uptake.

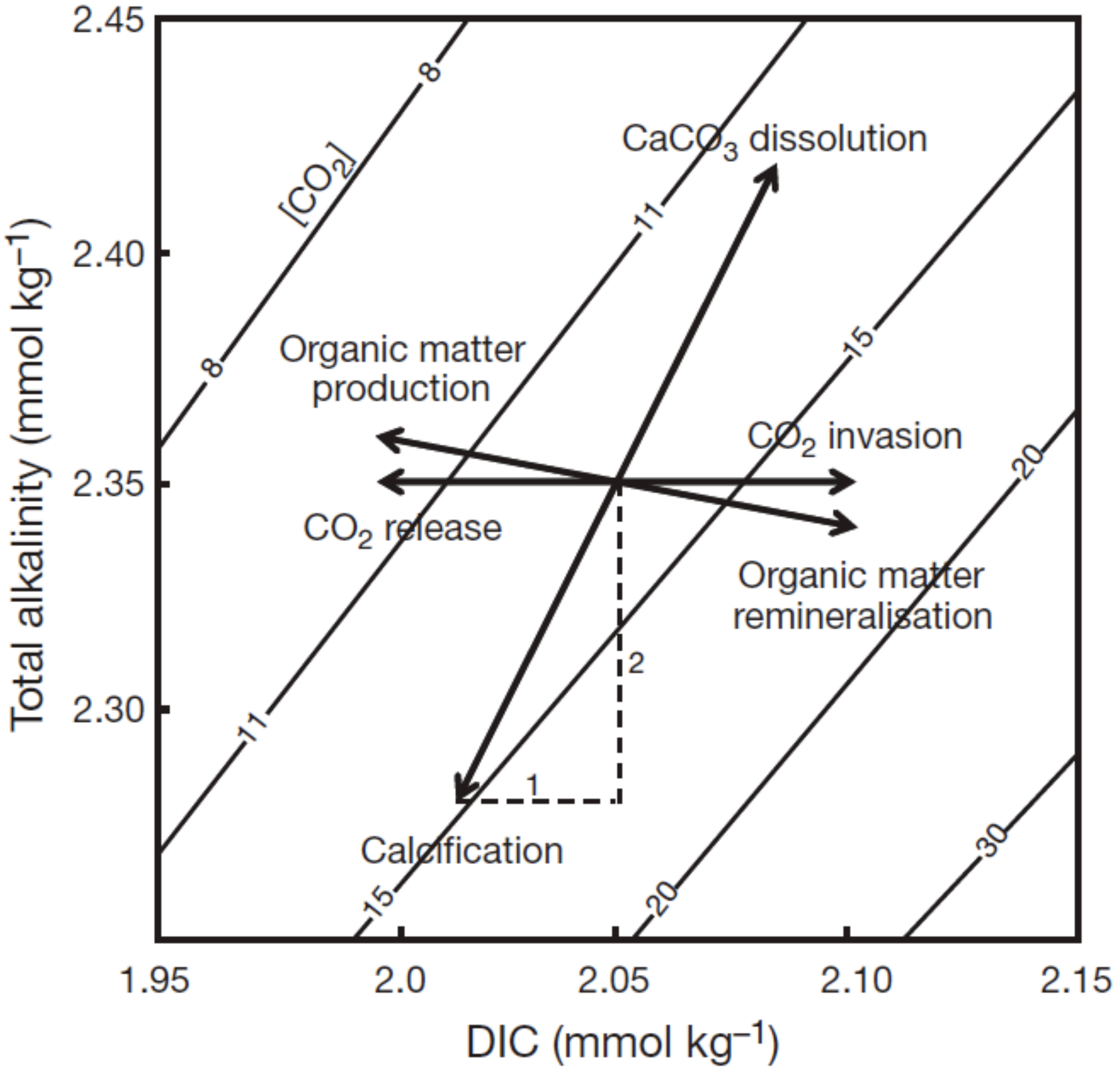
[5] An estimate of the oceanic carbon sequestration potential that could possibly be accessed by ocean pipes can be obtained from observed hydrographic and biogeochemical tracer distributions, assuming that (1) upwelled phosphate and a stoichiometric carbon equivalent (here we use molar C:N = 6.6) are taken up by the marine biota until pre-pipe surface phosphate concentrations are reached, (2) air-sea heat fluxes adjust the temperature of the upwelled water to pre-pipe surface temperatures, and (3) salinity and alkalinity of the upwelled water are mixed conservatively with ambient surface waters. Assumption (1) implies that any nitrate deficits of the upwelled waters are immediately compensated for by nitrogen fixation as implied by the proposal of *Karl and Letelier* [2008]. The hypothetical pipe-induced surface-water pCO_2 change can then be diagnosed from World Ocean

Physical/solubility C pump: enhanced downwelling (Zhou & Flynn, 2005)

Abstract. Downwelling ocean currents carry carbon into the deep ocean (the solubility pump), and play a role in controlling the level of atmospheric carbon. The formation of North Atlantic Deep Water (NADW) also releases heat to the atmosphere, which is a contributor to a mild climate in Europe. One possible response to the increase in anthropogenic carbon in the atmosphere and to the possible weakening of the NADW is modification of downwelling ocean currents, by an increase in carbon concentration or volume. This study assesses the costs of seven possible methods of modifying downwelling currents, including using existing industrial techniques for exchange of heat between water and air. Increasing carbon concentration in downwelling currents is not practical due to the high degree of saturation of high latitude surface water. Two of the methods for increasing the volume of downwelling currents were found to be impractical, and four were too expensive to warrant further consideration. Formation of thicker sea ice by pumping ocean water onto the surface of ice sheets is the least expensive of the methods identified for enhancing downwelling ocean currents. Modifying downwelling ocean currents is highly unlikely to ever be a competitive method of sequestering carbon in the deep ocean, but may find future application for climate modification.

Alkalinity enhancement

CO_2 as a function of DIC & TA: isocontours of $[CO_2]$ in μmol kg^{-1}



CO_2 sequestration in the ocean:

1. Increase strength of biological pump by ocean iron fertilization (OIF) -> DIC in surface ocean decreases

2. Increase TA by enhanced weathering

Pergamon

0360-5442(95)00035-6

Energy Vol. 20, No. 9, pp. 915–922, 1995

0360-5442/95 $9.50 + 0.00

SEQUESTERING ATMOSPHERIC CARBON DIOXIDE BY INCREASING OCEAN ALKALINITY

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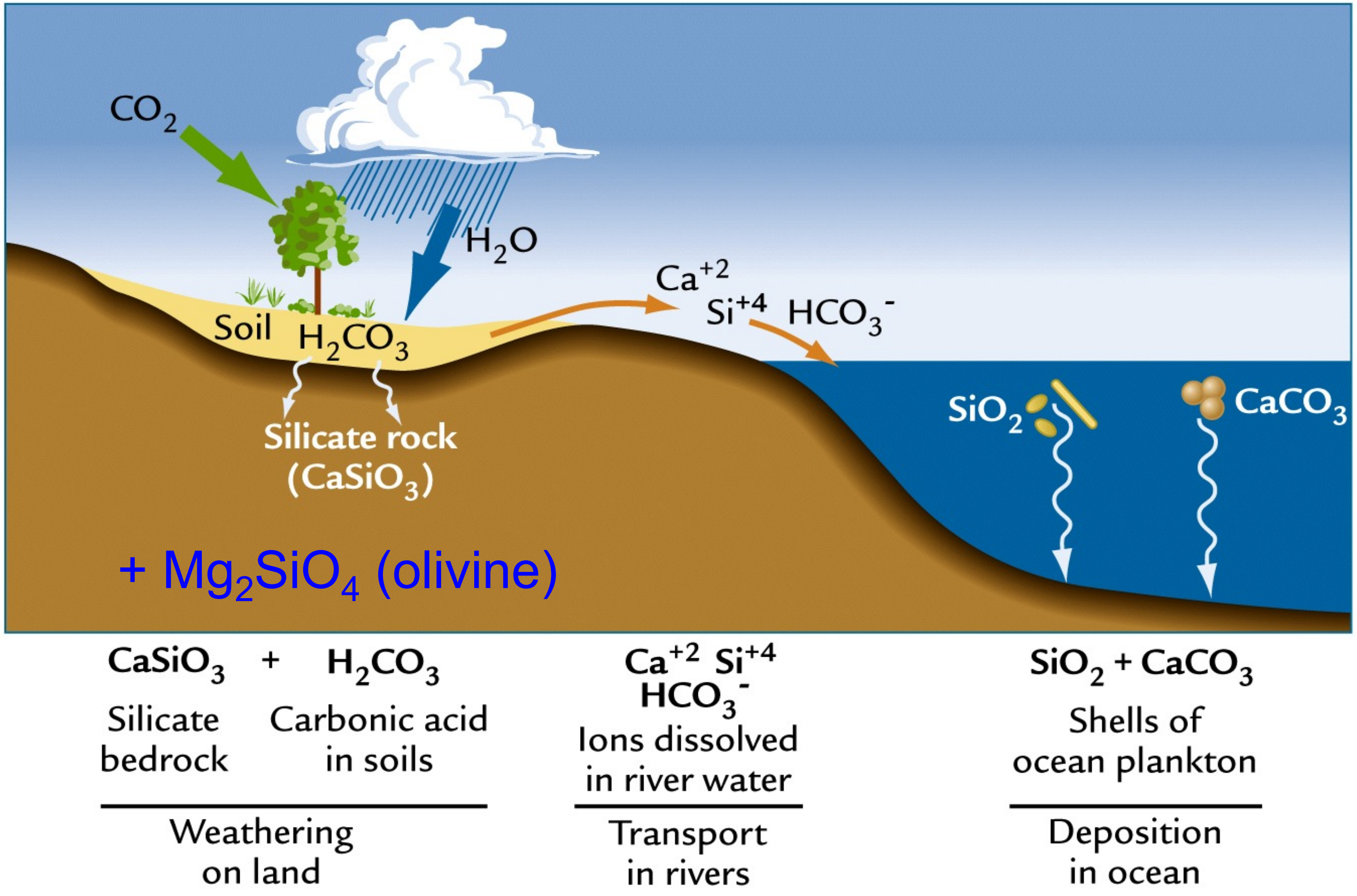
(Received 14 October 1994)

Abstract—We present a preliminary analysis of a geoengineering option based on the intentional increase of ocean alkalinity to enhance marine storage of atmospheric CO_2. Like all geoengineering techniques to limit climate change, with today's limited understanding of the climate system, this approach must be regarded as a potential strategic option that requires ongoing assessment to establish its potential benefits and side effects. CO_2 would be absorbed from the atmosphere by the oceans at an increased rate if ocean alkalinity were raised. Ocean alkalinity might be raised by introducing the dissolution products of alkaline minerals into the oceans. The limited deposits of naturally occurring soda ash (Na_2CO_3) are readily soluble and easily mined. Limestone ($CaCO_3$) is abundant in the Earth's crust but is not readily soluble. This analysis explores the potential feasibility and limits of such approaches.

Enhanced Weathering

The C cycle on long time scales: weathering of silicate rock



+ Mg_2SiO_4 (olivine)

(Ruddiman, 2000)

The net effect of weathering can be summarized into the basic equation
igneous rocks + acid volatiles ⇒ sedimentary rocks + salty ocean

Weathering rates depend on:

Surface to volume ratio of rock: mechanical weathering increases chemical weathering!

Temperature: reactions proceed faster in warmer climate

Precipitation: transport of dissolved substances (ions, molecules) via rivers to the ocean

Acidity of ground water: atmospheric CO_2 and organisms have an influence

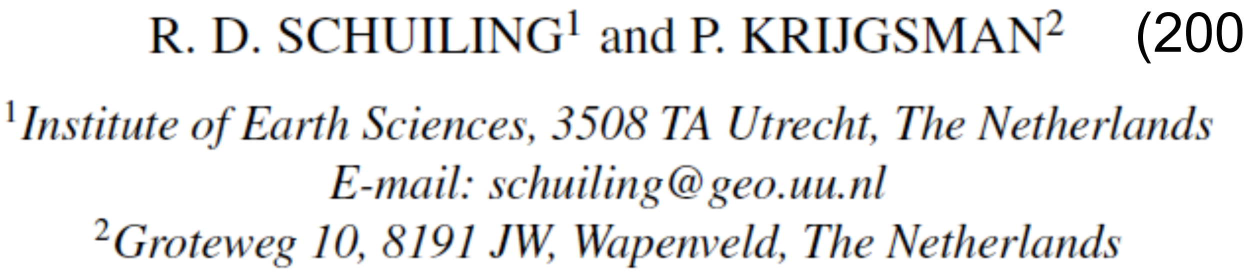
Artificially enhanced weathering of olivine

$Mg_2SiO_4 + 4\ CO_2 + 4\ H_2O \Rightarrow 2\ Mg^{2+} + 4\ HCO_3^- + H_4SiO_4$

+ 2 Mg^{2+}: increase total alkalinity (TA)!

Lackner 1995

ENHANCED WEATHERING: AN EFFECTIVE AND CHEAP TOOL TO SEQUESTER CO_2



R. D. SCHUILING[1] and P. KRIJGSMAN[2]

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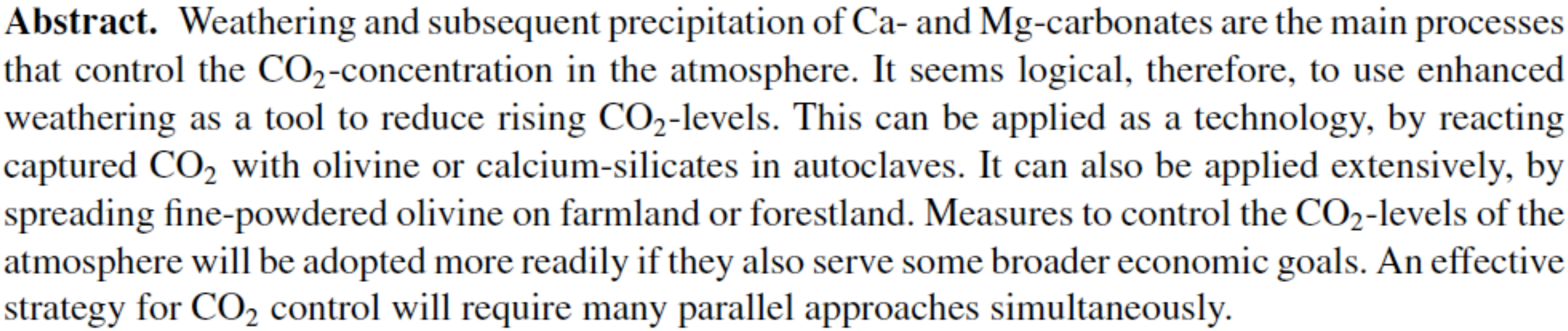
E-mail: schuiling@geo.uu.nl
[2]*Groteweg 10, 8191 JW, Wapenveld, The Netherlands*

(2006)

Requirements: small grain size (< 10 µm), high temperature, low pH
-> reactors or soils in tropical regions



Abstract. Weathering and subsequent precipitation of Ca- and Mg-carbonates are the main processes that control the CO_2-concentration in the atmosphere. It seems logical, therefore, to use enhanced weathering as a tool to reduce rising CO_2-levels. This can be applied as a technology, by reacting captured CO_2 with olivine or calcium-silicates in autoclaves. It can also be applied extensively, by spreading fine-powdered olivine on farmland or forestland. Measures to control the CO_2-levels of the atmosphere will be adopted more readily if they also serve some broader economic goals. An effective strategy for CO_2 control will require many parallel approaches simultaneously.

Total alkalinity

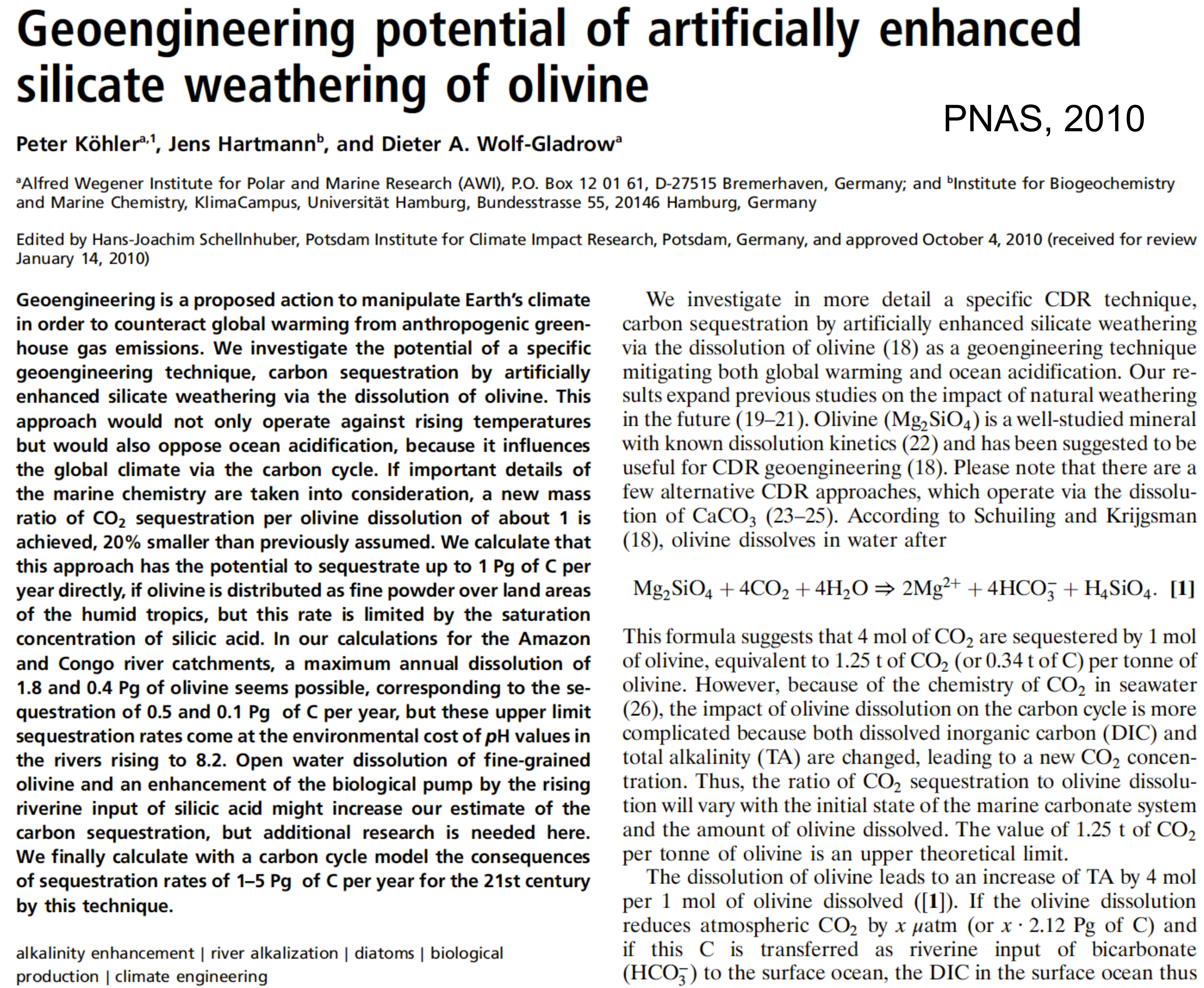
TA ≈ proton acceptors - proton donors

$$TA = [HCO_3^-] + 2\,[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + \text{minor components}$$

$$= [Na^+] + 2\,[Mg^{2+}] + 2\,[Ca^{2+}] + 2\,[Sr^{2+}] + \ldots$$
$$- [Cl^-] - [Br^-] - [NO_3^-] - \ldots$$
$$- TPO_4 + TNH_3 - 2\,TSO_4$$

$$\text{total phosphate} = TPO_4 = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

PNAS, 2010



Geoengineering potential of artificially enhanced silicate weathering of olivine

Peter Köhler[a,1], Jens Hartmann[b], and Dieter A. Wolf-Gladrow[a]

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Edited by Hans-Joachim Schellnhuber, Potsdam Institute for Climate Impact Research, Potsdam, Germany, and approved October 4, 2010 (received for review January 14, 2010)

Geoengineering is a proposed action to manipulate Earth's climate in order to counteract global warming from anthropogenic greenhouse gas emissions. We investigate the potential of a specific geoengineering technique, carbon sequestration by artificially enhanced silicate weathering via the dissolution of olivine. This approach would not only operate against rising temperatures but would also oppose ocean acidification, because it influences the global climate via the carbon cycle. If important details of the marine chemistry are taken into consideration, a new mass ratio of CO_2 sequestration per olivine dissolution of about 1 is achieved, 20% smaller than previously assumed. We calculate that this approach has the potential to sequestrate up to 1 Pg of C per year directly, if olivine is distributed as fine powder over land areas of the humid tropics, but this rate is limited by the saturation concentration of silicic acid. In our calculations for the Amazon and Congo river catchments, a maximum annual dissolution of 1.8 and 0.4 Pg of olivine seems possible, corresponding to the sequestration of 0.5 and 0.1 Pg of C per year, but these upper limit sequestration rates come at the environmental cost of *p*H values in the rivers rising to 8.2. Open water dissolution of fine-grained olivine and an enhancement of the biological pump by the rising riverine input of silicic acid might increase our estimate of the carbon sequestration, but additional research is needed here. We finally calculate with a carbon cycle model the consequences of sequestration rates of 1–5 Pg of C per year for the 21st century by this technique.

alkalinity enhancement | river alkalization | diatoms | biological production | climate engineering

We investigate in more detail a specific CDR technique, carbon sequestration by artificially enhanced silicate weathering via the dissolution of olivine (18) as a geoengineering technique mitigating both global warming and ocean acidification. Our results expand previous studies on the impact of natural weathering in the future (19–21). Olivine (Mg_2SiO_4) is a well-studied mineral with known dissolution kinetics (22) and has been suggested to be useful for CDR geoengineering (18). Please note that there are a few alternative CDR approaches, which operate via the dissolution of $CaCO_3$ (23–25). According to Schuiling and Krijgsman (18), olivine dissolves in water after

$$Mg_2SiO_4 + 4CO_2 + 4H_2O \Rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_4. \quad \textbf{[1]}$$

This formula suggests that 4 mol of CO_2 are sequestered by 1 mol of olivine, equivalent to 1.25 t of CO_2 (or 0.34 t of C) per tonne of olivine. However, because of the chemistry of CO_2 in seawater (26), the impact of olivine dissolution on the carbon cycle is more complicated because both dissolved inorganic carbon (DIC) and total alkalinity (TA) are changed, leading to a new CO_2 concentration. Thus, the ratio of CO_2 sequestration to olivine dissolution will vary with the initial state of the marine carbonate system and the amount of olivine dissolved. The value of 1.25 t of CO_2 per tonne of olivine is an upper theoretical limit.

The dissolution of olivine leads to an increase of TA by 4 mol per 1 mol of olivine dissolved ([**1**]). If the olivine dissolution reduces atmospheric CO_2 by x μatm (or $x \cdot 2.12$ Pg of C) and if this C is transferred as riverine input of bicarbonate (HCO_3^-) to the surface ocean, the DIC in the surface ocean thus

Potential for olivine dissolution

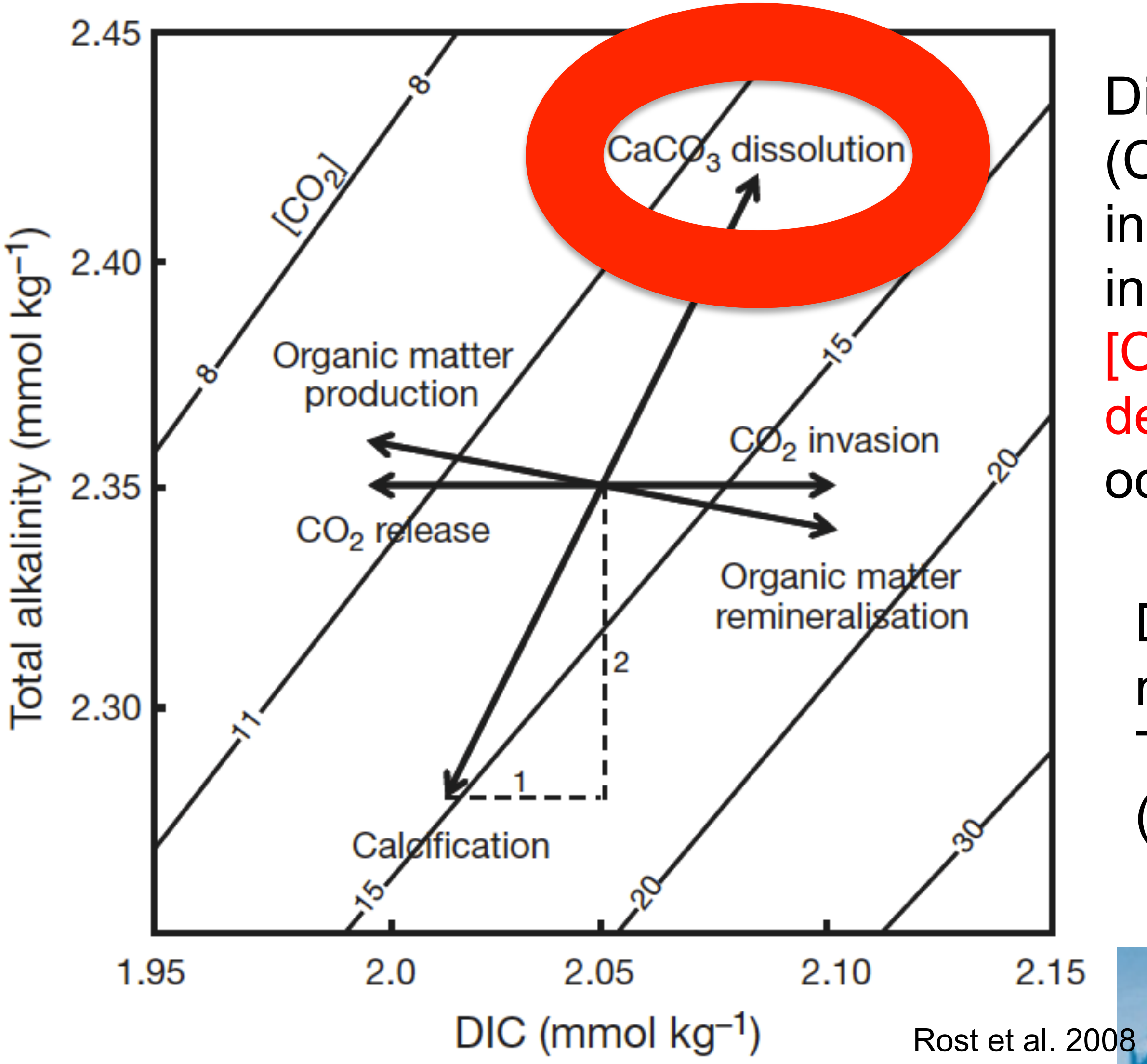
Consider olivine dissolution in catchment areas of Amazon & Congo.
1 g CO_2 sequestration ≈ 1 g olivine (-> huge amounts of olivine!)

Problems:
1. Increase of river pH from below 7 up to 8 or 9 (‘river alkalinization’).
2. Dissolution of silicic acid might limit potential to < 1 Pg C yr^{-1}.

-> find other ways to dissolve olivine

$CaCO_3$ dissolution

$CO_2 = f(DIC, TA, T, S)$



Rost et al. 2008

Dissolution of limestone ($CaCO_3$) leads to an increase of DIC and TA in the ratio of 1:2 -> [CO_2] and pCO_2 decrease (liming the ocean).

Dissolution of other minerals that lead to TA increase: soda ash (Na_2CO_3), olivine

PERGAMON
Energy Conversion & Management 40 (1999) 1803–1813
MANAGEMENT
www.elsevier.com/locate/enconman

Enhanced carbonate dissolution: a means of sequestering waste CO_2 as ocean bicarbonate

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Received 14 November 1998; accepted 26 February 1999

Abstract

The reaction of a mineral carbonate, such as limestone, with water and CO_2 to form bicarbonate in solution, is explored as a CO_2 mitigation strategy. Initial cost estimates for such a process range from \$18 to \$128 per tonne CO_2 sequestered, with an energy penalty of about 8% and with relatively low environmental impact. The regional availability and transport of water and mineral carbonate appear to be the primary determinants of the strategy's cost and applicability. The bicarbonate-rich waste effluent would be released into rivers or coastal waters, ultimately adding a small amount to the existing, very large bicarbonate reservoir in the ocean. For many applications, this form of 'marine' carbon sequestration appears to be less costly, less affected by national and international regulations, more environmentally friendly and more effective over the long term than direct CO_2 injection into the ocean. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon; CO_2; Carbon dioxide; Fossil fuel; Sequestration; Mitigation; Storage; Calcium; Carbonate; Bicarbonate; Limestone; Dissolution; Weathering; Disposal

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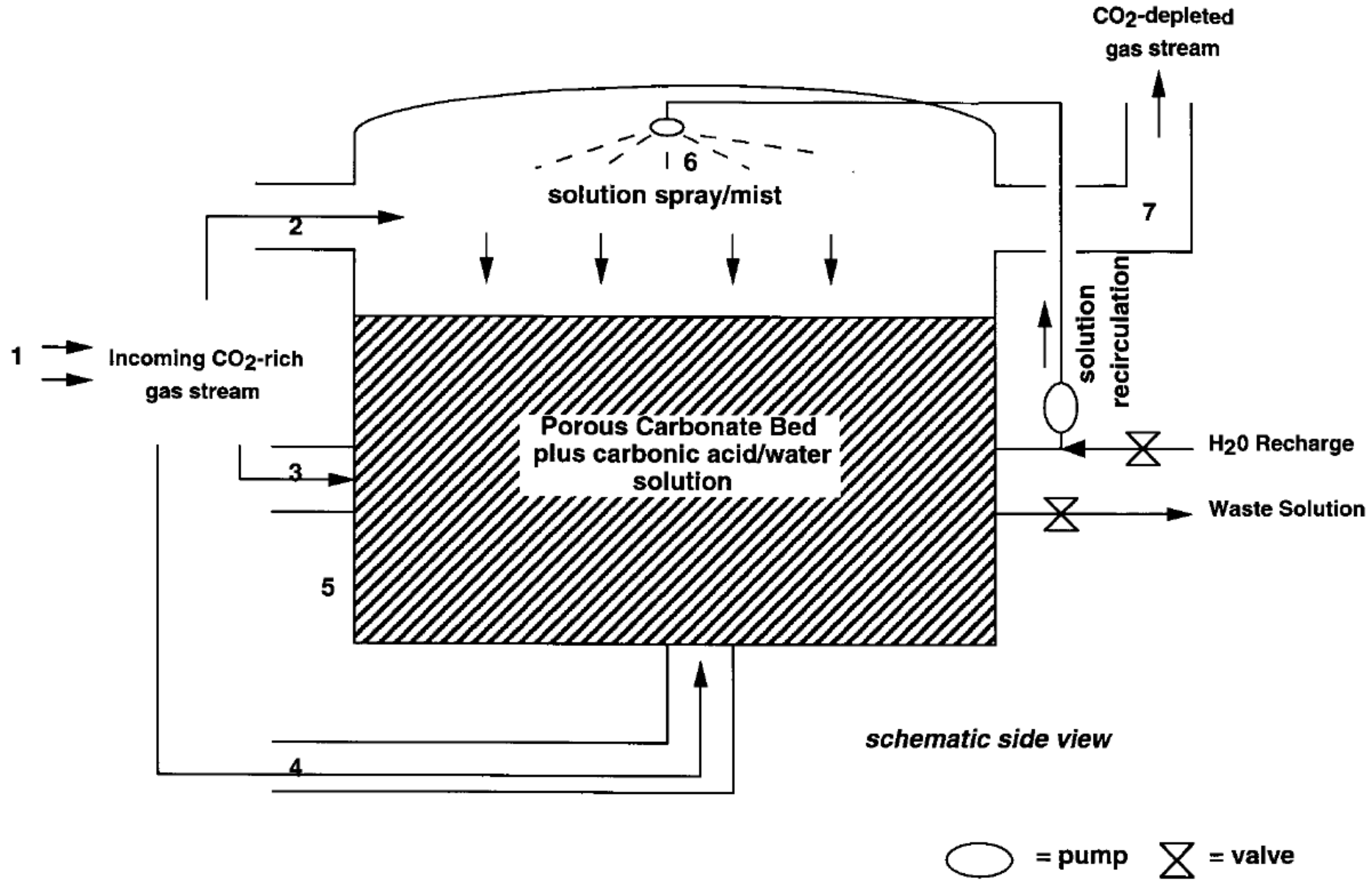

Fig. 1. An example of a possible C_2SEA reactor design.

Liming the ocean

$CaCO_3 \rightarrow CaO + CO_2$

CaO = lime

CO_2 -> CCS (carbon capture & storage)

$CaO + H_2O + 2\ CO_2 \rightarrow Ca^{2+} + 2\ HCO_3^-$

Final remarks

Large scale experiment (Revelle & Suess, 1957): anthropogenic CO_2 emissions & climate change & ocean acidification

Finish this experiment (mitigation) or adapt to the consequences or counteract/combat the effects (climate- or geo-engineering)

Some climate-engineering methods (iron fertilization, enhanced silicate weathering) have the potential to sequester large amount of CO_2 in the ocean (order of 1 Pg C yr^{-1}).

These methods might have (not well known) side-effects on marine ecosystems (general problem for CO_2 sequestration in the ocean).

Climate-engineering: trade-off or torture?

Sustainable development

Thanks for your attention!