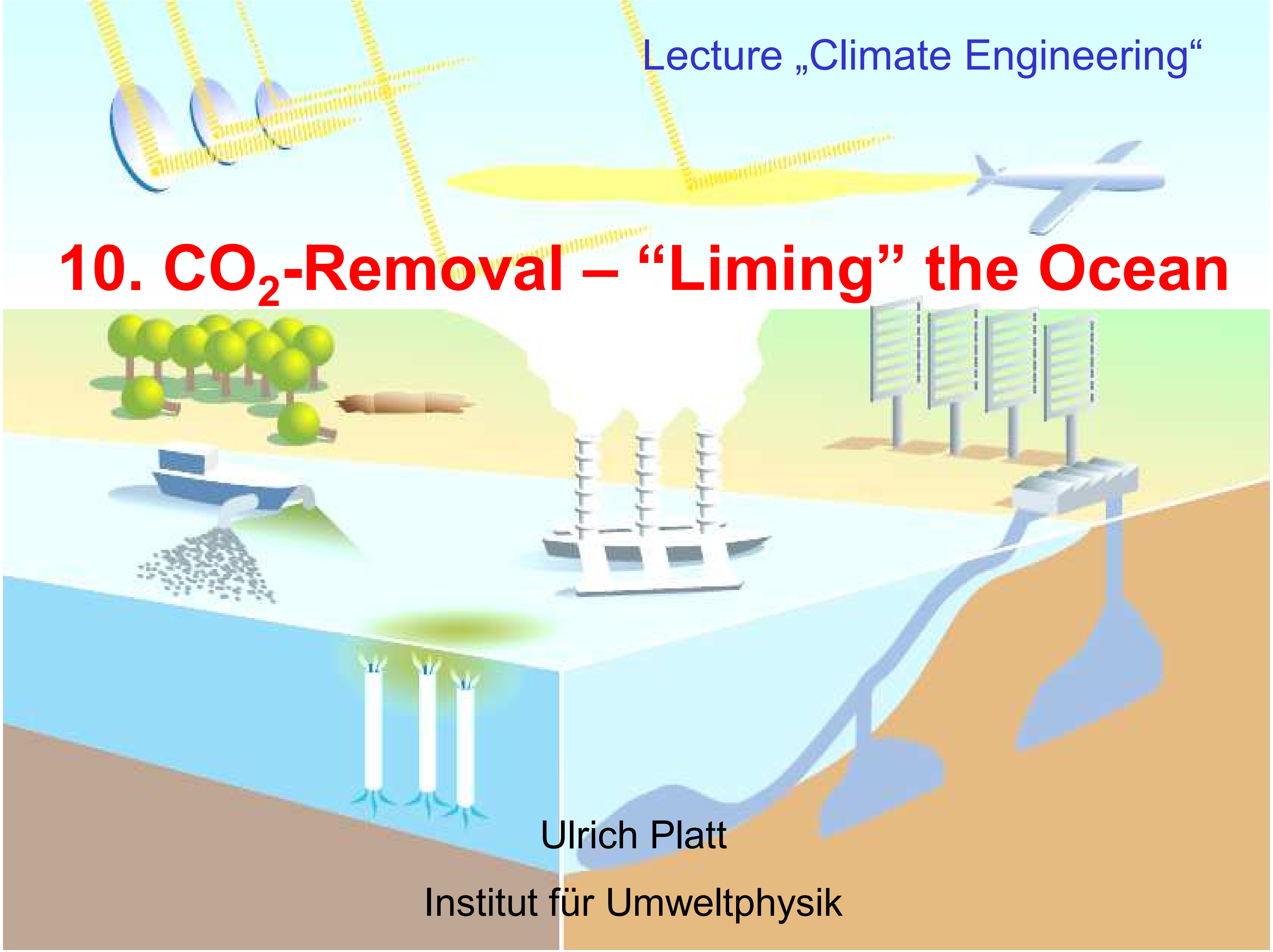
Lecture „Climate Engineering“

10. CO_2-Removal – “Liming” the Ocean



Ulrich Platt

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Lecture Program of „Climate Engineering

Part 1: Introduction to the Climate System (4 sessions)

1. Introduction and scope of the lecture
2. The Climate System – Radiation Balance
3. Elements of the Climate System - Greenhouse Gases, Clouds, Aerosol
4. Dynamics of the Climate System - Sensitivity, Predictions

Part 2: Climate Engineering Methods - Solar Radiation Management, SRM

1. SRM – Reflectors in space
2. SRM – Aerosol in the Stratosphere
3. SRM – Cloud Whitening
4. SRM – Anything else

Part 3: Climate Engineering Methods – Carbon Dioxide Removal, CDR

1. Direct CO_2 removal (CDR) from air
2. Alkalinity to the ocean (enhanced weathering)
3. Ocean fertilization
4. Removal of other greenhouse gases

Part 4: CE – Effectiveness, Side Effects (3 sessions)

1. Comparison of Techniques, characterisation of side effects
2. Other parameters than temperature
3. Summary

Nachricht (FAZ 27.6.2012):

Unterirdische CO_2-Lager Einigung auf Kohlendioxid-Speicherung

27. 6. 2012 · Bund und Länder haben sich auf einen Kompromiss zur umstrittenen unterirdischen Speicherung von Kohlendioxid geeinigt: Die verpresste CO_2-Menge soll begrenzt werden und geringer sein als bisher geplant. Zudem können die Länder unter bestimmten Bedingungen Speicher in ihrem Gebiet verhindern.

Nach monatelangen Verhandlungen gibt es eine Einigung über die unterirdische Speicherung von klimaschädlichem Kohlendioxid in Deutschland. Der Vermittlungsausschuss von Bundestag und Bundesrat beschloss am Mittwochabend einen Kompromiss. Demnach soll die verpresste CO_2-Menge auf 1,3 Mio. t pro Jahr und Speicher begrenzt werden - zunächst waren drei Millionen Tonnen geplant. Zudem gibt es eine Länderklausel, mit der Bundesländer unter bestimmten Bedingungen Speicher in ihrem Gebiet verhindern können. Schleswig-Holstein und Niedersachsen hatten darauf gedrungen.

In der Energiebranche wird der CCS-Technologie (Carbon Capture and Storage) wegen allgemeiner Bedenken und Proteste trotz der Einigung wenig Aussicht auf Erfolg in Deutschland vorausgesagt. Eine Regelung ist aber wichtig, damit Zuschüsse etwa für den Neubau von Kohlekraftwerken fließen können. EU-Beihilfeleitlinien fordern eine CCS-Regelung. Die Bundesregierung hätte gerne eine Regelung ohne Ausstiegsklauseln gehabt und hält CCS für eine klimafreundliche Technologie. In der Industrie oder bei Kohlekraftwerken wird CO_2 abgefangen und per Pipeline in unter-irdische Speicher verpresst. Bürger fürchten aber ein unkontrolliertes Entweichen des Gases.

Literature

Hangx S.J.T. and Spiers C.J. (2009), Coastal spreading of olivine to control atmospheric CO_2 concentrations: A critical analysis of viability, Int. J. Greenhouse Gas Control 3, 757-767.

Harvey L.D.D. (2008), Mitigating the atmospheric CO_2 increase and ocean acidification by adding limestone powder to upwelling regions, J. Geophys. Res. 113, C04028.

Kheshgi H.S. (1995), Sequestering atmospheric carbon dioxide by increasing ocean Alkalinity, Energy 20, 915–922.

Köhler P., Hartmann J., Wolf-Gladrow D.A. (2010), Geoengineering potenzial of artificially enhanced silicate weathering of olivine, Proc. National Academy of Sciences, S. 1- 6.

Körtzinger A. (2003), A significant CO_2 sink in the tropical Atlantic Ocean associated with the Amazon River plume, Geophys. Res. Lett. 30, 2287.

Lenton T.M. and Britton C. (2006), Enhanced carbonate and silicate weathering accelerates recovery from fossil fuel CO_2 perturbations, Global Biogeochem. Cycles 20, GB3009.

Rau G.H. (2008), Electrochemical splitting of calcium carbonate to increase solution alkalinity: Implications for mitigation of carbon dioxide and ocean acidity, Environ. Sci. Technol. 42, 8935–8940.

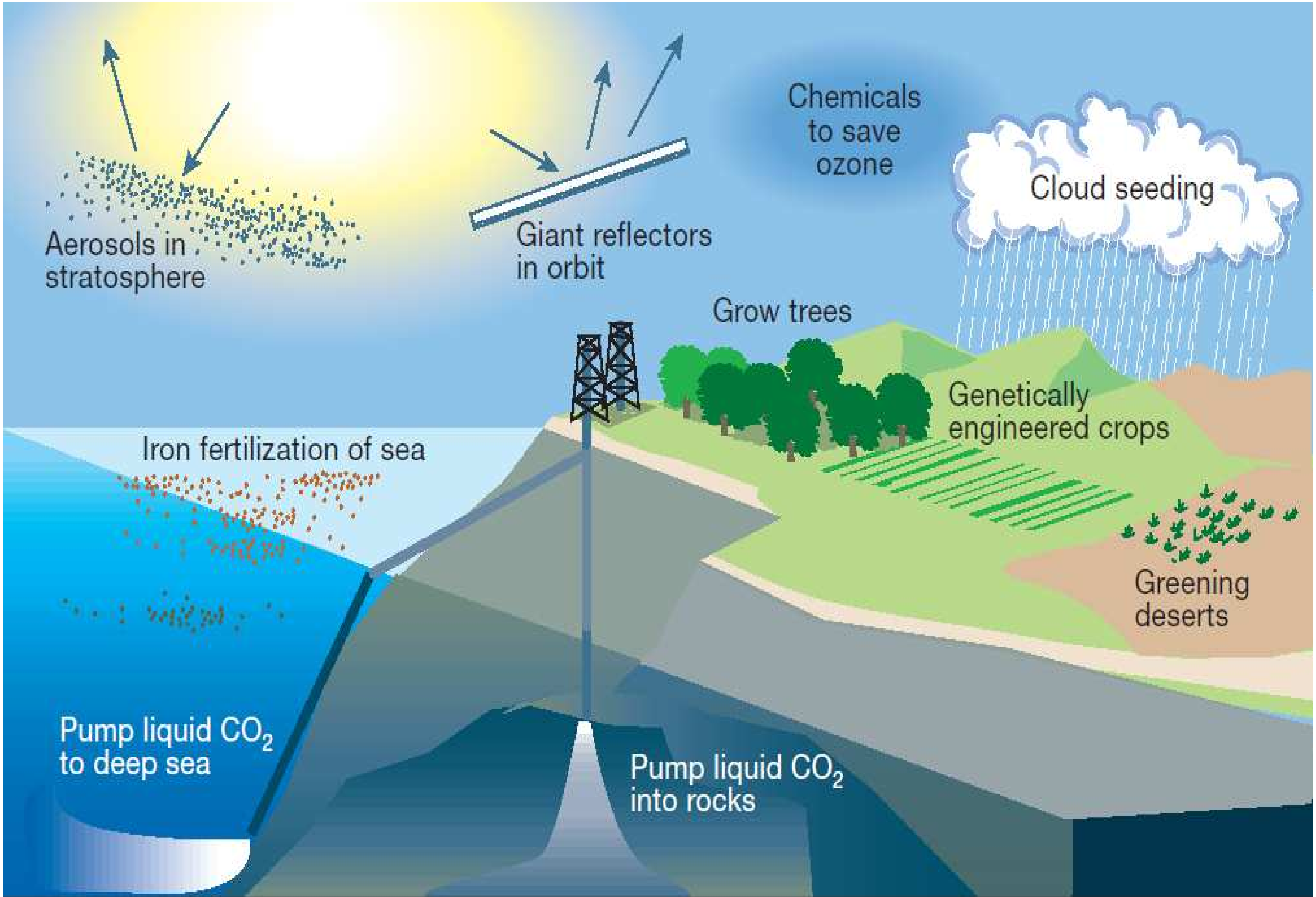
Riebesell U., Körtzinger A., and Oschlies A. (2009), Sensitivities of marine carbon fluxes to ocean change, Proc. Natl. Acad. Sci. (PNAS) 106, 20602–20609.

Schuiling R.D. and Krijgsman P. (2006), Enhanced weathering: An effective and cheap tool to sequester CO_2, Clim. Change 74, 349–354.

Couce E., Irvine P.J., Gregorie L.J., Ridgwell A., Hendy E.J. (2013), Tropical coral reef habitat in a geoengineered, high-CO_2 world, Geophys. Res. Lett. 40, 1–6, doi:10.1002/grl.50340.

Contents of Today's Lecture

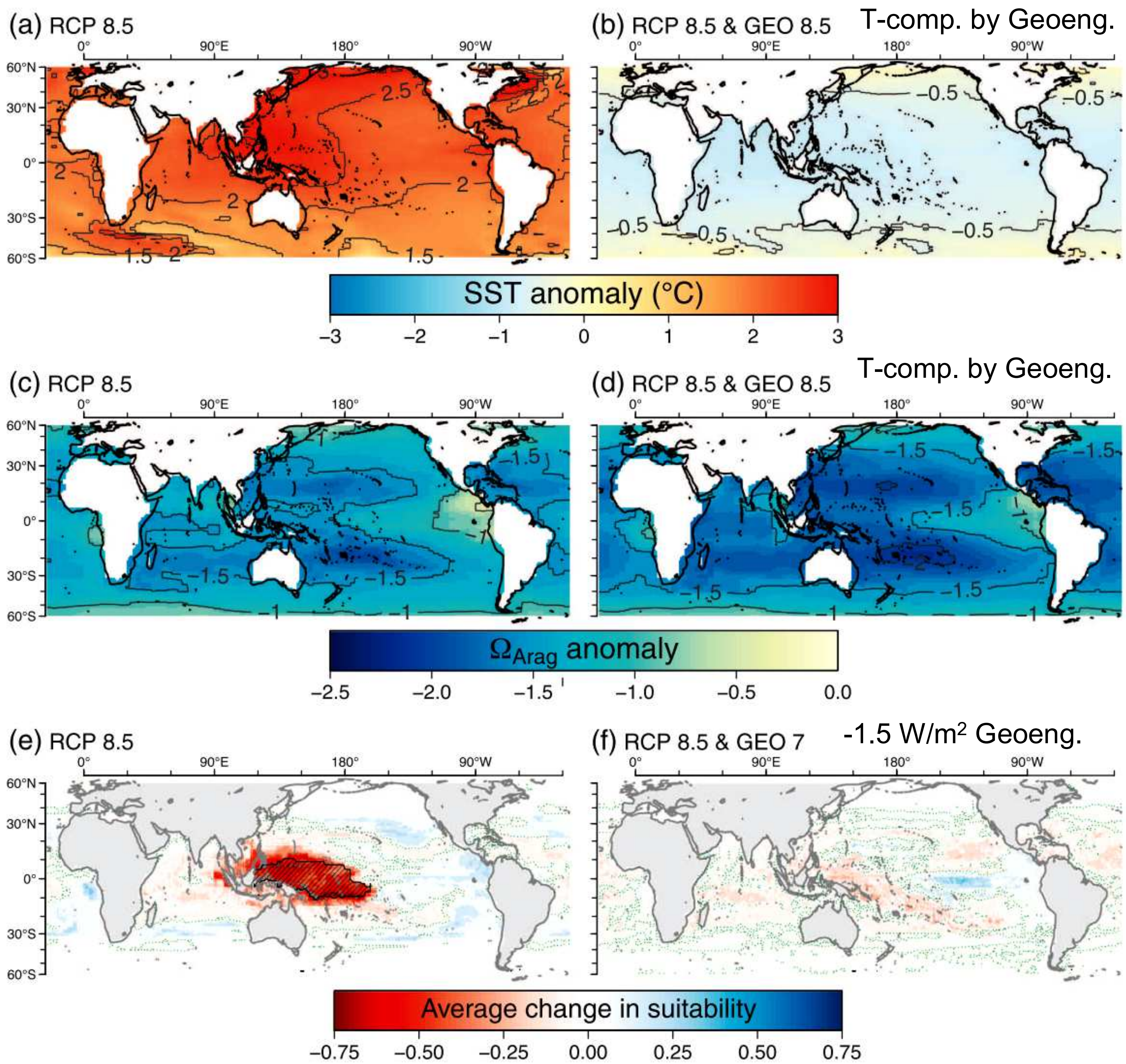
- Inorganic Carbon Chemistry in the Ocean
- What happens if we add alkalinity to the ocean?
- Weathering processes
- Feasibility of adding alkalinity to the oceans
- Technical questions
- Side effects?
- Model calculations
- Conclusions



Schematic representation of various climate-engineering proposals (courtesy B. Matthews).

Keith, David, 2001: Geoengineering, *Nature*, **409**, 420.

Aragonit
Saturation
Anomaly



Couce et al. 2013

The Idea:

1) Obtain suitable alkaline minerals from quarries (Steinbrüchen)
2) Grind it to fine powder (which dissolves relatively rapidly)
3) Put powder to ocean (or into large rivers)

UPTAKE OF CO_2 BY THE OCEANS

Remember Lecture 3

ATMOSPHERE $CO_2(g)$

$\downarrow\uparrow$

OCEAN $CO_2{\cdot}H_2O$

$K_1 = 9\times10^{-7}$ M $\quad CO_2{\cdot}H_2O \rightleftarrows HCO_3^- + H^+$

$K_2 = 7\times10^{-10}$ M $\quad HCO_3^- \rightleftarrows CO_3^{2-} + H^+$

Higher CO_2:

→ Lower pH

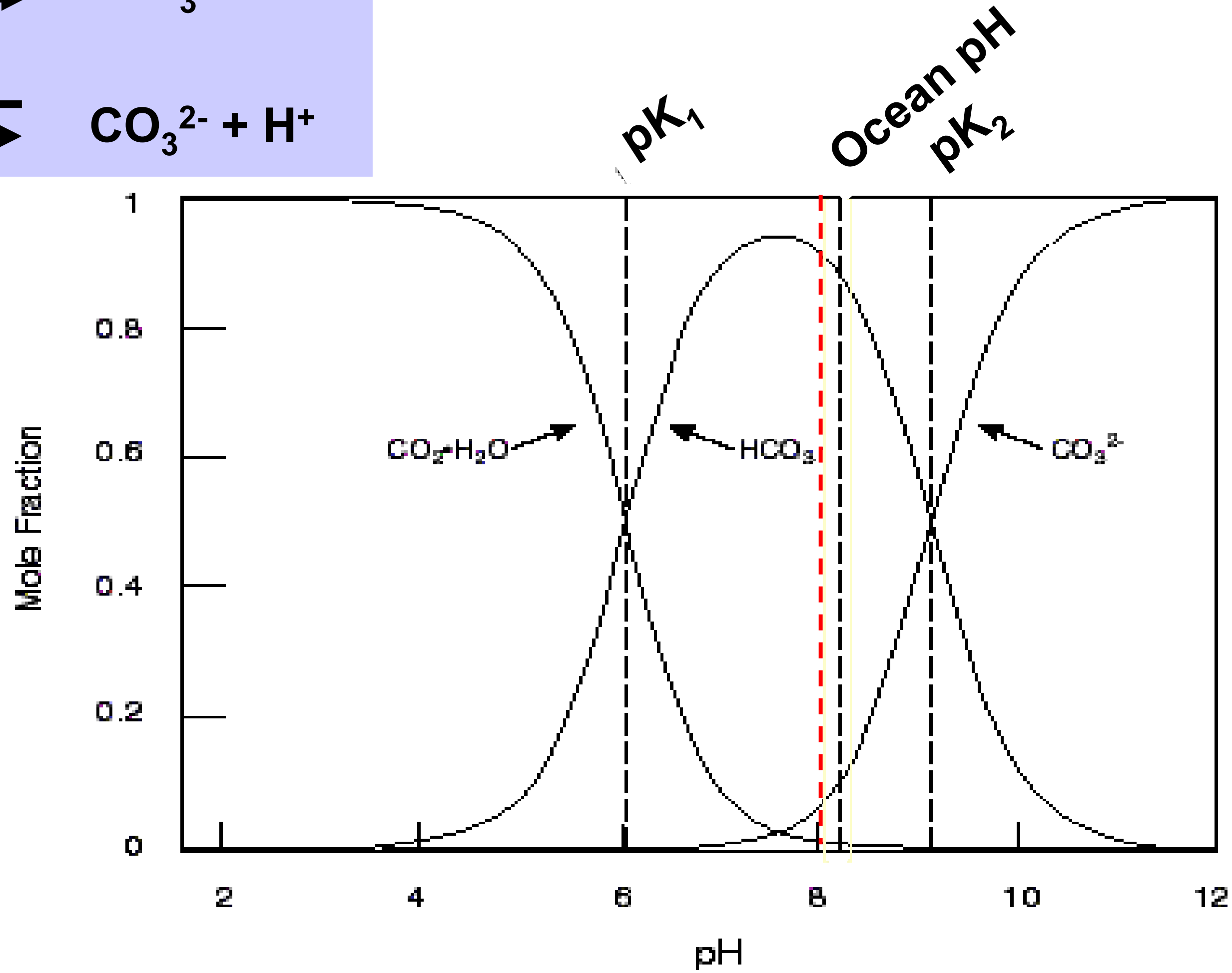
→ More HCO_3^-, Less CO_3^{2-}

$$K_1 = \frac{[HCO_3^-]\cdot[H^+]}{[CO_2]} \quad \frac{\text{Mols}}{\text{liter}}$$

$$K_2 = \frac{[CO_3^{2-}]\cdot[H^+]}{[HCO_3^-]}$$

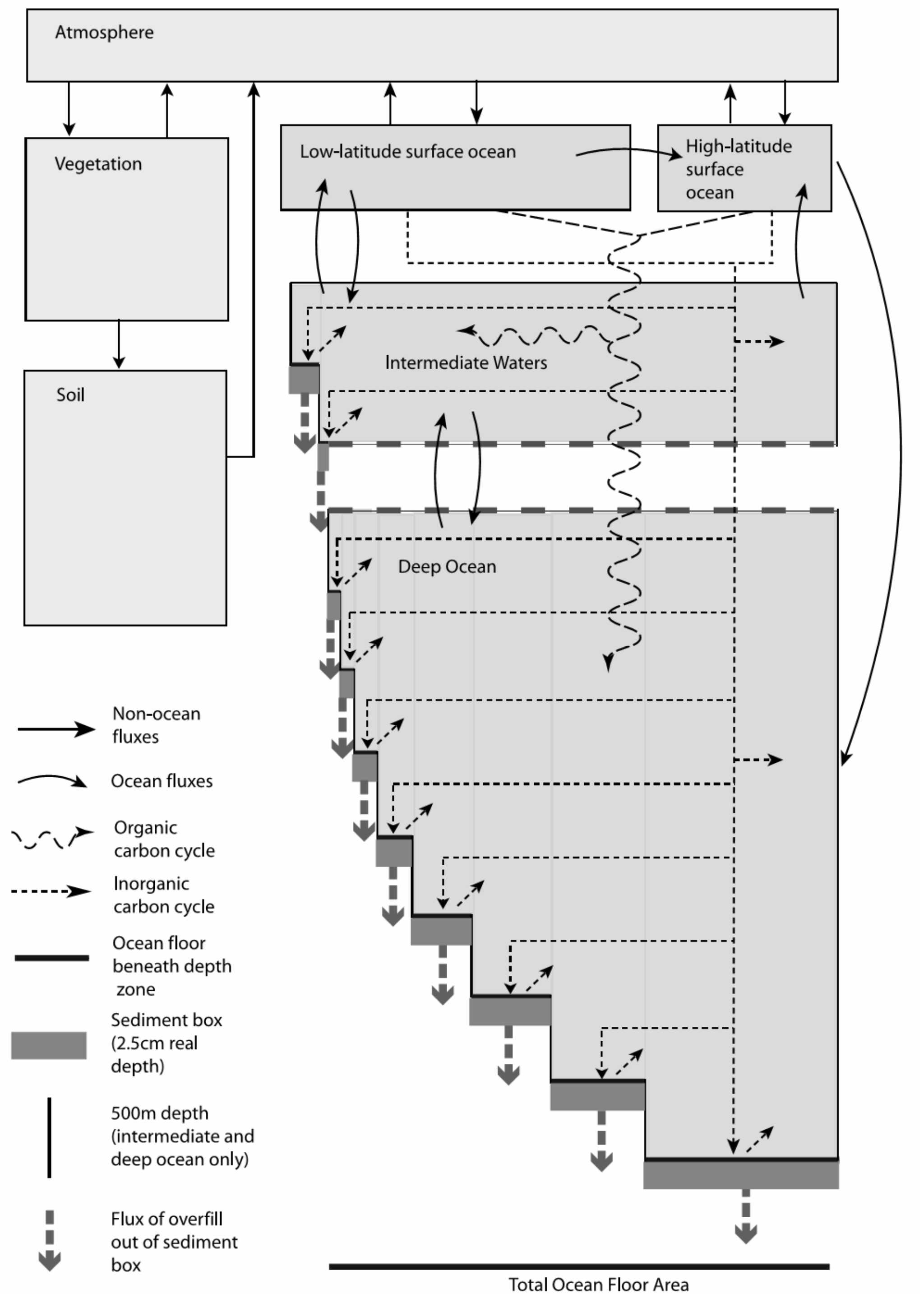
Net uptake:

$$CO_2(g) + CO_3^{2-} \longrightarrow 2HCO_3$$



Global Carbon-Cycle Model

Lenton 2000,
Lenton and Britton 2006



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Riebese
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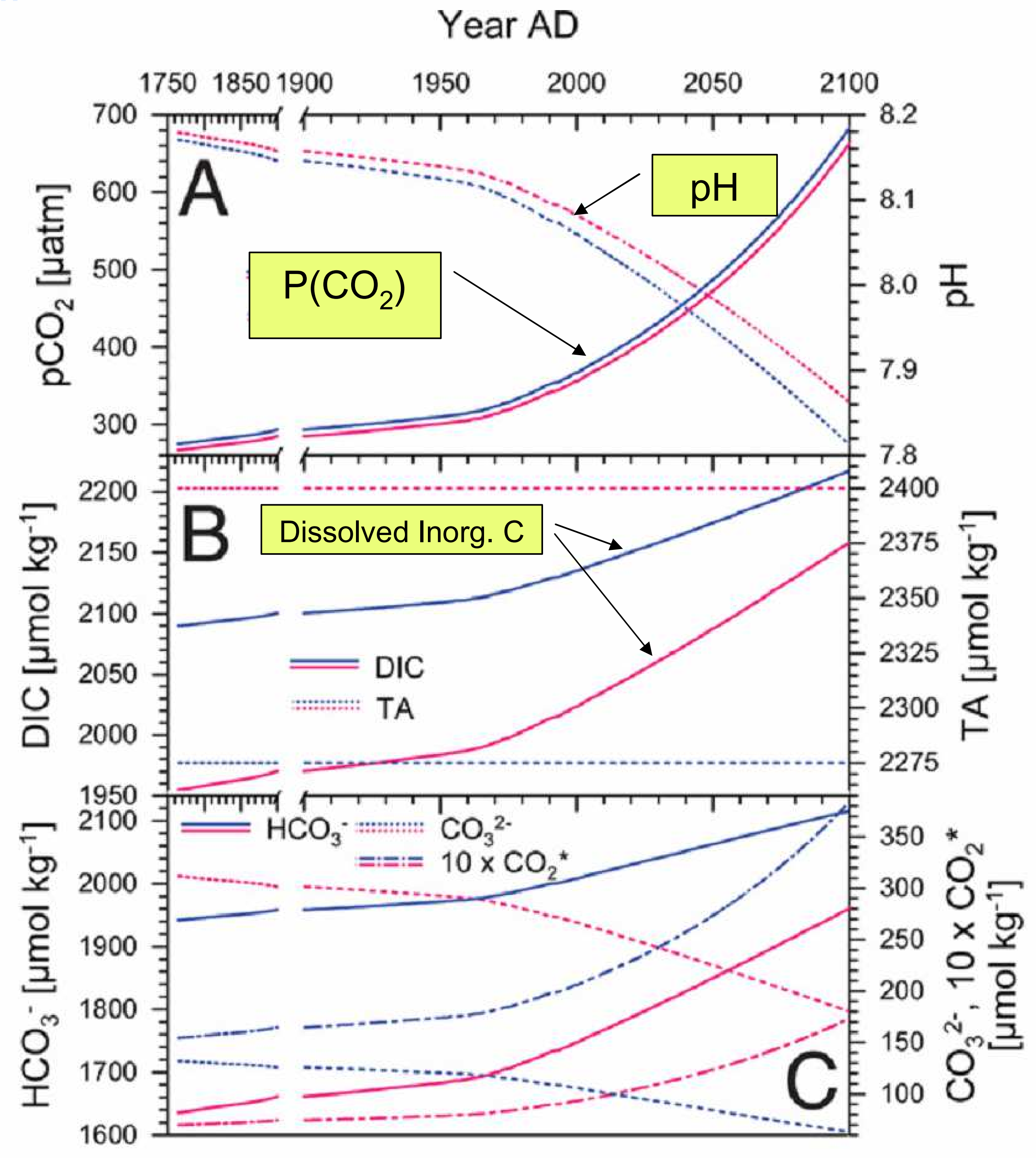
2009

Changes in cold (blue) and warm (red) surface waters between 1750 and 2100 under prescribed (A) atmo-spheric CO_2 increase.

→ Lower pH
→ Higher Dissolved Inorganic Carbon (DIC)



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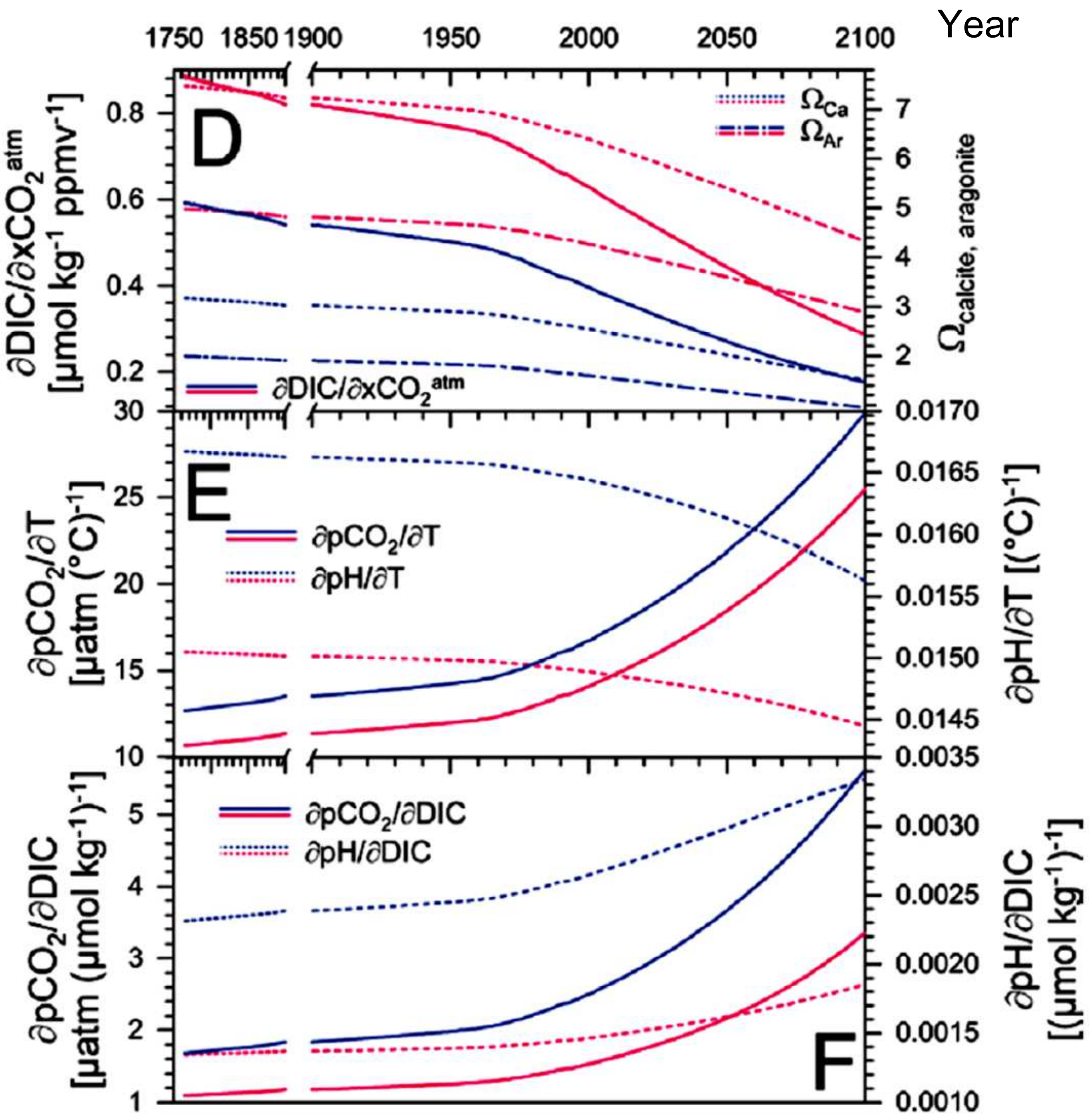
Conditions in cold (blue) and warm (red) surface waters, 1750-2100 under prescribed atmospheric CO_2 increase.

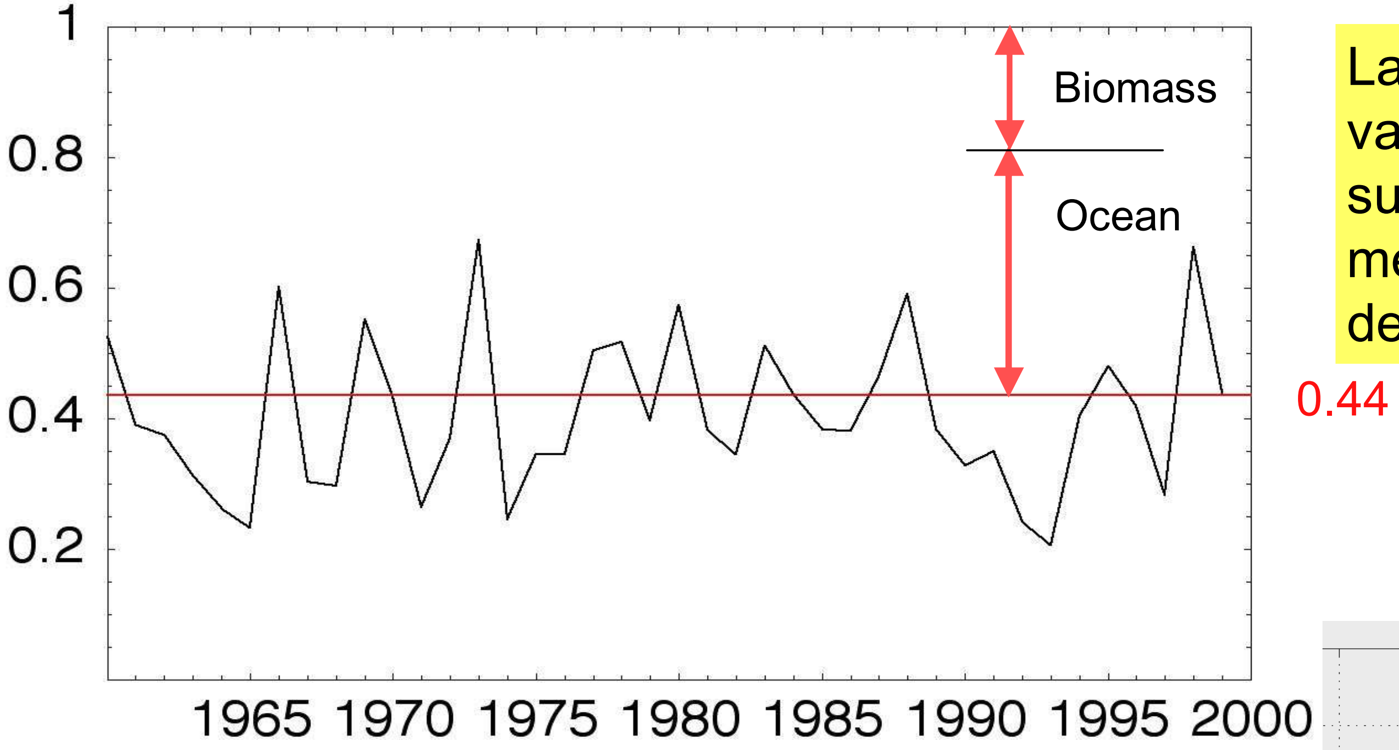
D: CO_2-uptake ratio and saturation states of calcite and aragonite.

E: Temperature sensitivities of pCO_2 and pH.

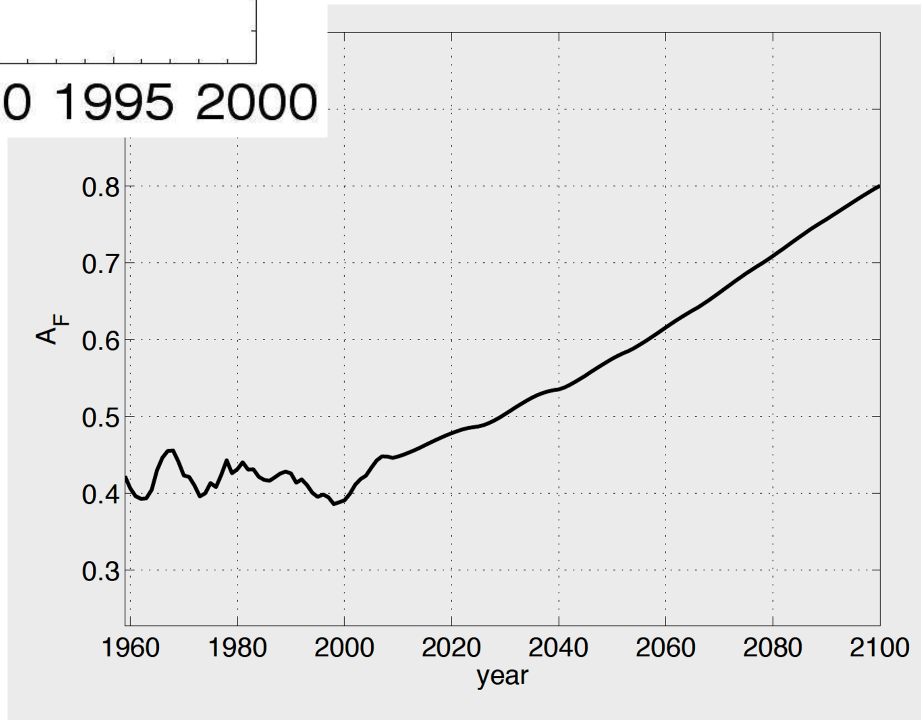
F: Chemical (i.e., CO_2) sensitivities of CO_2 and pH.



The „Airborne Fraction“ of emitted CO_2



Large inter-annnual variations, but surprisingly constant mean during recent decades.



Model predictions:

Terenzi and Khatiwala, Tellus 2009

Solution (?): Add Alkalinity to the Ocean

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ (1)

$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$ (2)

Net: $Ca(OH)_2 + 2\ CO_2 \rightarrow Ca(HCO_3)_2$

Problem:

$Ca(OH)_2$ must be produced from limestone:

$CaCO_3$ + heat $\rightarrow CaO + CO_2$ (CaO: quick lime)

$CaO + H_2O \rightarrow Ca(OH)_2$

Nevertheless:
Burning lime releases one CO_2 per mole of $CaCO_3$, formation of calcium bicarbonate binds two molecules of CO_2 per mole of lime.

However:
In the ocean enhancing bicarbonate reduces carbonate,
→ less than 2 molecules of CO_2 are consumed per $Ca(OH)_2$ added.

Reducing Atmospheric CO_2 by „Liming the Ocean“*, System 1

Kheshgi 1995

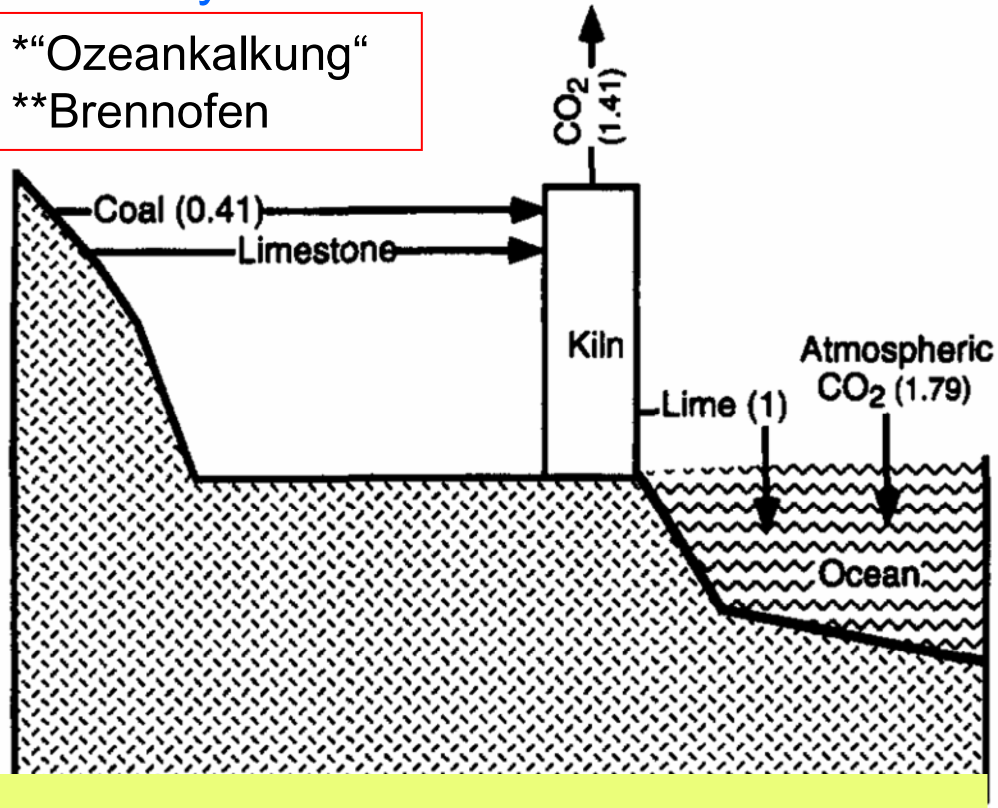
*“Ozeankalkung“
**Brennofen

$CaCO_3$ + 178 kJ/mol → CaO + CO_2
(1 atm, 25°C)

In Sea Water:

CaO + 1.79 CO_2 + 0.79 H_2O + ...

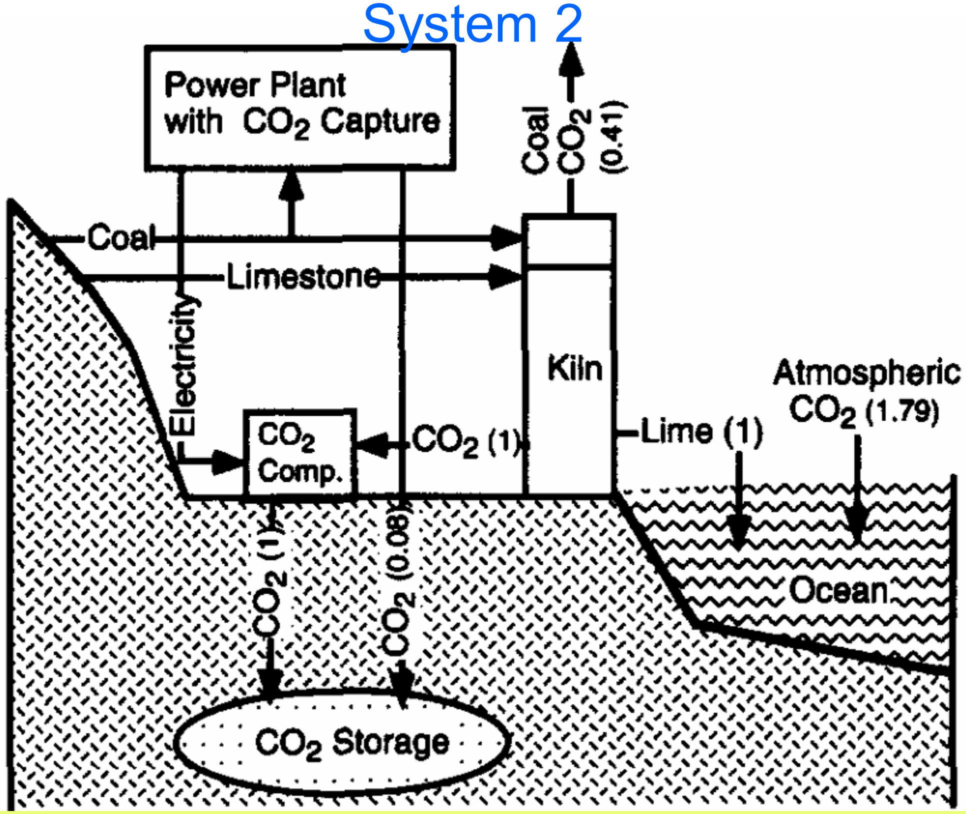
→ Ca^{2++} + 1.62 HCO_3^- + 0.17 CO_2^{2-} + ...



Conceptual process:
1) Limestone is converted to lime by a kiln**. Combustion- and decomposition gases are emitted to the atmosphere.
2) Dissolution products of lime are put into ocean, → enhanced oceanic uptake of CO_2. (mole flow rates relative to produced lime in parentheses). Production of 1 mole of CaO leads to emission of 0.41 mole CO_2 from burned coal + 1 mole from $CaCO_3$.
→ 1.41 moles CO_2 emitted to the atmosphere.
3) Each mole CaO dissolved in the ocean leads to absorption of 1.79 moles CO_2.
→ net removal of 1.79-1.41 = 0.38 mole CO_2 per mole CaO produced.

Reducing Atmospheric CO_2 by „Liming the Ocean“, System 2

Kheshgi 1995



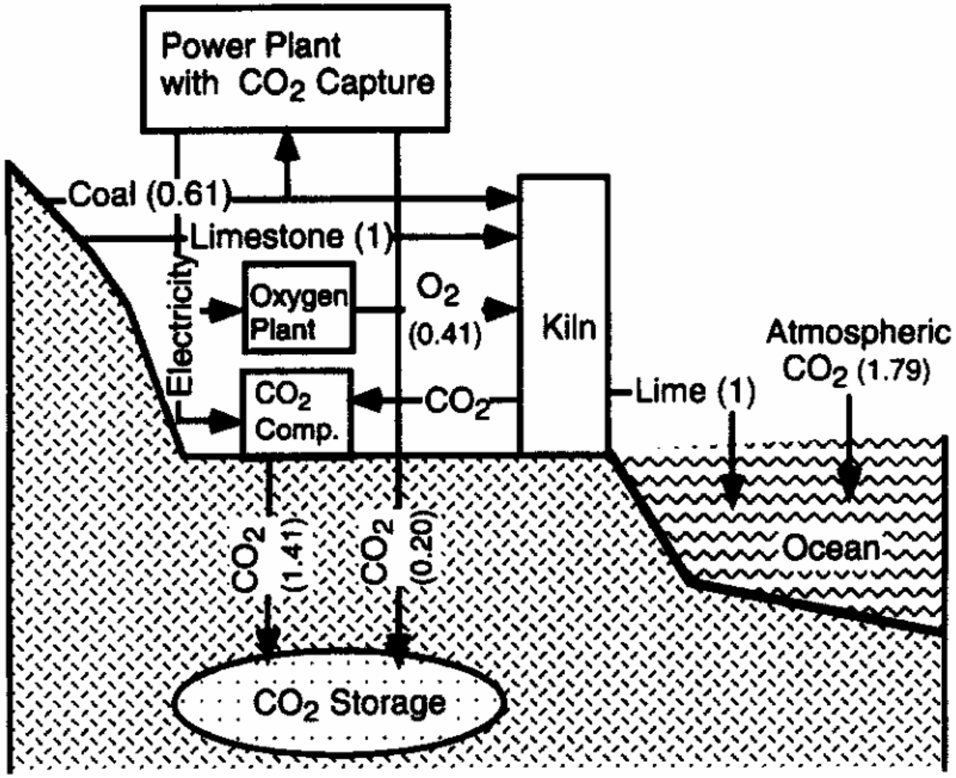
Similar to System 1, but with capture and storage of the CO_2 from limestone. Combustion gases are emitted to the atmosphere. Dissolution products of lime are put into the ocean, resulting in enhancement of the oceanic uptake of atmospheric CO_2. Mole flow rates relative to that of produced lime shown in parentheses. For each mole of CaO produced, one mole of CO_2 from $CaCO_3$ decomposition must be compressed and stored, electricity is required for this task, which requires an additional 0.08 mole of carbon in coal to be burned for power generation.

→ net removal of 1.79-0.41 = 1.38 mole CO_2 per mole CaO produced.

→ Plus 1.08 mole of CO_2 to be stored (underground).

Reducing Atmospheric CO_2 by „Liming the Ocean“, System 3

Kheshgi 1995



As System 2 but combustion and decomposition CO_2 captured and stored (requires Kiln with oxygen feed). Dissolution products of lime are put into the ocean, → enhancement of oceanic CO_2 uptake. For each mole of CaO produced 0.41 mole of O_2 must be separated from air. Electricity is required to separate O_2 and compress the 1.41 moles CO_2 for storage, which requires an additional 0.20 mole of C in coal to be burned, and requires additional storage of 0.20 mole of CO_2.

→ net removal of 1.79-0 = 1.79 mole CO_2 per mole CaO produced.

→ Plus 1.28 mole of CO_2 to be stored (underground).

An Easier Way?

→ Just put minerals into the ocean or into rivers or on the soil

Mineral weathering is a natural process!

(but very slow!)

Source: http://www.limeplus.com.au/news_sept05.php

CO_2-Uptake by Mineral Weathering

Olivine (Forsterite):

$Mg_2SiO_4(s) + 2\ CO_2(g) + 2\ H_2O(l) \rightarrow 2\ MgCO_3(s) + H_4SiO_4(aq)$ (1a)

Pyroxenoid (Wollastonite):

$CaSiO_3(s) + CO_2(g) + 2H_2O(l) \rightarrow CaCO_3(s) + H_4SiO_4(aq)$ (1b)

Serpentine:

$Mg_3Si_2O_5(OH)_4(s) + 3\ CO_2(g) + 2\ H_2O(l) \rightarrow 3\ MgCO_3(s) + 2\ H_4SiO_4(aq)$

Weathering (and thus CO_2 uptake) occurs naturally, however very slowly (annual CO_2 uptake < 0.2 GtC)

Artificial enhancement by higher temperatures (100-185^{o}C) and higher p(CO_2) (40-150 atm). → Too much energy needed

Possible Alternative: Put large amounts of suitable minerals (e.g. olivine) as powder (r = 0.3mm) to the surface [Schuiling and Krijgsman 2006].

A layer of 1.2 mm of olivine on the entire surface of Earth (or about 4 mm on all land surface) would be sufficient to remove all CO_2 from the Atmosphere

Enhanced Weathering

Olivine dissolution (neglecting Fe):

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

→ 4 moles of CO_2 are sequestered per mole of olivine
→ Equivalent to ≈1.25 t of CO_2 per t of olivine

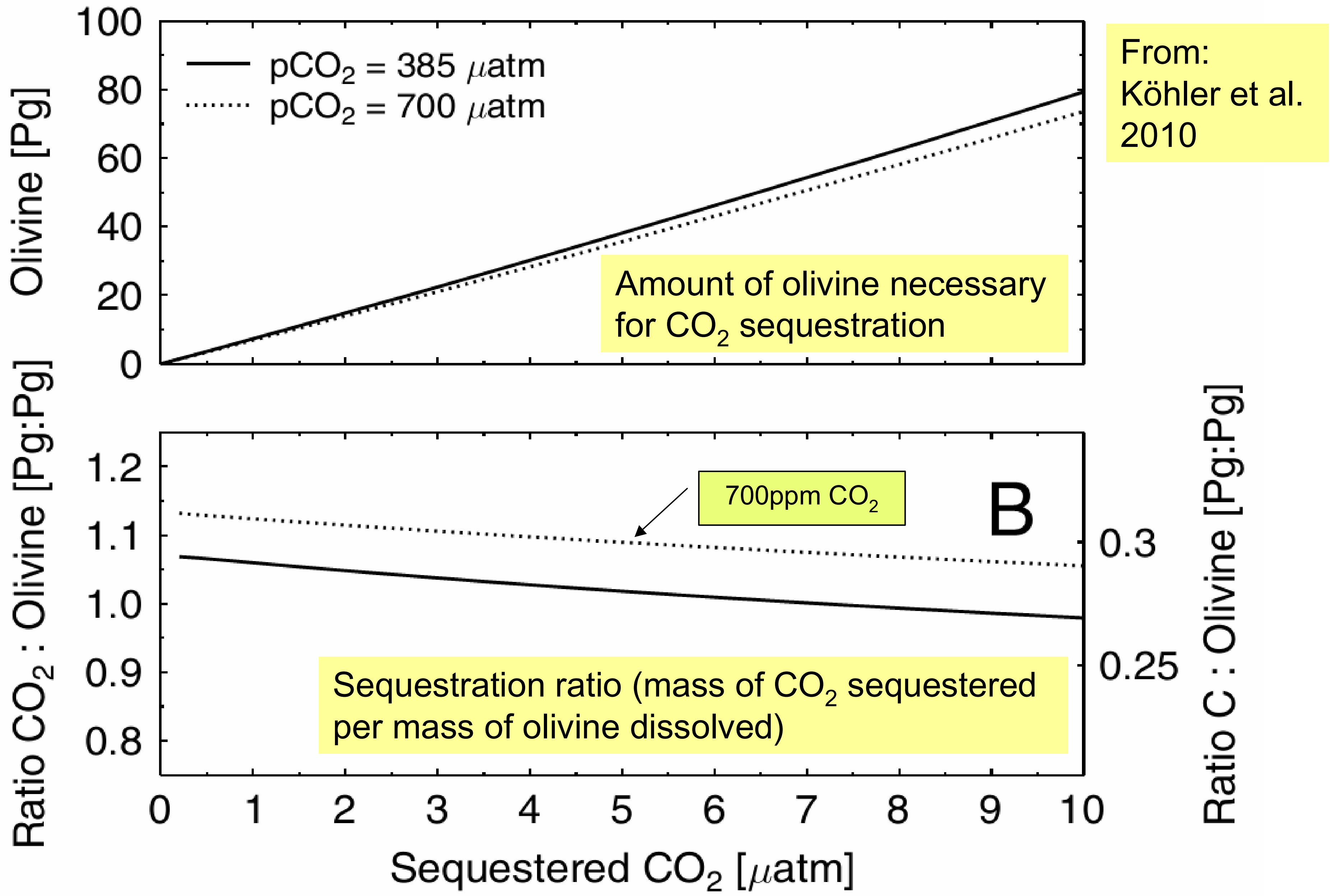
Problem:
Sea water CO_2 – HCO_3^- - $CO_3^=$ equlibrium is disturbed

→ Above CO_2 – uptake figure is a theoretical maximum

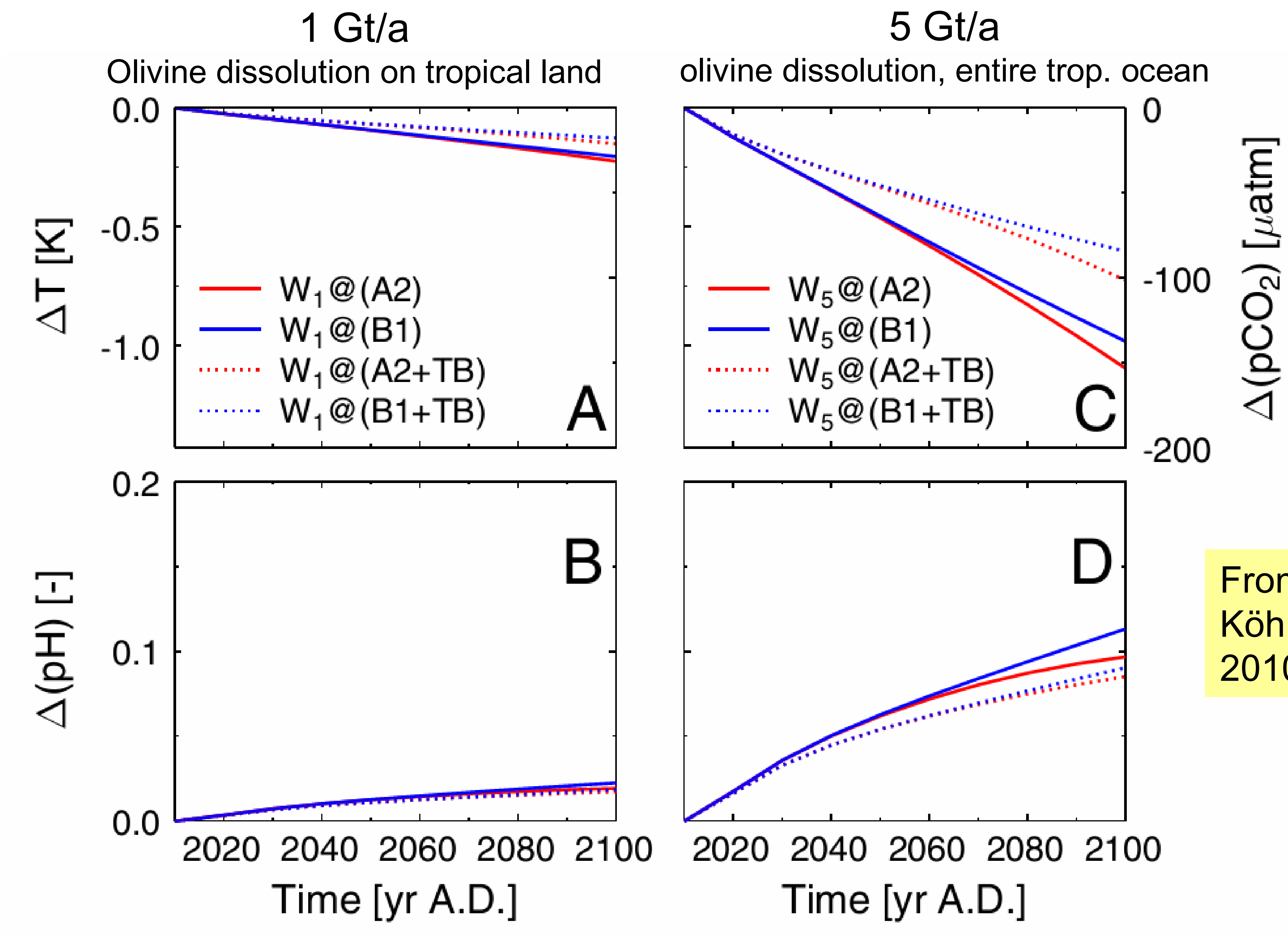
Köhler et al. 2010

The Effect and Efficiency of Olivine Dissolution in the Ocean

(p_{CO2} = 385 or 750 ppmv)



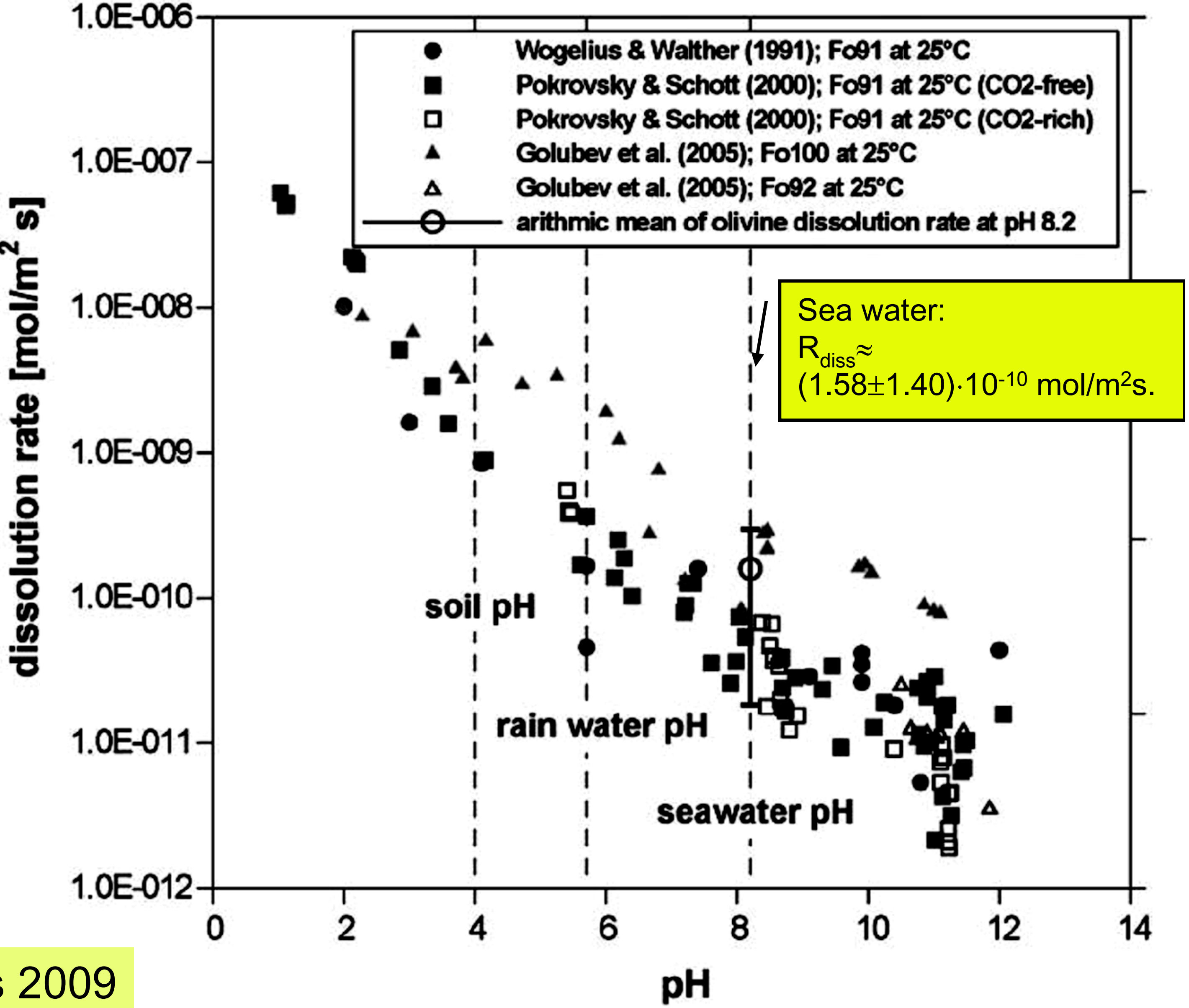
Change in Temperature and pH due to Olivine addition to the Ocean (2010-2100)



From:
Köhler et al.
2010

Problem: Dissolution of Minerals is slow!

Olivine dissolution rate R_{diss} (mol/m^{2}s) in water vs. pH (25^{o}C).
Sea water (pH ≈8.2): R_{diss}≈ (1.58±1.40)·10^{-10} mol/m^{2}s. (one order of magnitude variability).
Decreasing pH to 5.7 (rain water pH) and 4.0 (acid soil pH) increases R_{diss} by approx. one and two orders of magnitude, resp.



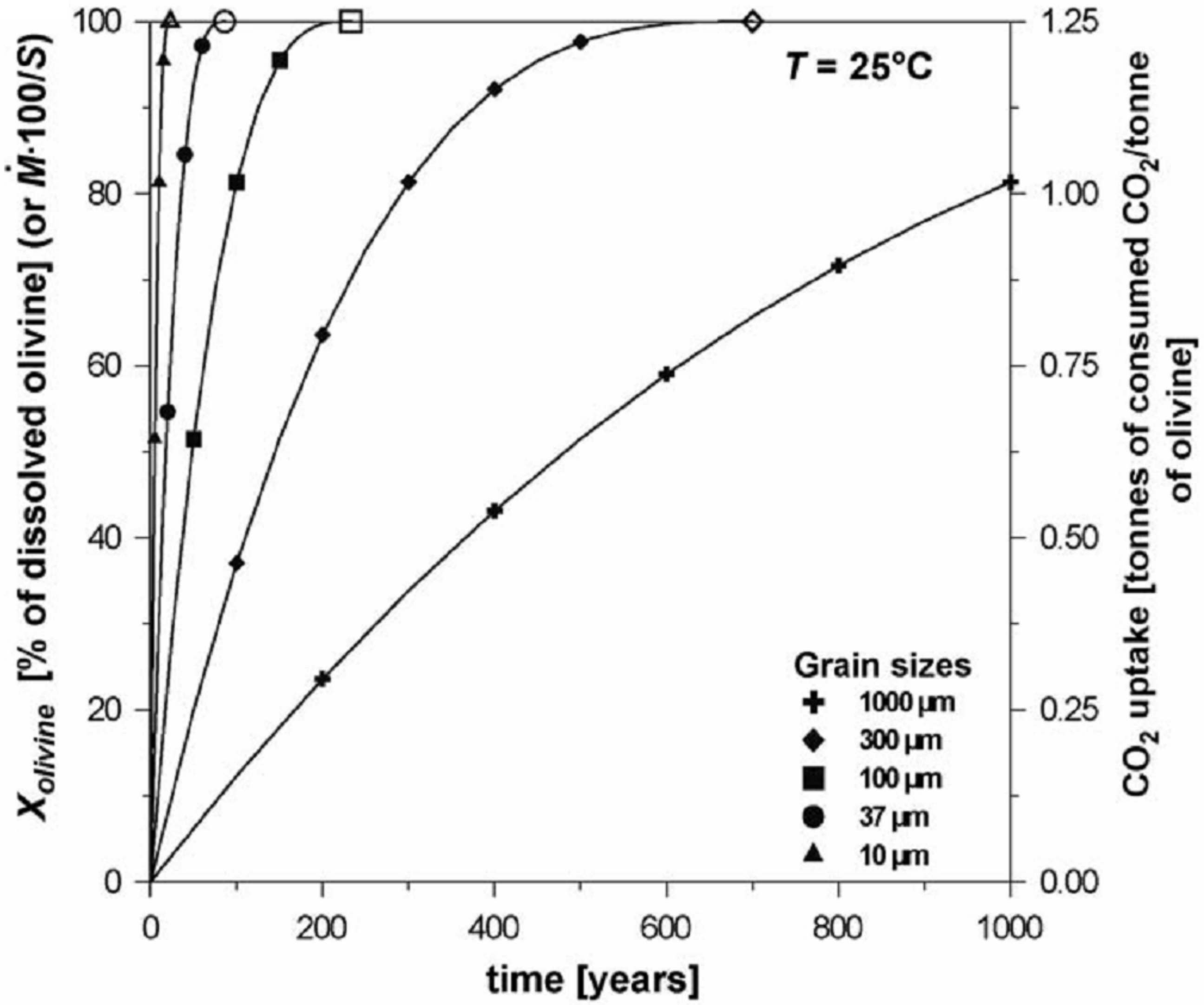
Hangx and Spiers 2009

The Effect of Grain Size (25°C)

Percentage of dissolved Olivine as function of time for different grain size:

10μm grains dissolve within a few years

100 μm grains within a century

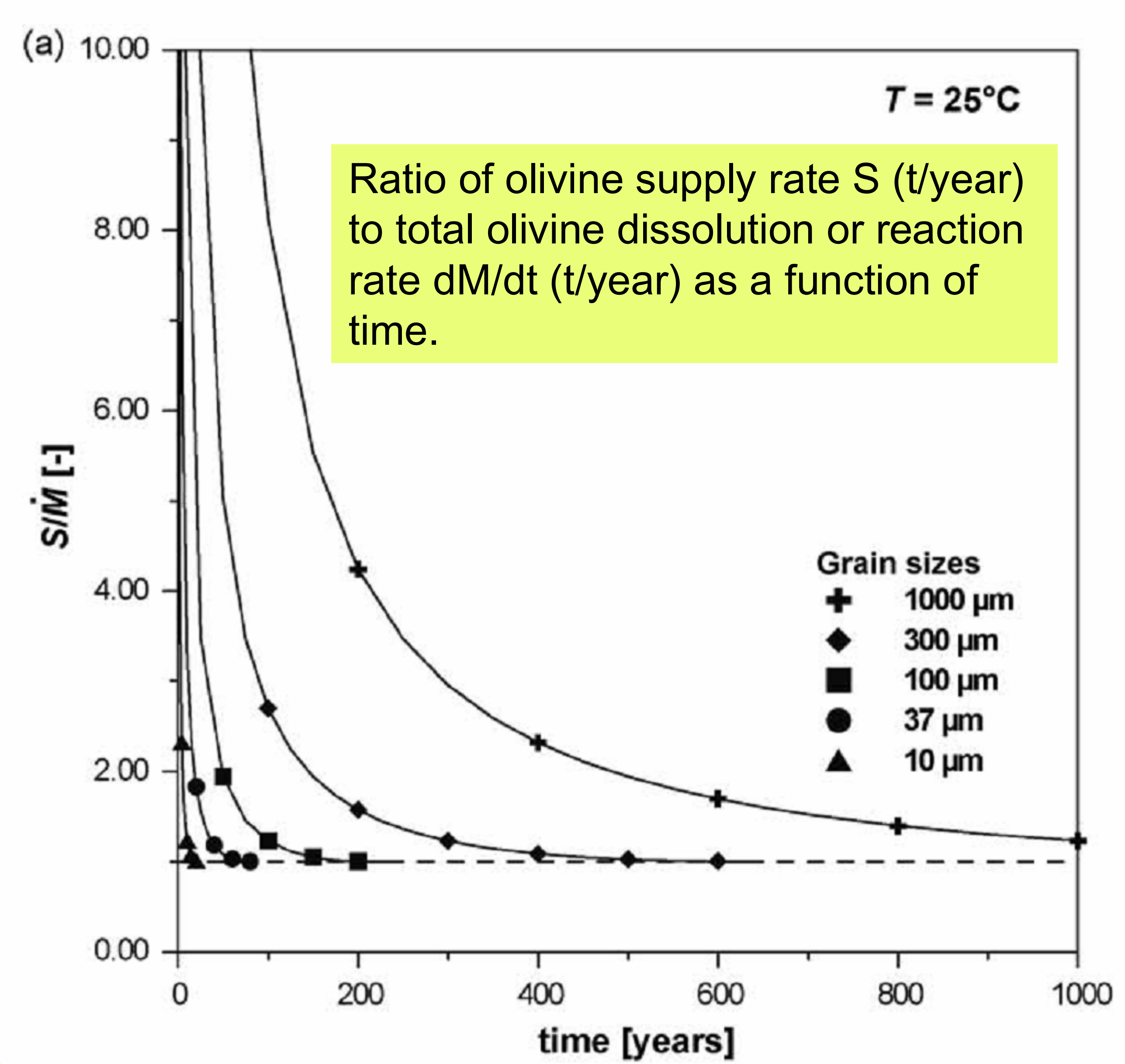


Hangx and Spiers 2009

Problem: Initially much more Olivine would be needed

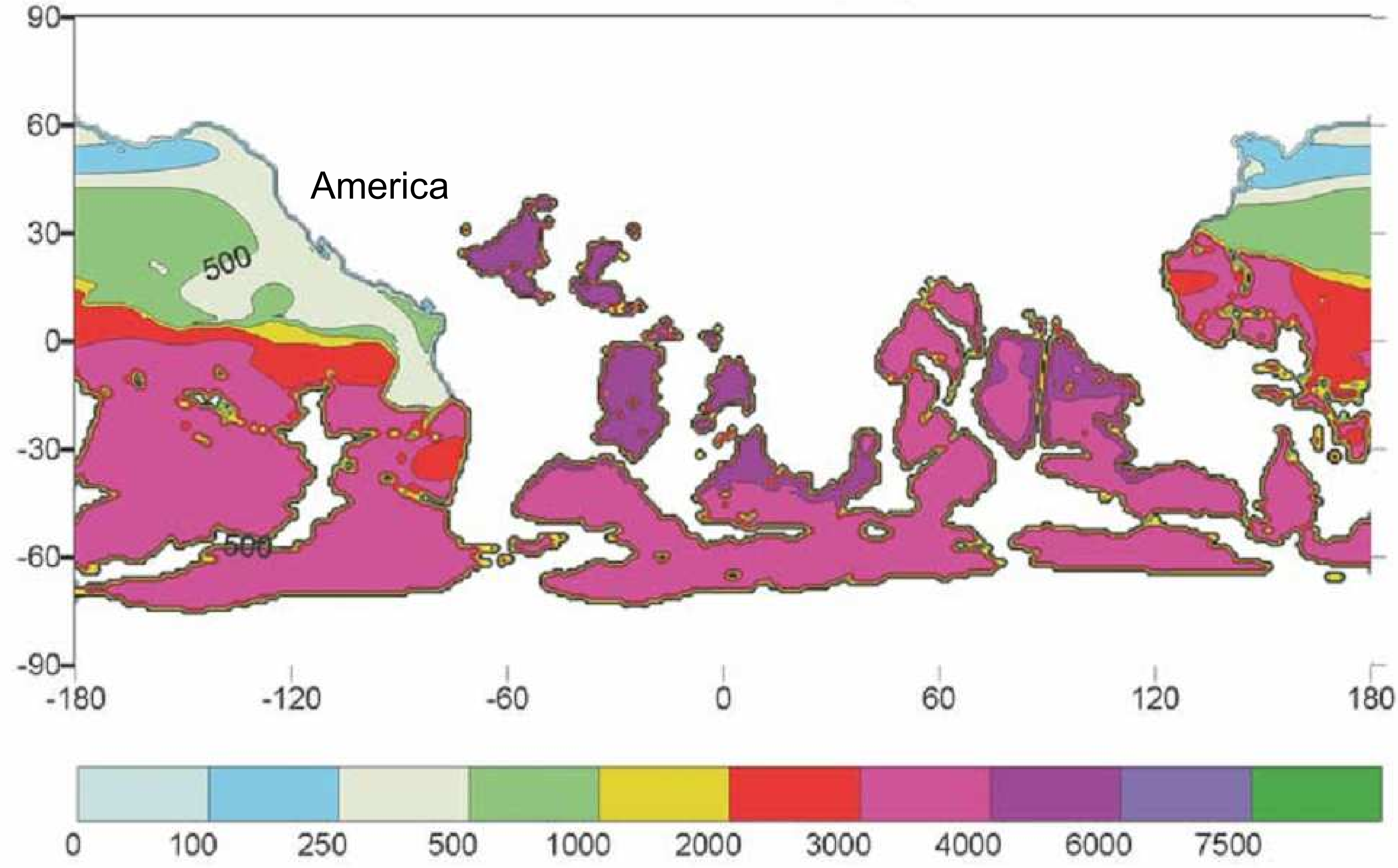
Large Input required initially, less input required when steady state (between input and dissolution) is approached.

Olivine dissolution rate: 5Gt/a



Hangx and Spiers 2009

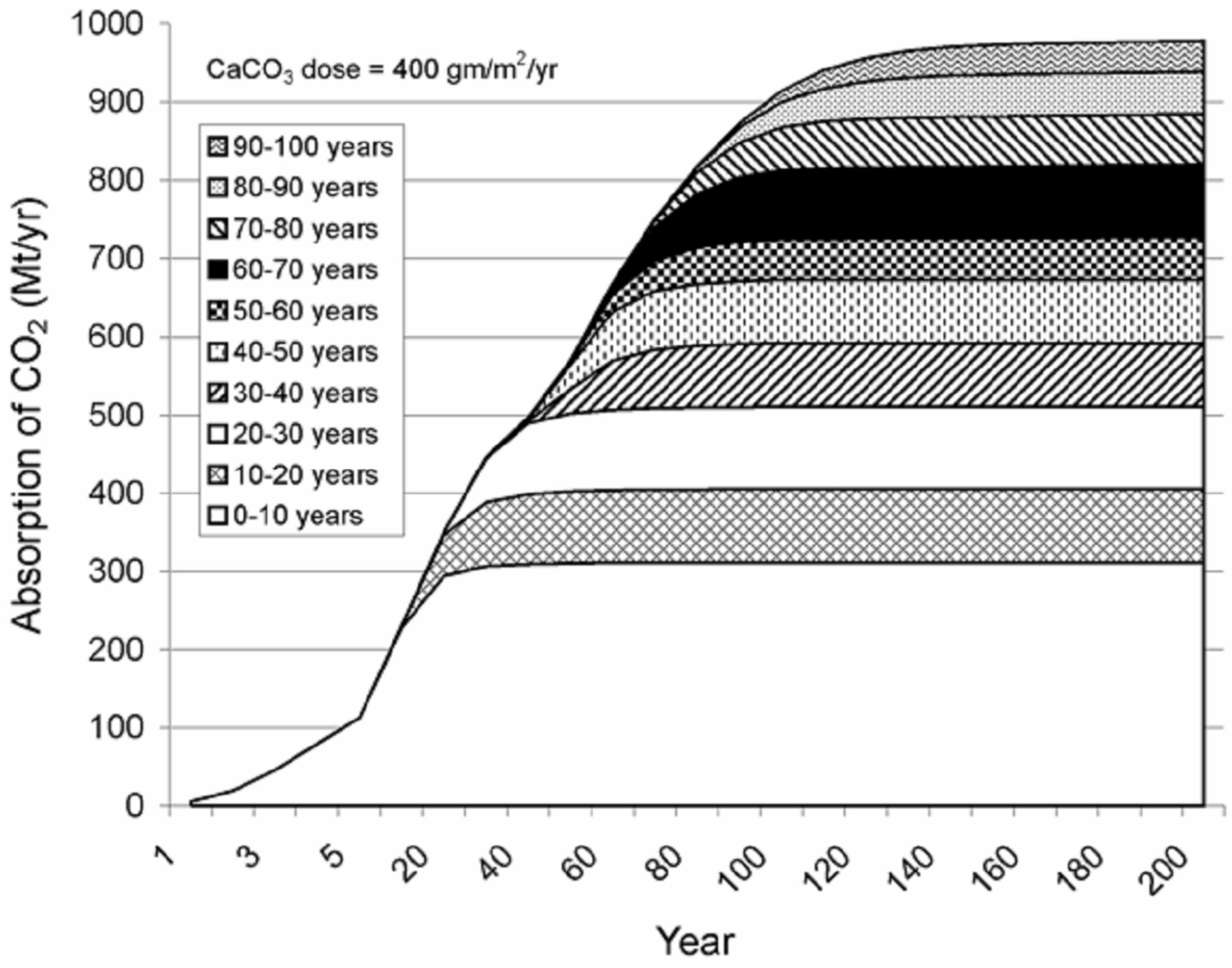
Calcite Saturation Depth in the Ocean



White areas: undersaturation not reached

How Much CO_2 can be Absorbed How Soon?

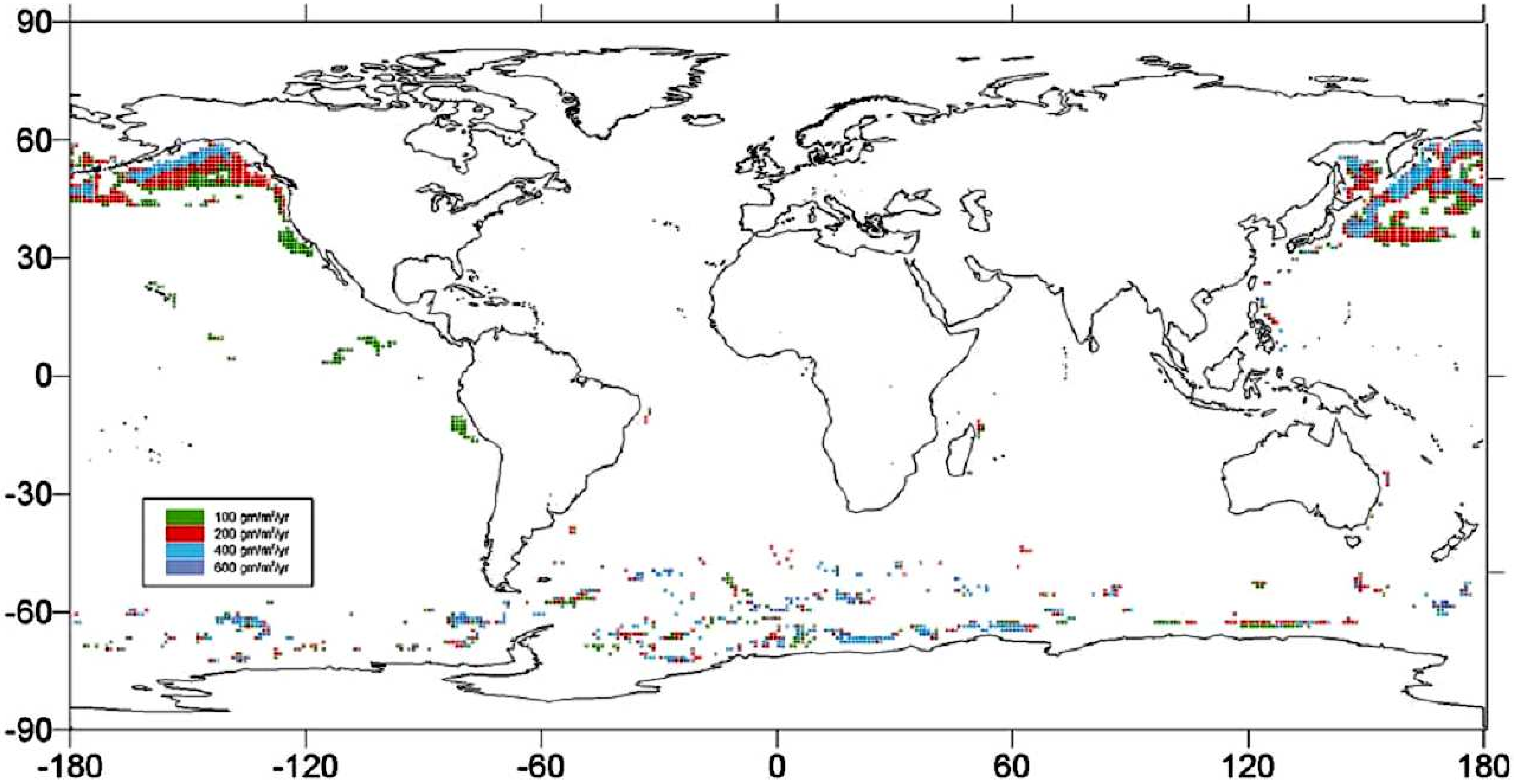
Harvey 2008



Rate of absorption of atmospheric CO_2 resulting from applying $CaCO_3$ powder at a rate of 400 g $m^{-2}a^{-1}$ grouped according to columns in 10-year upwelling time bins.

Where to Put the Carbonate?

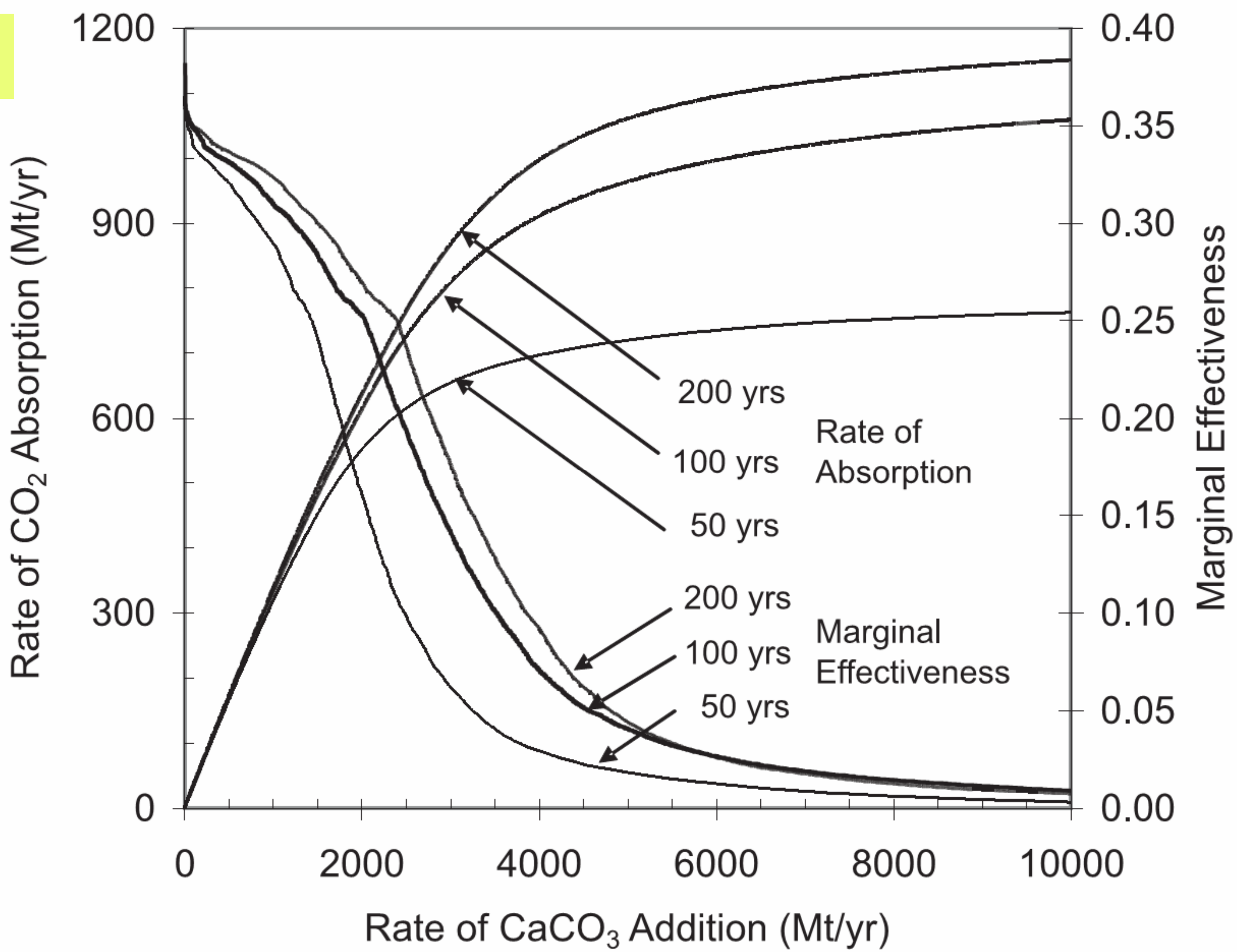
Harvey 2008



Distribution of the rate of addition of limestone powder (g $m^{-2}a^{-1}$) that maximizes the total absorption of CO_2 in year 50, at a total application rate of 4 Gt a^{-1}.

Another Problem: Difficult to Add Enough Alkalinity

Harvey 2008



Rate of atmospheric CO_2 absorption with increasing rate of $CaCO_3$ addition, beginning with the most effective column/dose increment combinations then going to progressively less effective combinations.

Energy Efficiency fo the Measure

The mass efficiency of oliviene addition in sequestering CO_2 is approximately unity

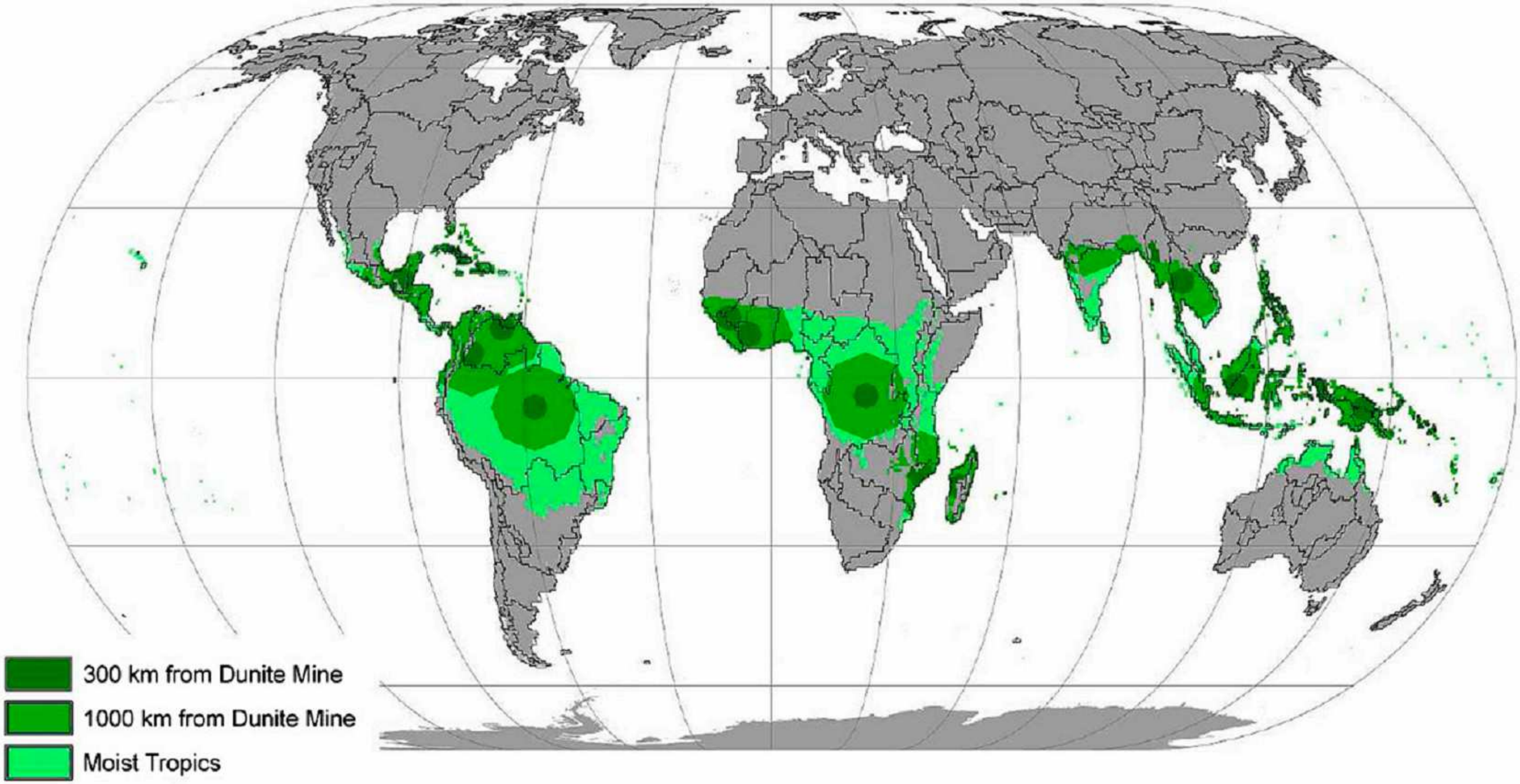
→ To offset present anthropogenic CO_2 output
$\approx$30 Gt of Olivin/year would be required

Mining will require a few % of energy offset by liming the ocean

Grinding to 10μ particles (which dissolve within 1-2 years) will require additional several % of energy offset

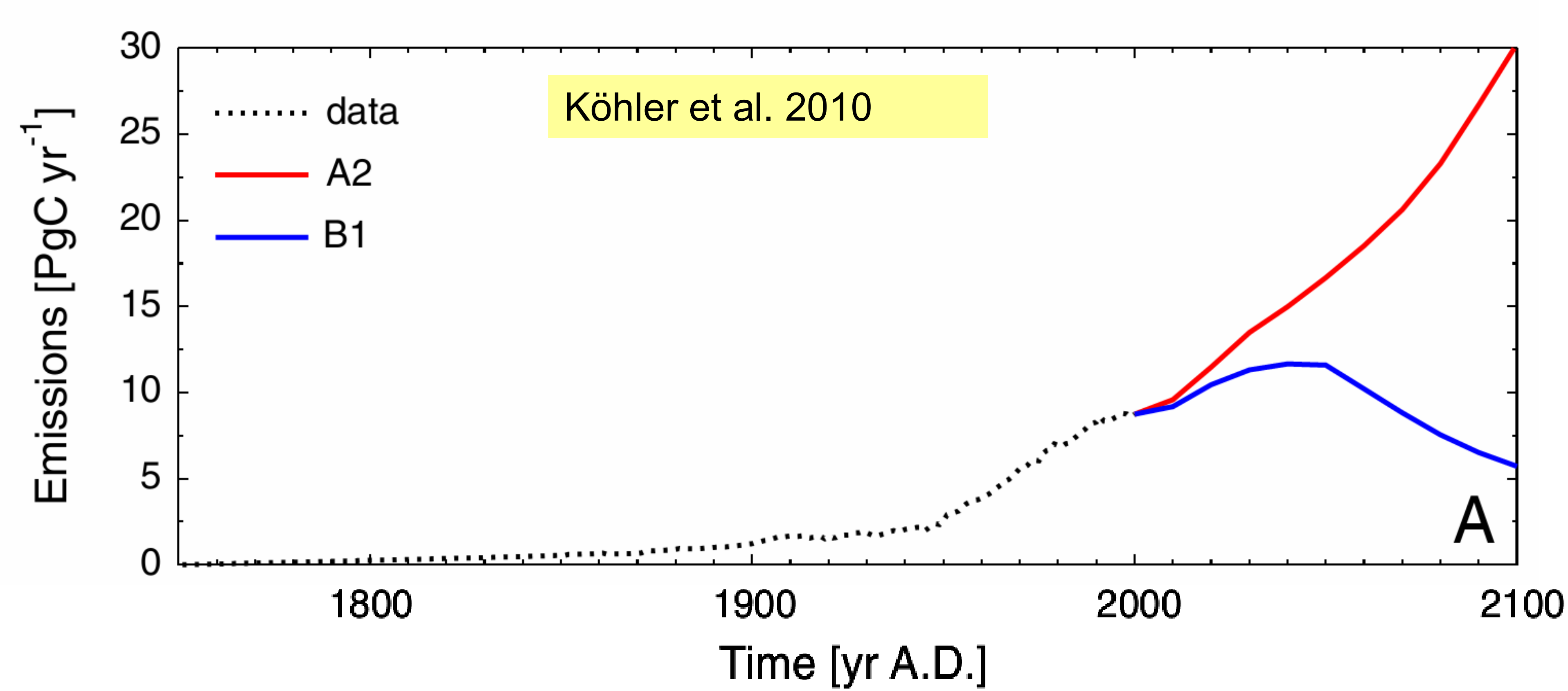
Transport distance (of olivine) is critical.
→ Put olivine powder to large rivers
(e.g. Amazone, Congo) for free transport

Location of some Active Dunite (Olivine) Mines



Köhler et al. 2010

A2- and B1 IPCC Emission Scenarios

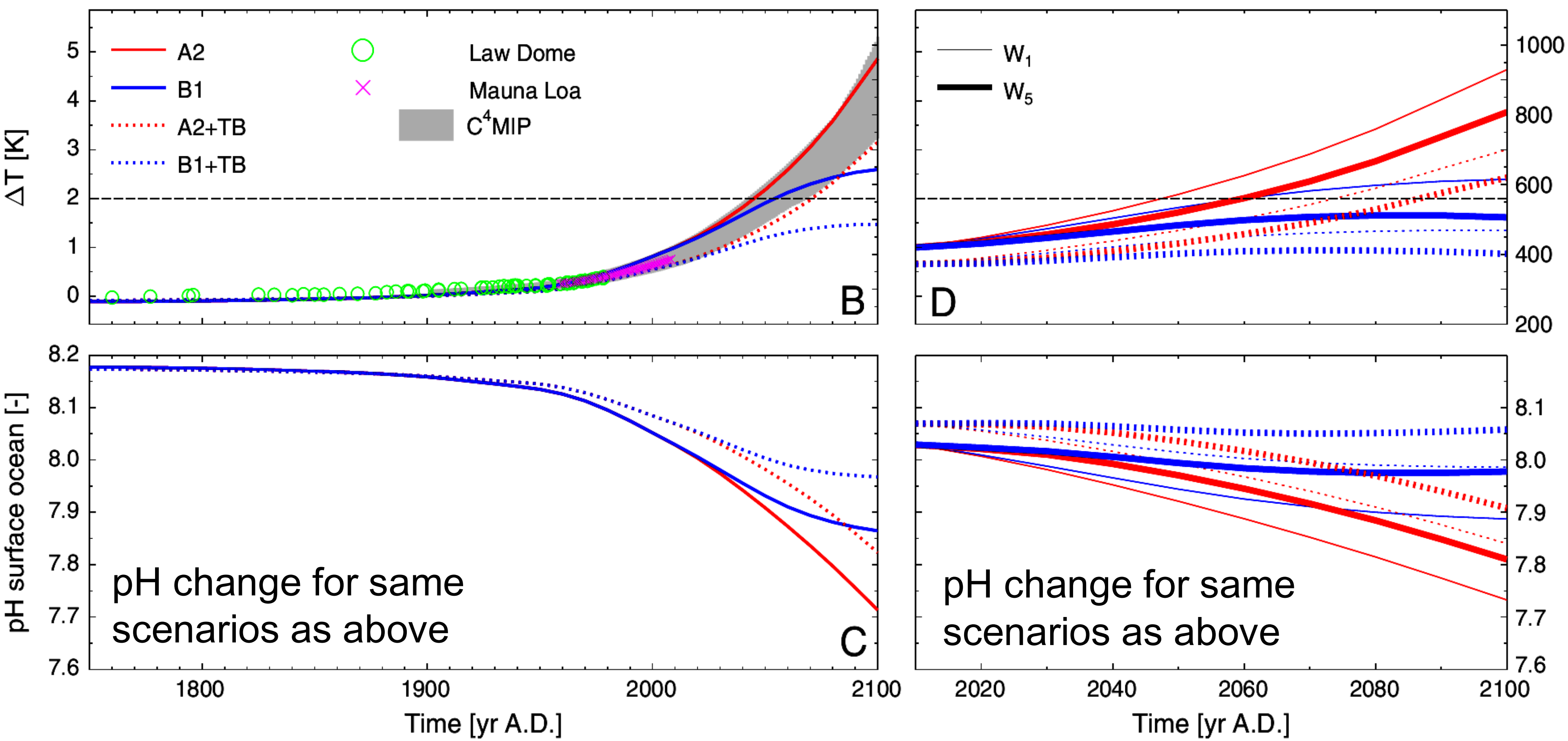


Sum of anthropogenic emissions from fossil fuel combustion (A.D. 1750–2000) and land use change (A.D. 1850–2000; before A.D. 1850: linear extrapolation of land use change to zero in A.D. 1750) (50). A.D. 2000–2100: Projected emission for A2 and B1 scenarios.

Modelled Climate Effect of Adding Alkalinity to the Ocean

From: Köhler et al. 2010

$P(CO_2)$ [µatm]



(B) Global transient temperature rise (derived from transient climate sensitivity of 2 K for 2x preindustrial CO_2 and atmospheric CO_2 (right y-axis). The gray area covers the range of results from coupled carbon cycle-climate simulations for the A2 emission scenario C^4MIP. (D) Impact of enhanced silicate weathering (2010–2100). Global temperature rise and simulated atmospheric pCO_2 (right yaxis) for A2 and B1 scenarios with and without dynamical terrestrial carbon storage for three different weathering strengths [W1 (thin line): 1Pg of C per year; W5 (bold line): 5Pg of C per year].

Cost of Liming (Adding Alkalinity to the Ocean)

Olivin (or calcium carbonate) are available (close to quarries) for several 10$/t.

→ Neglecting cost of transport and grinding this would translate in several 10$/t of CO_2 removed

→ Cost of 20-40$/t of CO_2 were estimated.

Conclusions

- Adding alkalinity to the ocean could – in principle – be a solution to the CO_2 problem
- It would (as all CDR-measures) also (largely) solve the ocean acidification problem
- However, there is no leverage ($L \approx 1$), approximately 1 t of mineral has to be added to the ocean per t of CO_2 emitted (or 3.7 t of mineral per ton of C)
- Changes to ocean chemistry may have unintended consequences (e.g. due to silicate being a nutrient)
- This amounts to about 30 Gt mineral per year. In comparison present global annual production of carbonate (limestone) is about 3 Gt. However, limestone is available in the Earth‘s crust in very large quantities.