



Mini-conference on Vulnerabilities of the Carbon-Climate-Human System



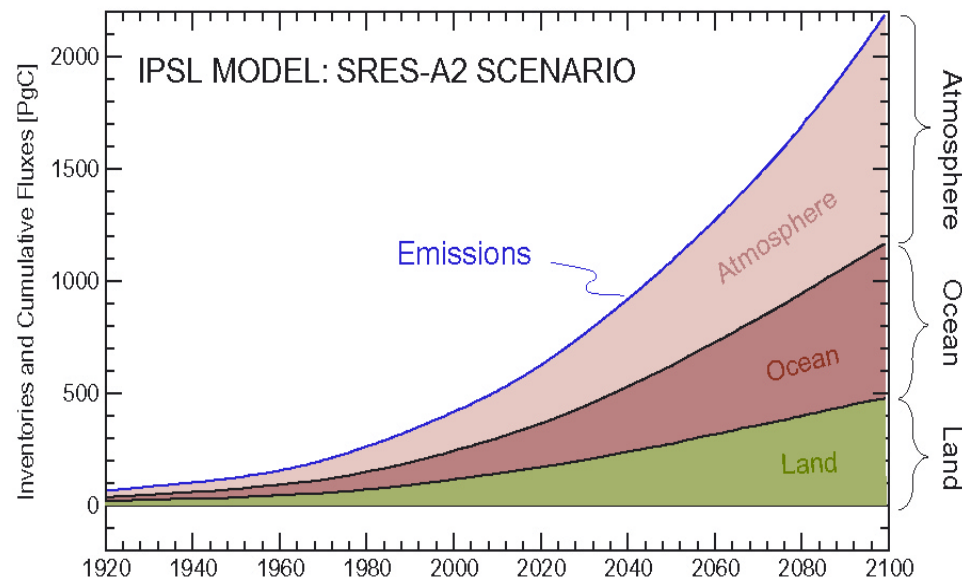
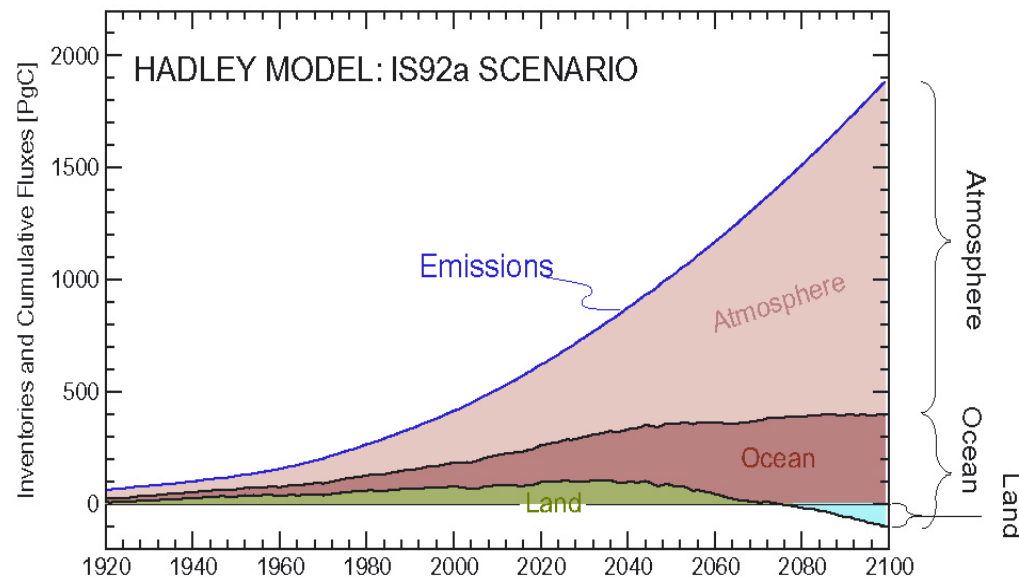
*Vulnerabilities of the calcium-carbonate
cycle: positive and negative feedbacks*

Christopher L. Sabine
NOAA/PMEL
Seattle, WA USA

Wednesday, 15 June 2005

UNESCO, Paris, France

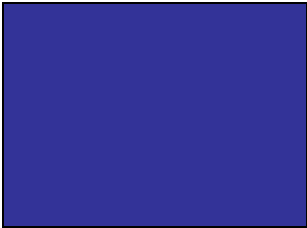
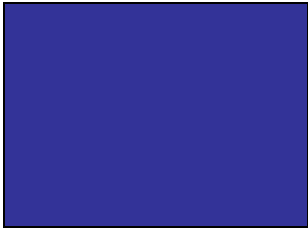
CARBON-CYCLE / CLIMATE SYSTEM FEEDBACKS



Current level of understanding, projected into the future:

- Predictive models differ significantly in future predictions.
- Cannot improve predictions without better understanding of the controlling processes.
- This is no longer just an academic issue
- Disagreements in predictions impact baseline targets for emissions reduction.
- Sequestration cost targets are \$10-35/t of C.
- Differences between models imply differences in ecosystem services of trillions of dollars.
- = big incentive for research.

The Global Carbon Budget [Pg C]. Positive values represent atmospheric increase (or ocean/land sources), negative numbers represent atmospheric decrease (sinks).

	1800-1979	1980-1999
Atmospheric increase	116 \pm 4	65 \pm 1
Emissions (f. fuel, cement)		
Ocean Inventory		
Net terrestrial	+50 \pm 28	-15 \pm 9
<i>Land-use change</i>	+82 to +162	+24 \pm 12
<i>*Resid. terrestrial sink</i>	-32 to -112	-39 \pm 18

First 180 years the ocean absorbed 57% of FF emissions

Last 20 years the ocean absorbed 31% of FF emissions

Relative to total emissions the ocean absorbed 44% and 36%

There are a number of feedbacks in the global carbon cycle and between the carbon and climate systems that we must understand if we are ever to predict the future role of the ocean as a sink for CO_2

Carbon Cycle Change	Climate Feedback	direction
CO_3^{2-} decrease	Less efficient uptake	positive
Calcification decrease	lower natural CO_2 production	negative
CaCO_3 dissolution-sed.	higher CO_3^{2-} increasing uptake	negative
CaCO_3 dissolution-water	higher CO_3^{2-} /lower org. transport	Neg./pos.
Increasing SST	Convert ocean HCO_3^- to CO_2	positive
Increased stratification	Reduced mixing and transport	positive
Increased stratification	Lower productivity and uptake	positive
Increased dust input	Increased productivity-N fixers	negative
Ecosystem structure	Lower or higher productivity	Pos./neg.
CH_4 hydrate release	Increased greenhouse forcing	Positive

2005 Headlines on CO₂ & Coral Reefs

Ocean acidification represents "potentially a gigantic problem for the world." -Dr. Carol Turley, Plymouth Marine Laboratory, Feb. 7, 2005.

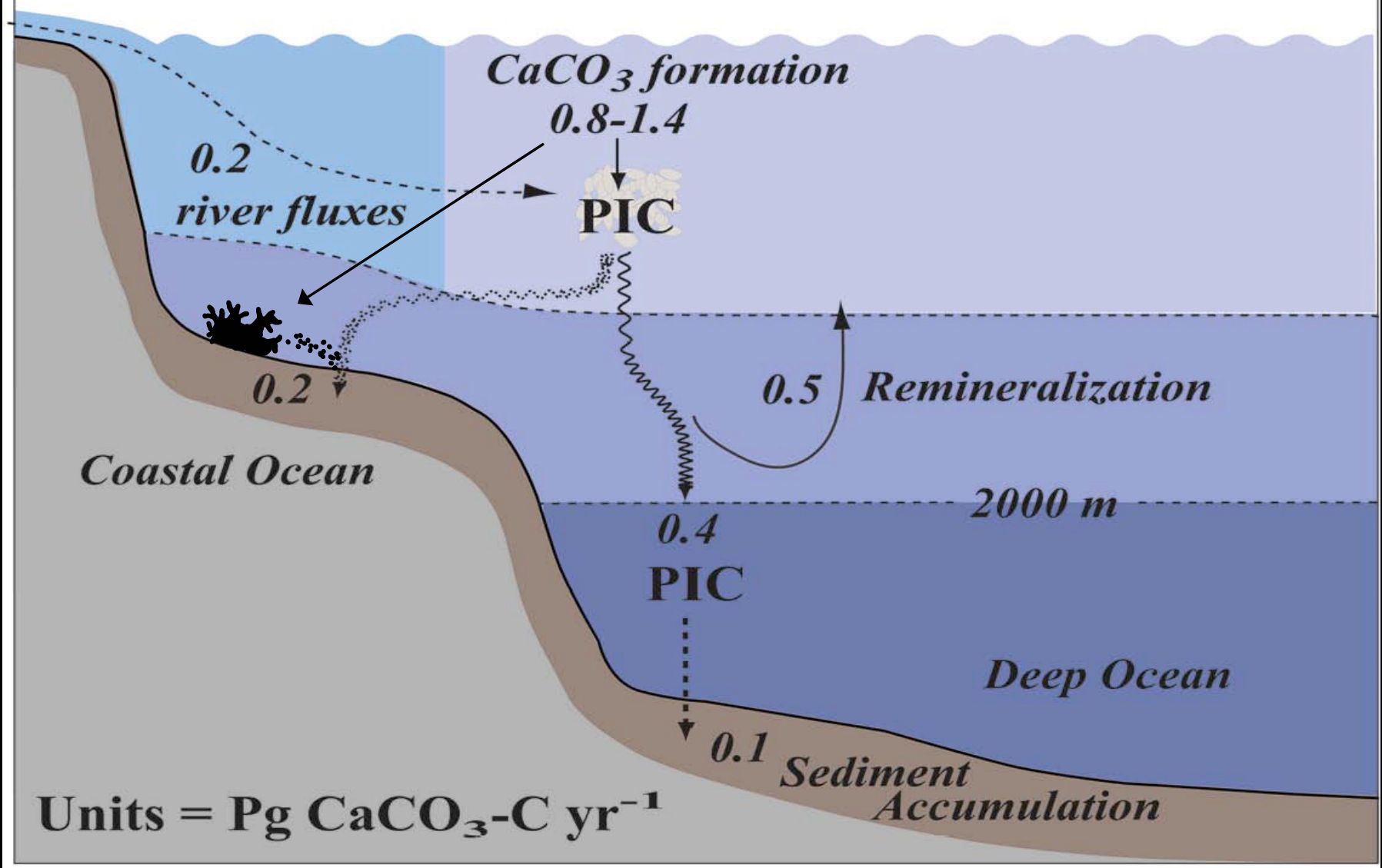
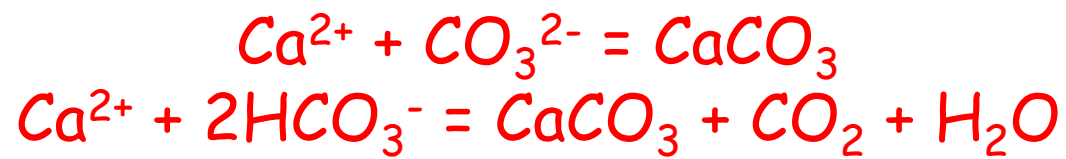
"Scientists warn growing acidity of oceans will kill reefs" Paul Brown, environment correspondent, The Guardian

"As an ecosystem our grandchildren will not see coral reefs any more" - Professor Jonathan Erez, Hebrew University of Jerusalem - BBC News, Feb. 13, 2005

"If CO₂ levels continue to rise, the oceans could be more acidic in 2100 than they have been for 400 million years." Ulf Riebesell - BBC News, Feb. 07, 2005.

"The Other CO₂ Problem: Ocean Acidification," GCC News, Feb. 05, 2005.

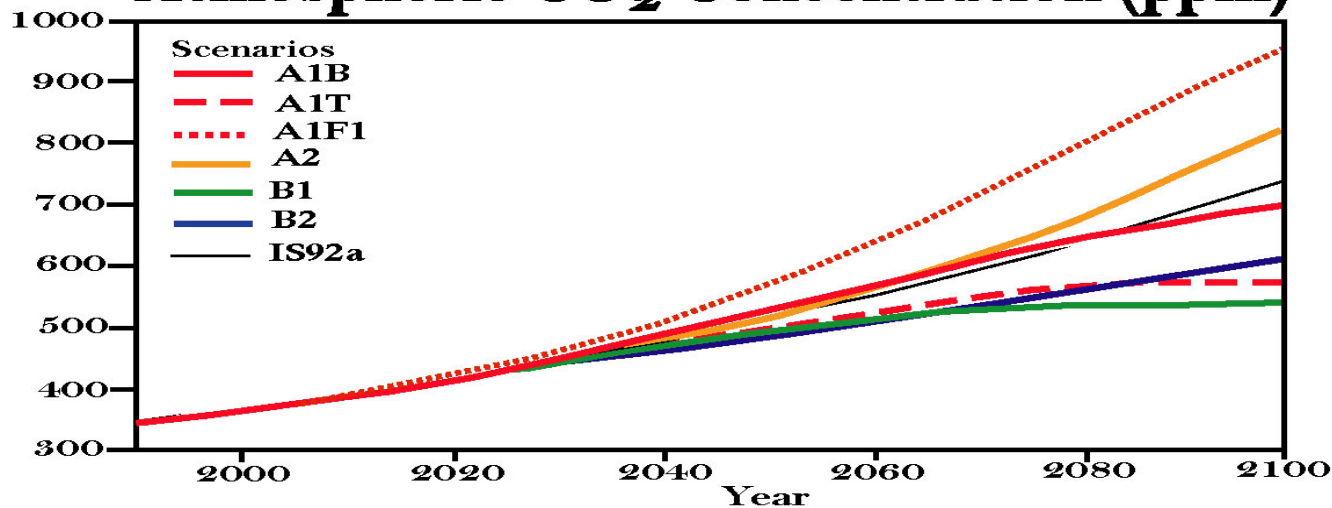
"The world scientific community is only just waking up to this." Cape Argus, Feb. 5, 2005



CO_2 is an acid gas...as we add CO_2 to the surface waters we are reducing the buffering capacity of the ocean and its ability to continue to take up CO_2 from the atmosphere

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Atmospheric CO₂ Concentration (ppm)



Under IPCC "Business as Usual" the pH of surface seawater drops by 0.4 pH units by 2100. CO₃²⁻ in surface water drops by 48% from pre-industrial values.

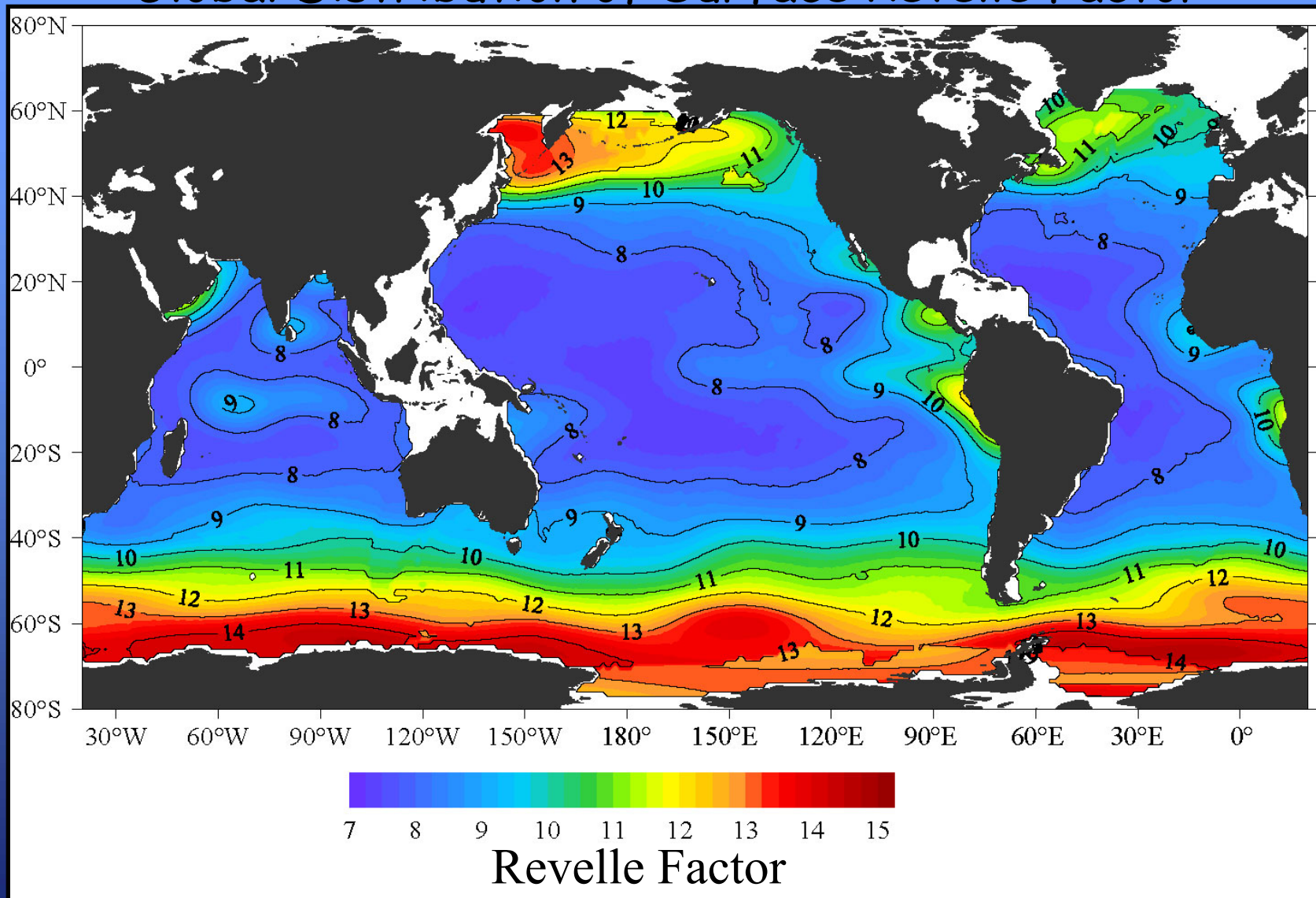
	Glacial	Pre-industrial	Present	2XCO ₂	3XCO ₂	Atmosphere
CO ₂ (g)	180	280	380	560	840	
	(56)	(0)	(36)	(100)	(200)	Surface ocean
Gas Exchange						
CO ₂ (aq) + H ₂ O ⇌ H ₂ CO ₃	7	9	13	18	25	
Carbonic acid	(29)	(0)	(44)	(100)	(178)	
H ₂ CO ₃ ⇌ H ⁺ + HCO ₃ ⁻	1666	1739	1827	1925	2004	
Bicarbonate	(4)	(0)	(5)	(11)	(15)	
HCO ₃ ⁻ ⇌ H ⁺ + CO ₃ ²⁻	279	222	186	146	115	
Carbonate	(20)	(0)	(-16)	(-34)	(-48)	
H ⁺ x 10 ⁻⁹	4.79	6.92	8.91	12.3	17.4	
Hydrogen Ion Concentration	(45)	(0)	(29)	(78)	(151)	
Ω Ca	6.63	5.32	4.46	3.52	2.77	
Omega Calcite	(20)	(0)	(-16)	(-34)	(-48)	
Ω Ar	4.26	3.44	2.9	2.29	1.81	
Omega Aragonite	(19)	(0)	(-16)	(-33)	(-47)	
	1952	1970	2026	2090	2144	DIC
	(1)	(0)	(2.8)	(6.1)	(8.8)	
	8.32	8.16	8.05	7.91	7.76	pH

% Change from Pre-industrial Values

Average Surface Water DIC Increase in 2000 ~ 1.2 μmol kg⁻¹ yr⁻¹

Modified from Feely et al., (2001)

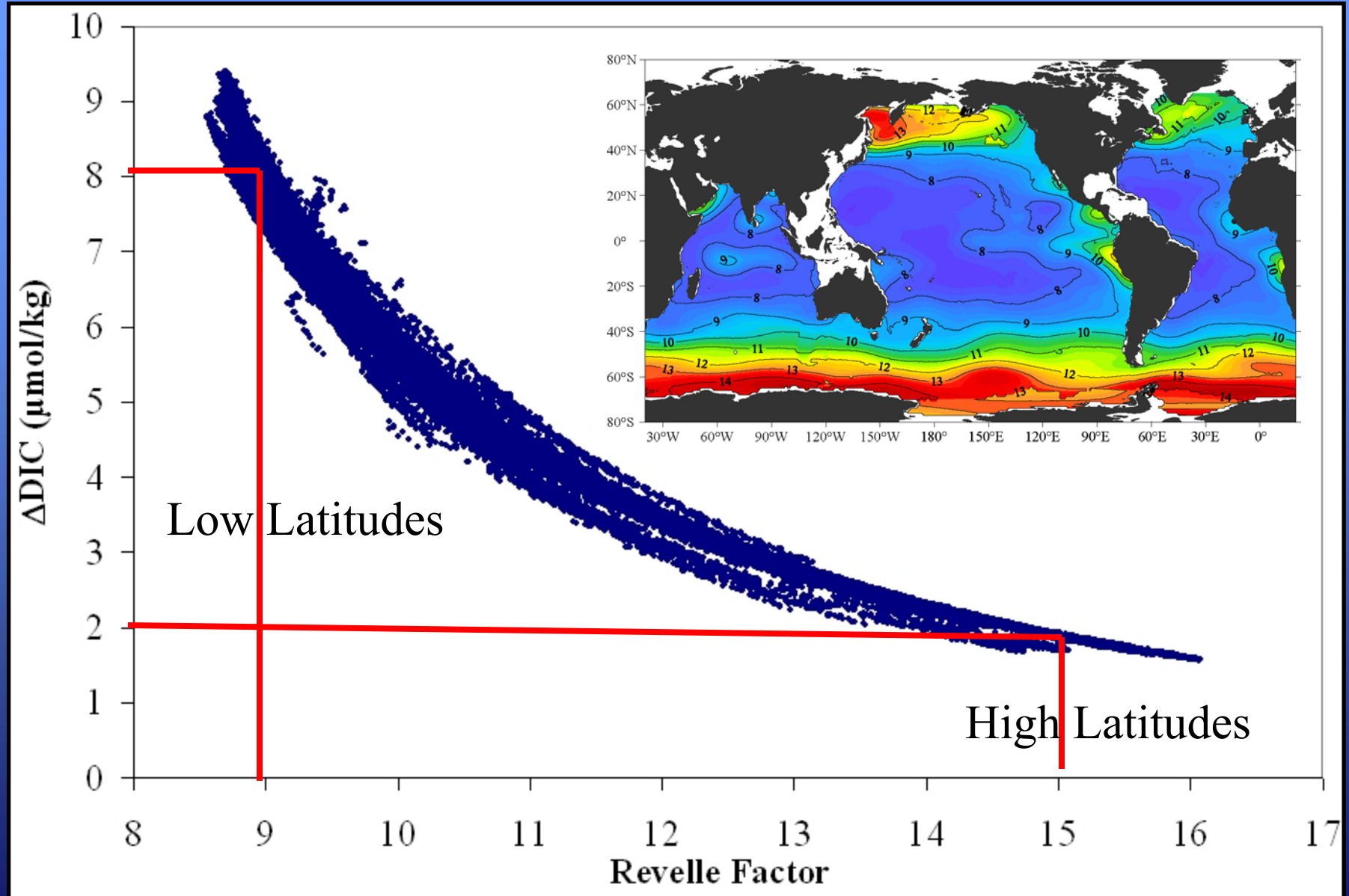
Global Distribution of Surface Revelle Factor



R. Revelle, H.E. Suess,
Tellus 9, 18 (1957)

$$\frac{(\Delta f\text{CO}_2 / \Delta \text{TCO}_2)}{(f\text{CO}_2 / \text{TCO}_2)}$$

ΔDIC for a 10 ppm change in pCO_2 as a function of Revelle Factor

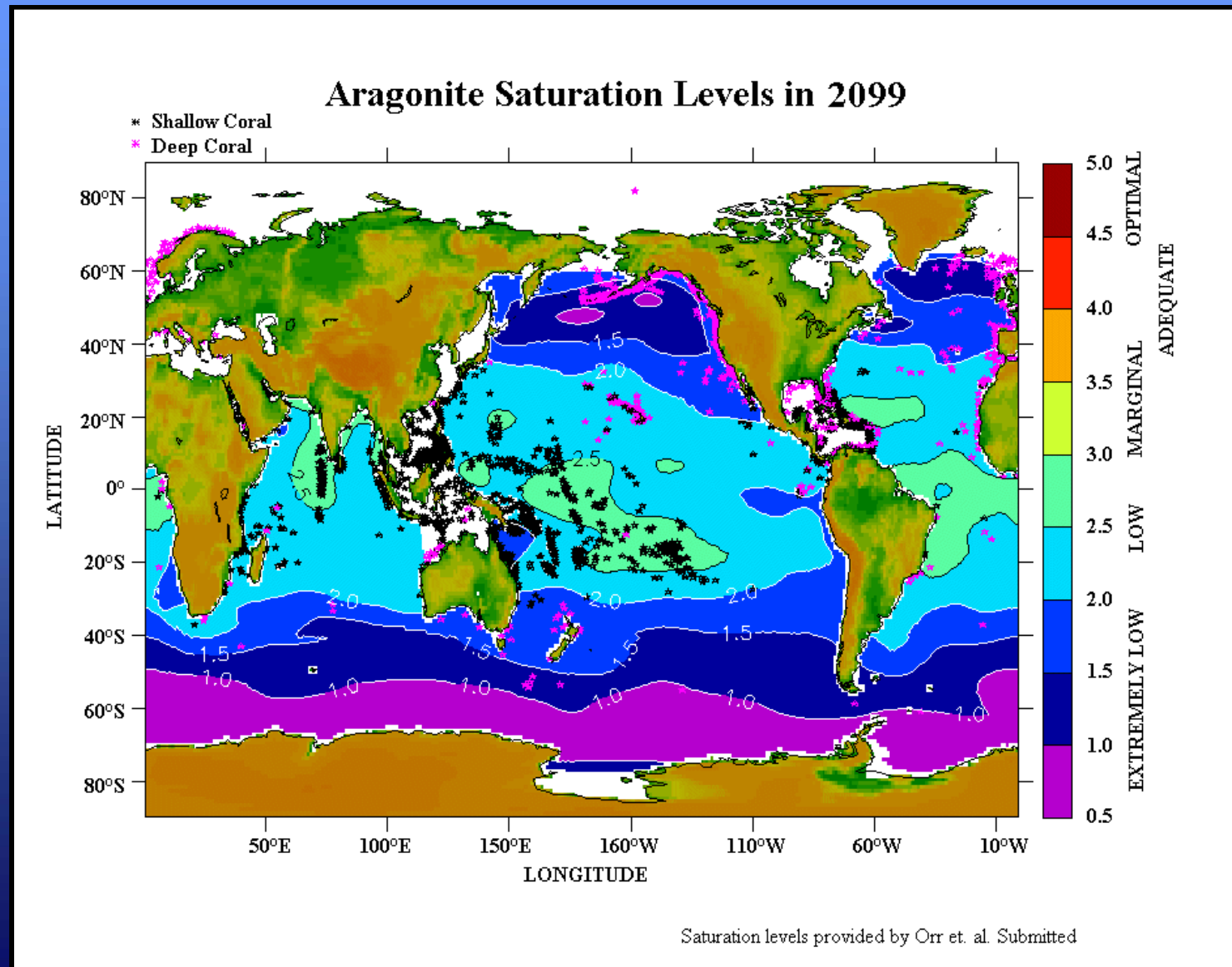


Modern Revelle Factors have already increased by 1 since preindustrial

CaCO_3 prod. currently releases $\sim 1 \text{ PgC yr}^{-1}$ to the atmosphere,
as CO_3^{2-} concentrations drop calcification is expected to
decrease

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Warm water corals have primarily formed in aragonite saturation levels > 4 , can survive at levels > 3.5 , and generally stop growing < 3

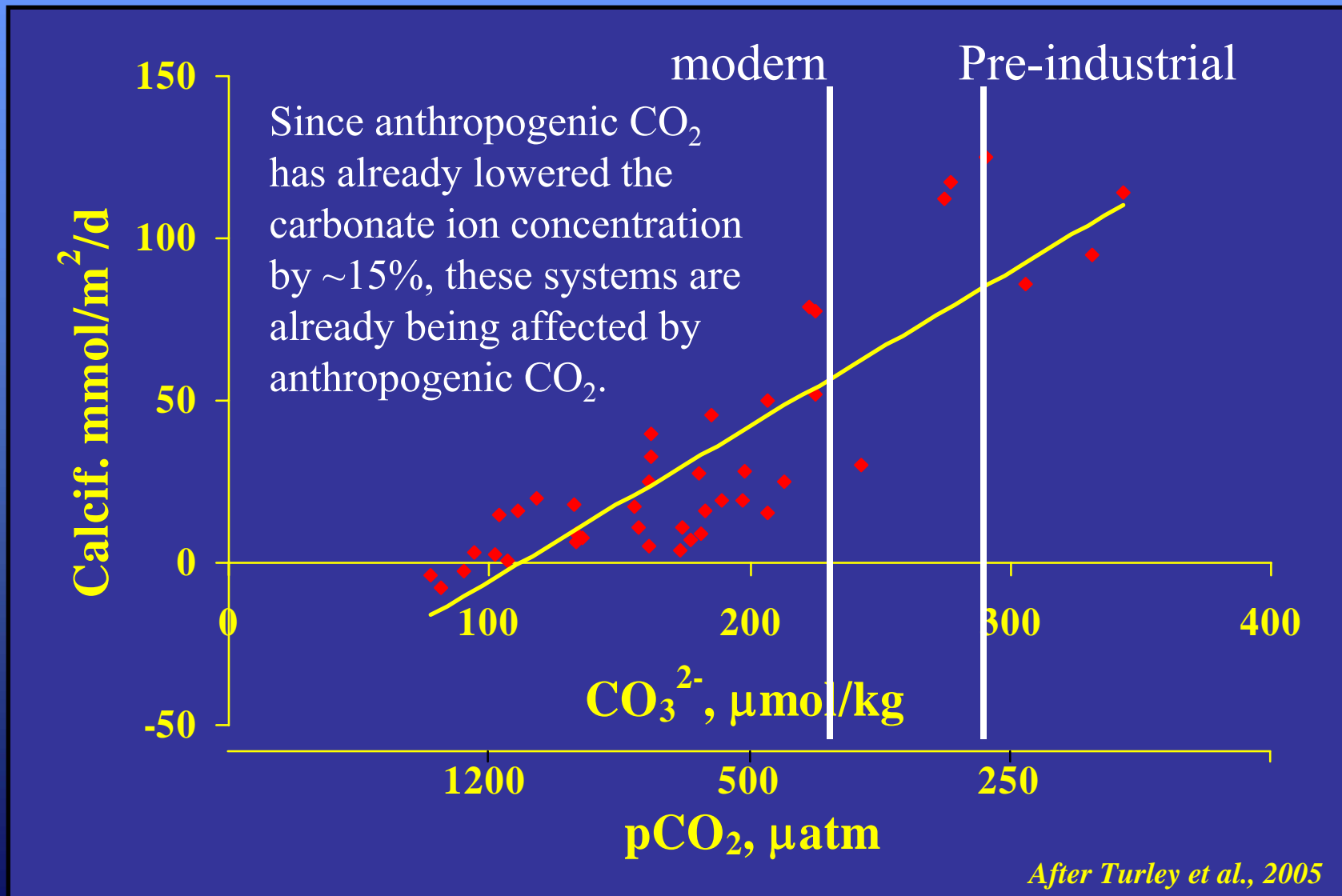


Effects of doubled CO₂ on coral calcification

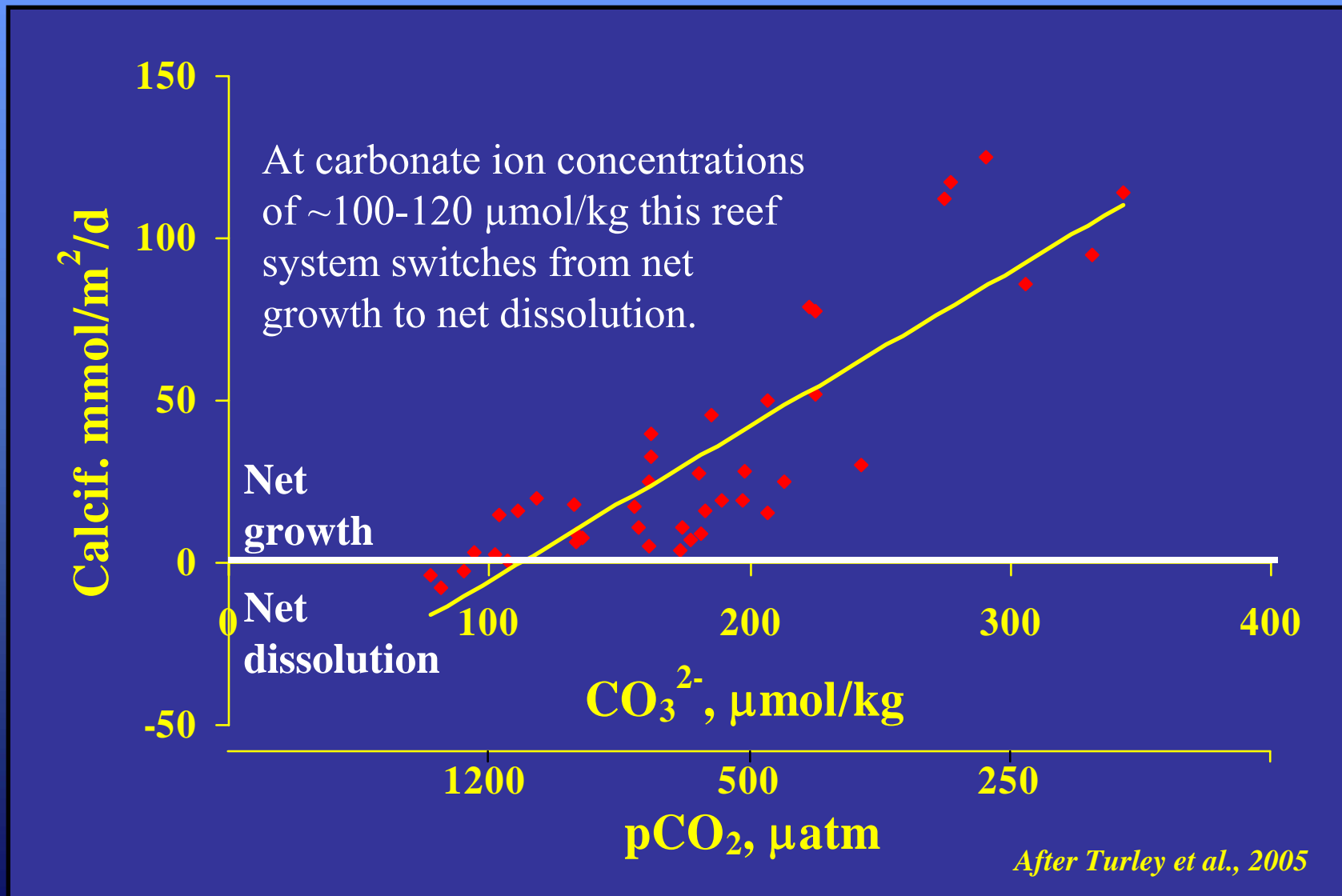
Organism/ System	Manipulation	% Change in Calc'n	Reference
<i>Corallina</i>	1	-44	Gao 1993
<i>Porolithon</i>	2	-25	Agegian 1985
<i>Amphiroa</i>	3	-36	Borowitzka 1981
<i>Turbinaria</i>	2	-15	Marubini et al. 2003
<i>Stylophora</i>	2	-15	
<i>Goniastrea</i>	2	-16	
<i>Acropora</i>	2	-18	
<i>Porites</i>	2	-18	
	1	-19	Marubini et al. 2001
<i>Acropora</i>	2	-37	Schneider & Erez 2000
<i>Porites</i>	2	-27	Marubini & Atkinson 1999
<i>Porites/ Montipora</i>	2	-51	Langdon et al. (2003)
<i>Montipora</i>	3	-22	Langdon et al. (2003)
Gr. Bahama Banks*	4	-82	Broecker & Takahashi 1964
			Broecker et al. 2001
B2 mesocosm*	1,3,4	-54	Langdon et al. 2000
Monaco mesocosm	1	-21	Leclercq et al. 2000

* dominated by coralline algae

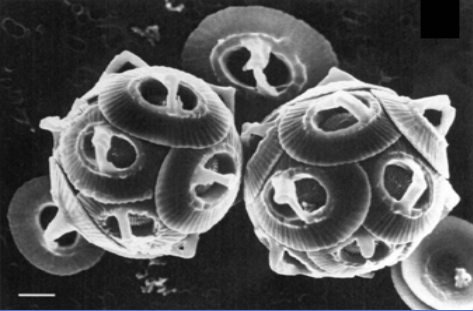


There appears to be a linear decrease in the calcification rate of coral reef systems with decreasing carbonate ion concentrations.



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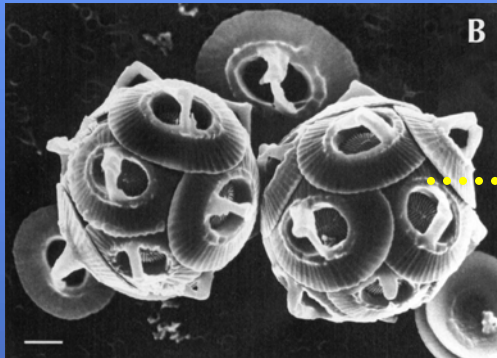
Major planktonic calcifiers

	group	mineral form	generation time	# of extant species
	Coccolithophores autotroph	calcite	day(s)	~250
	Foraminifera heterotroph (many with autotrophic symbionts)	calcite	weeks	~4000
	Pteropods heterotroph	aragonite	months	~30

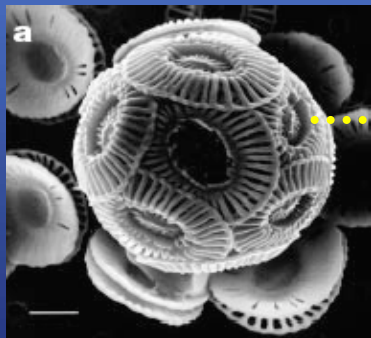
Response to elevated CO_2 (decreased pH, Ω or $[\text{CO}_3^{2-}]$)

Today's world

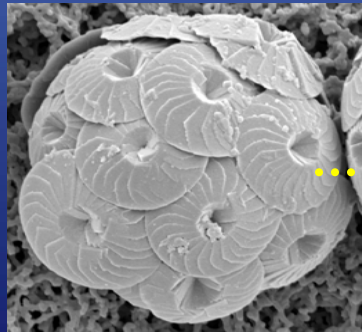
pCO_2 : 280-380 ppmV



Gephyrocapsa oceanica



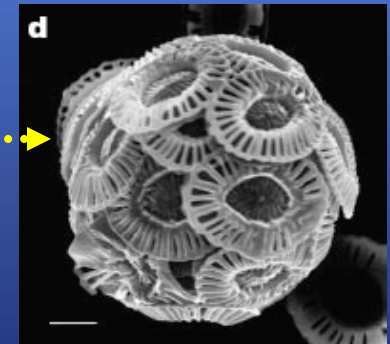
Emiliana huxleyi



Calcidiscus leptoporus

High- CO_2 world

pCO_2 : 580-720 ppmV



Riebesell et al. (2000), Nature; Langer et al. subm.

CO_2 out-gassing as a consequence of CaCO_3 production

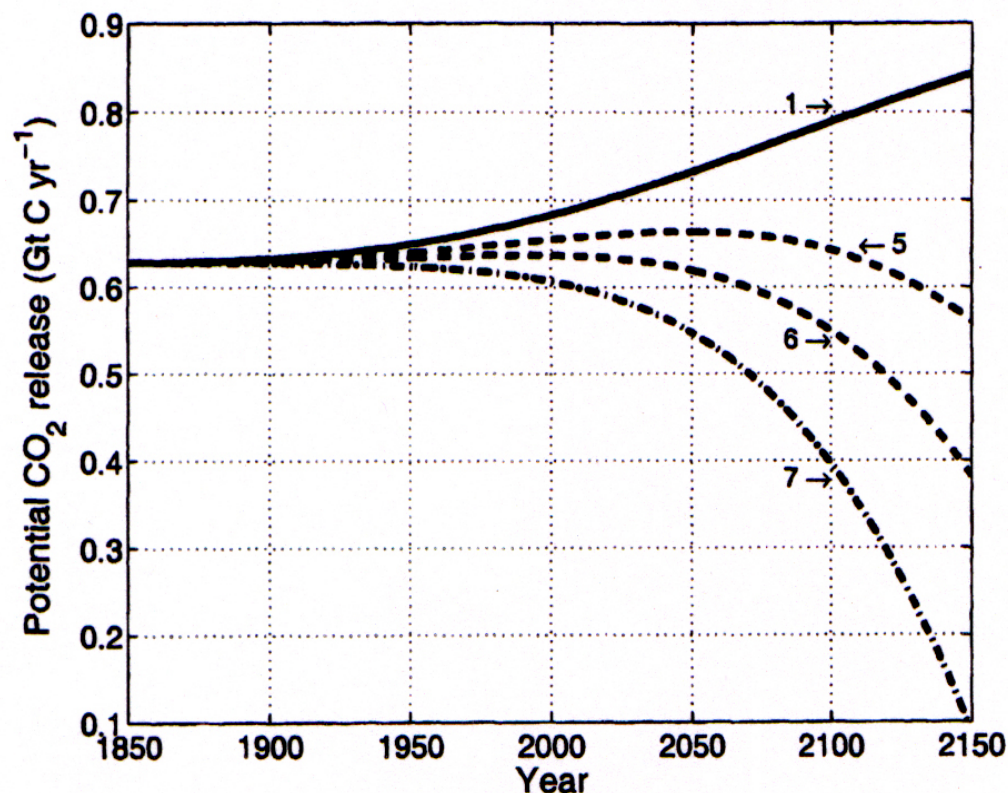
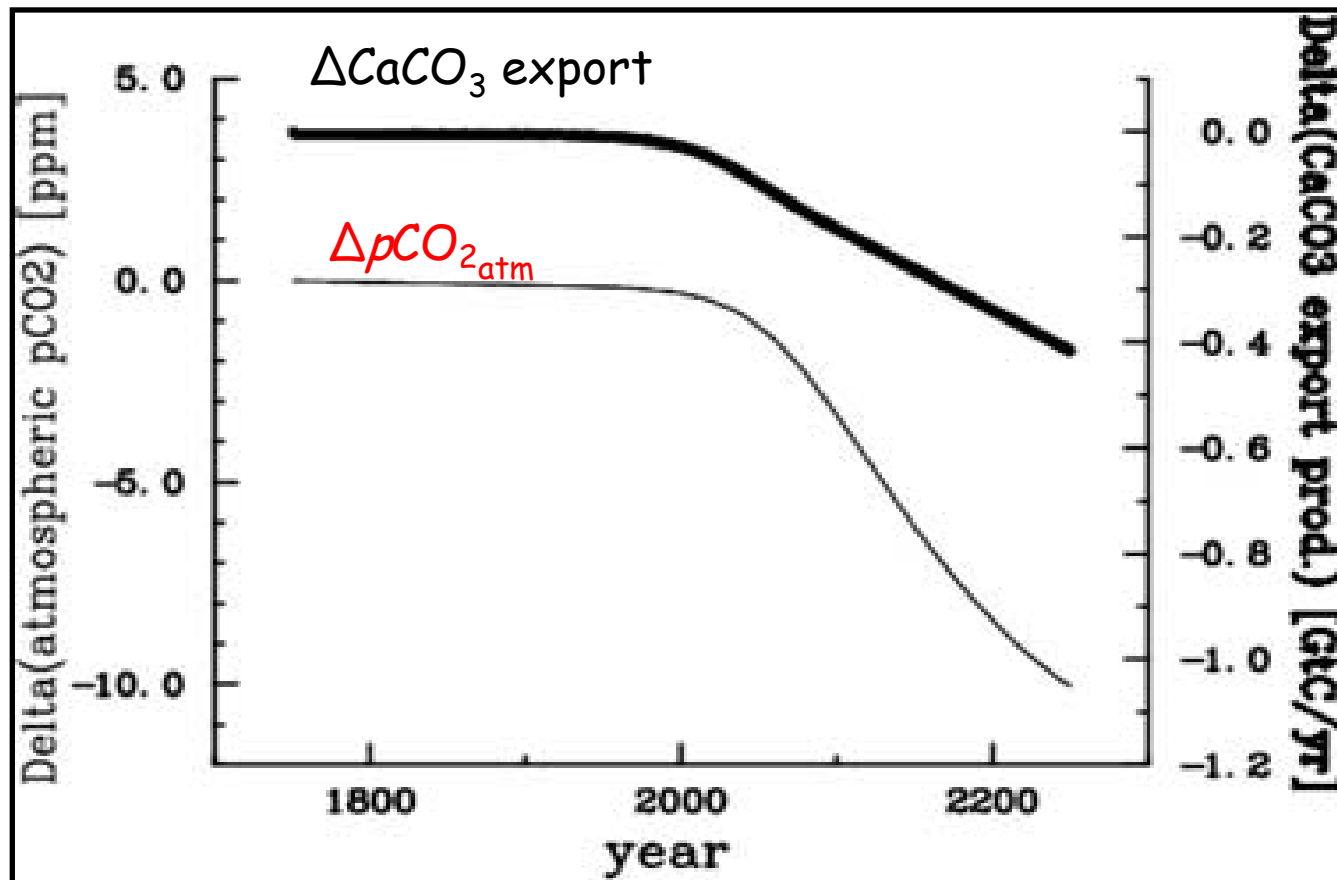


Figure 4. Potential CO_2 release in Gt C yr^{-1} from 1850 to 2150 when annual CaCO_3 production remains constant at 1 Gt C yr^{-1} (scenario 1, solid line), PIC/POC ratio decreases as in *E. huxleyi* at a 16/8 L/D cycle (scenario 5, dashed line), or at a 24/0 L/D cycle (scenario 6, dashed line), and PIC/POC ratio decreases as in *G. oceanica* (scenario 7, dashed- dotted line).

Zondervan et al. (2001)

Changes in calcification out-gassing in the future result in an uncertainty of at least 1 Pg C yr^{-1}

40% reduction in CaCO_3 export corresponds to
10 ppm reduction in atmospheric CO_2



Heinze 2004, GRL 31

(assuming CaCO_3 export = 1Pg C yr^{-1})

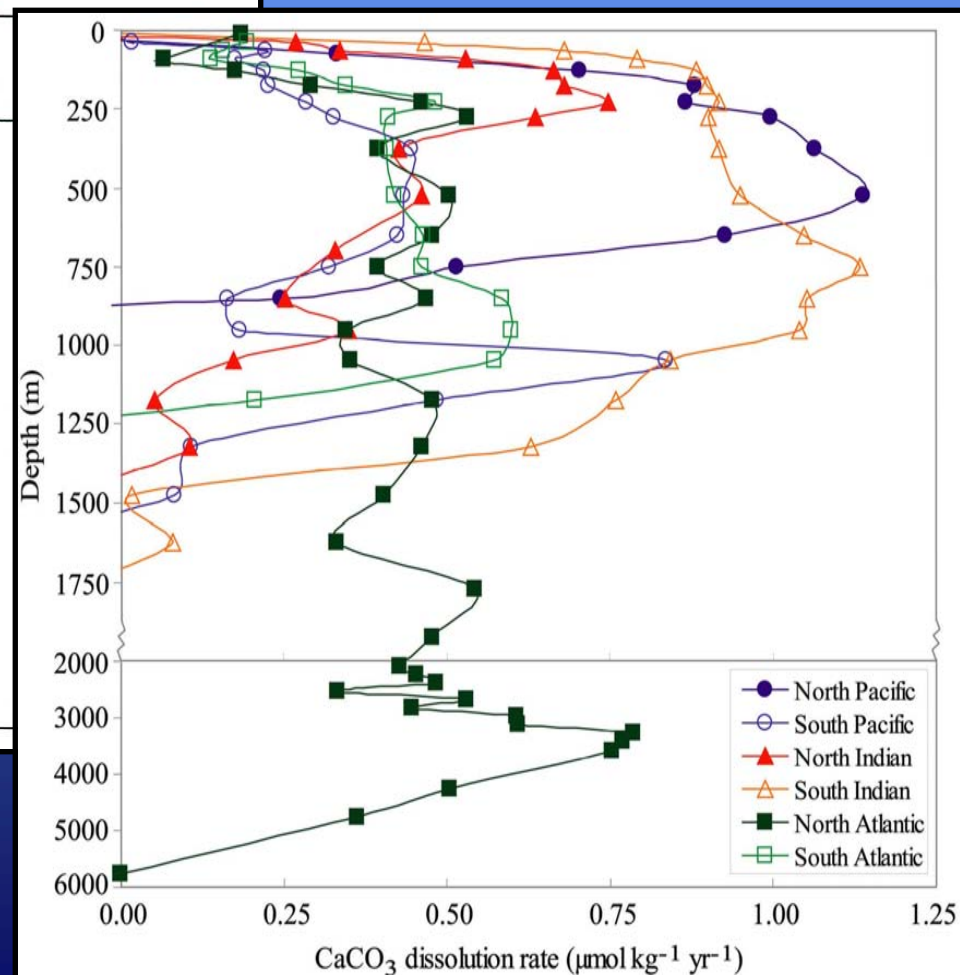
In addition to reduced CaCO_3 production, exported CaCO_3 particles are dissolving at shallower depths

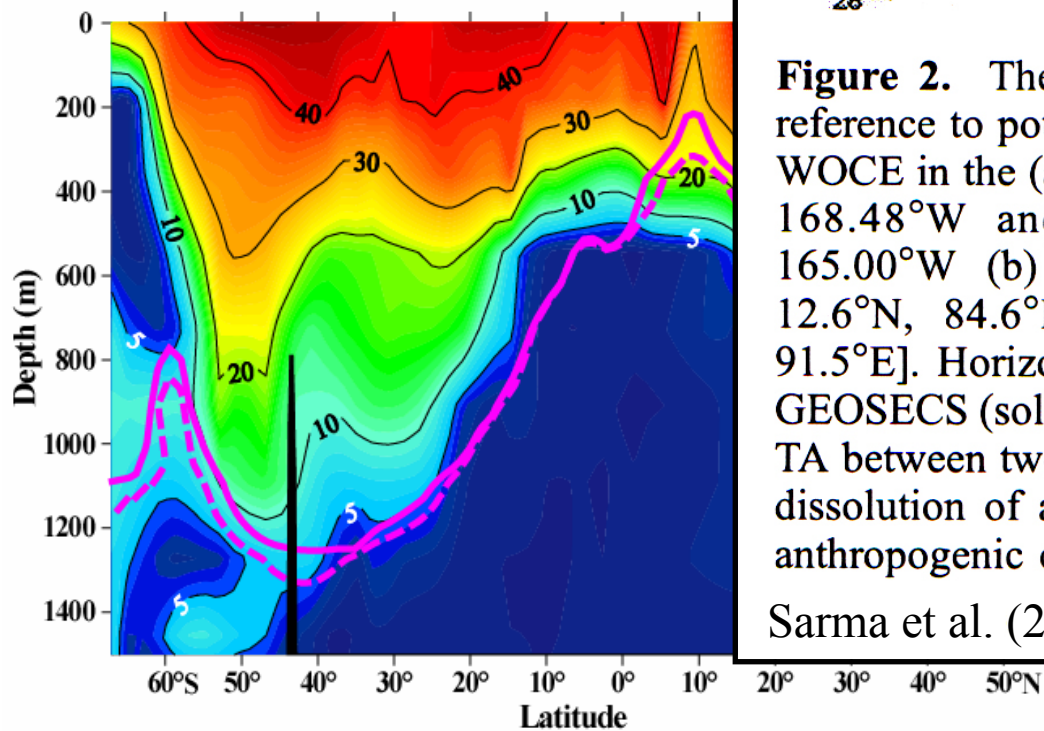
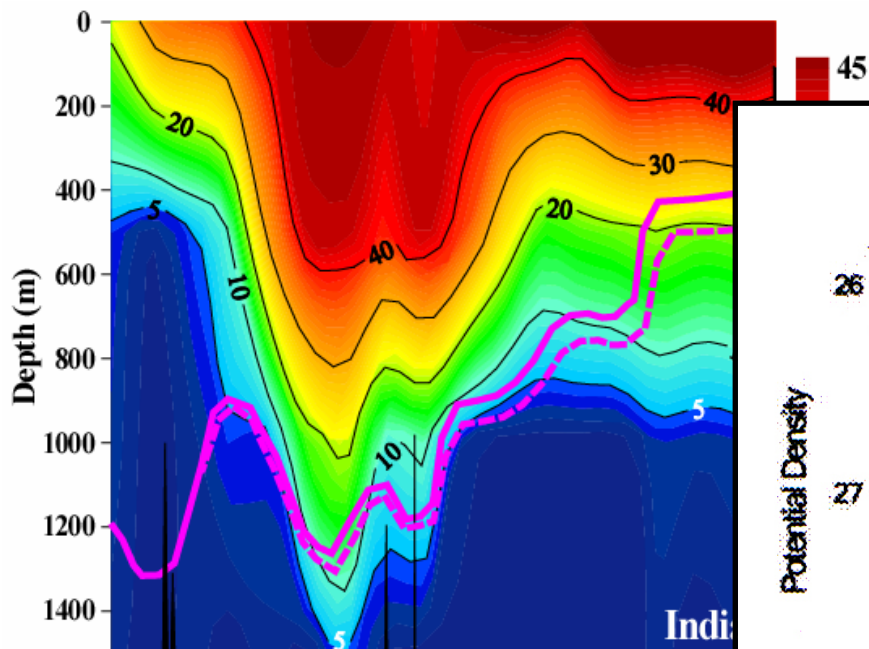
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Increased stratification	Lower productivity and uptake	positive
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Ecosystem structure	Lower or higher productivity	Pos./neg.
CH_4 hydrate release	Increased greenhouse forcing	Positive

The available sediment trap and water chemistry data indicate that as much as 60% of CaCO_3 production dissolves in shallow waters

Table 1. Sediment trap particulate CaCO_3 dissolution fluxes in the Pacific Ocean. The difference between the mean carbonate flux in the upper trap and the lower trap defines the dissolution flux. In all but one of the deepwater cases, the CaCO_3 flux collected in the midwater trap is higher than the carbonate flux collected in the deepwater trap. The dissolution rates are derived from the differences in CaCO_3 sediment trap fluxes between the upper and lower sediment traps divided by the depth range between the traps.

Location	Trap depth range (m)	Dissolution rate ($\mu\text{mol kg}^{-1} \text{ year}^{-1}$)
<i>Shallow sediment traps</i>		
Northwestern Pacific	100–1000	0.12
Equatorial Pacific	105–320	0.67
Northwestern Pacific	500–1000	0.02
Northeastern Pacific	200–1000	0.10
<i>Deep sediment traps</i>		
Northwestern Pacific	2000–4000	0.003–0.006
Equatorial Pacific	2300–3600	0.005–0.014
2°59.8'N 135°1.0'E	1592–3902	0.012
4°7.5'N 136°16.6'E	1769–4574	0.013
0°0.2'N 175°09.7'E	1357–4363	0.005
0°01'N 175°02'E	2200–4300	—
13°00'N 175°01'E	1500–5100	0.006
00°04'N 139°45'W	2284–3618	0.005–0.014
11°58'S 135°02'W	1292–3594	0.003
50°0'N 145°0'W	1000–3800	0.024





Modern Aragonite Saturation Horizon

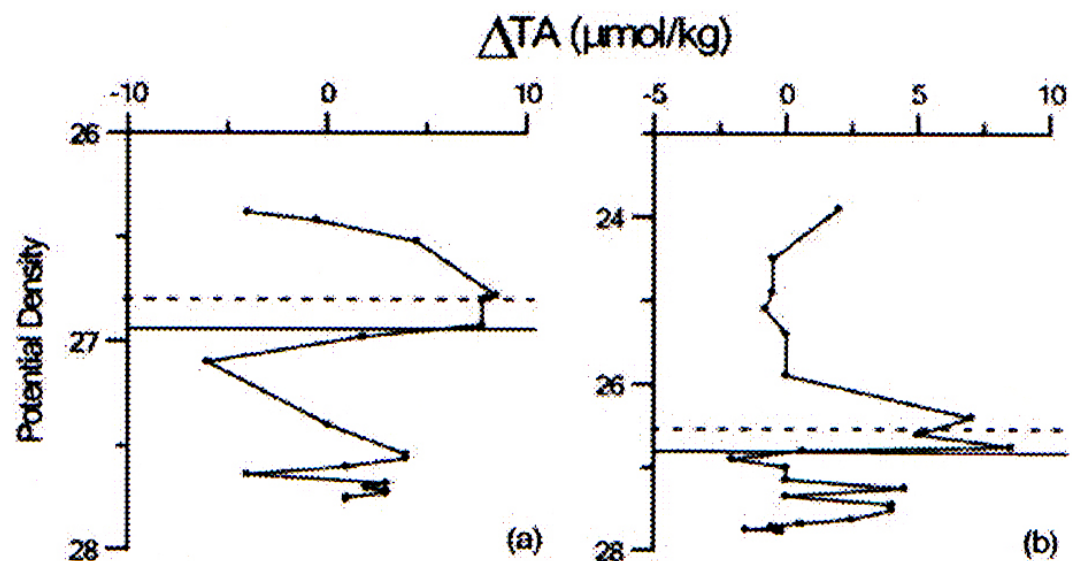
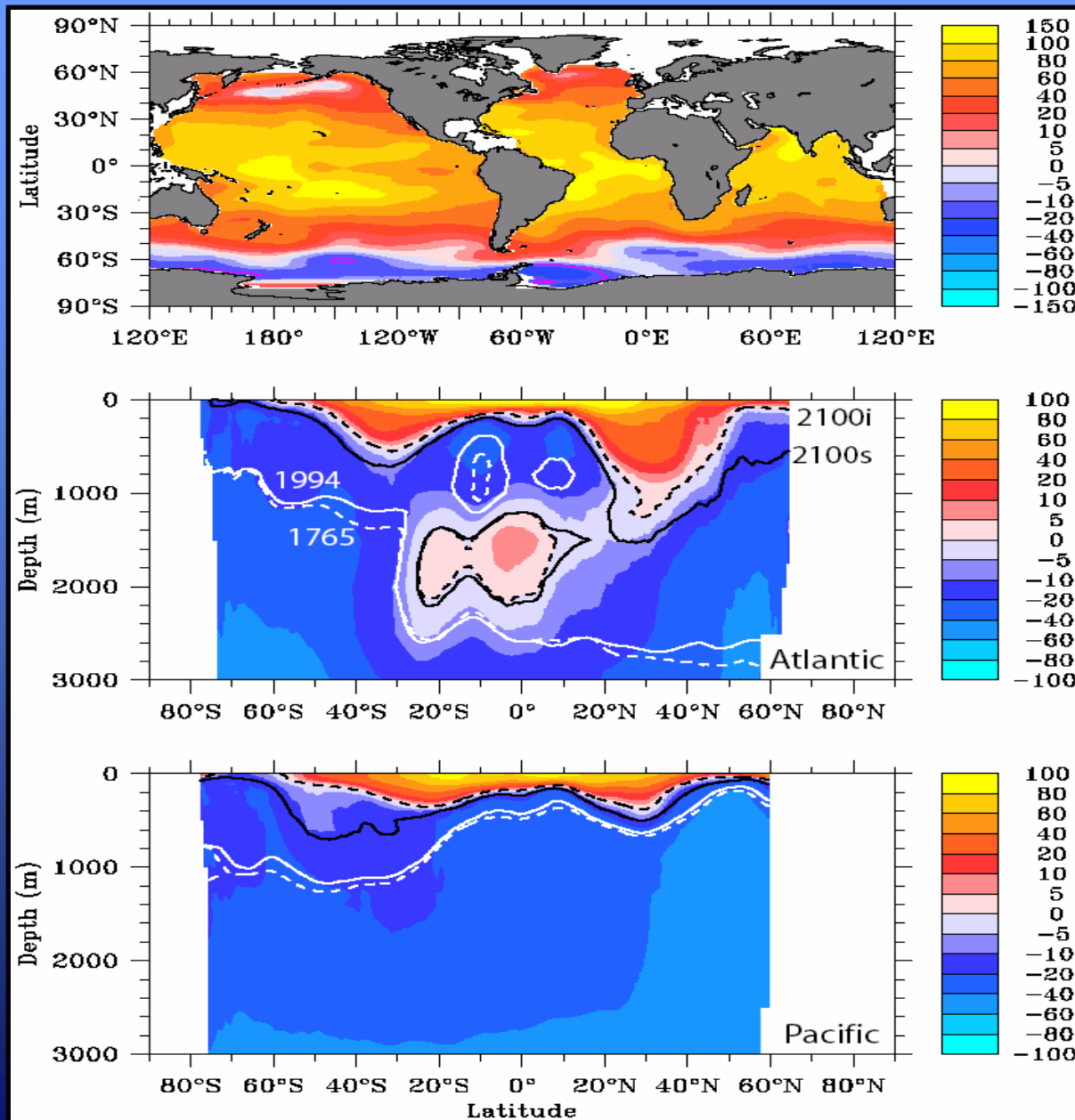


Figure 2. The change in total alkalinity ($\mu\text{mol/kg}$) with reference to potential density (σ_0), between GEOSECS and WOCE in the (a) North Pacific [GEOSECS #213, 30.97°N , 168.48°W and WOCE leg P15NA, #50, 31.00°N , 165.00°W] (b) North Indian Ocean [GEOSECS #446, 12.6°N , 84.6°E and WOCE leg I09, #241, 13.86°N , 91.5°E]. Horizontal lines show aragonite saturation during GEOSECS (solid line) and WOCE (dashed line). Increase in TA between two horizontal lines represents the influence of dissolution of aragonite skeletal material due to increased anthropogenic carbon inputs during past two decades.

Sarma et al. (2002)

Feely et al. (2004)

By 2100 large changes in saturation state

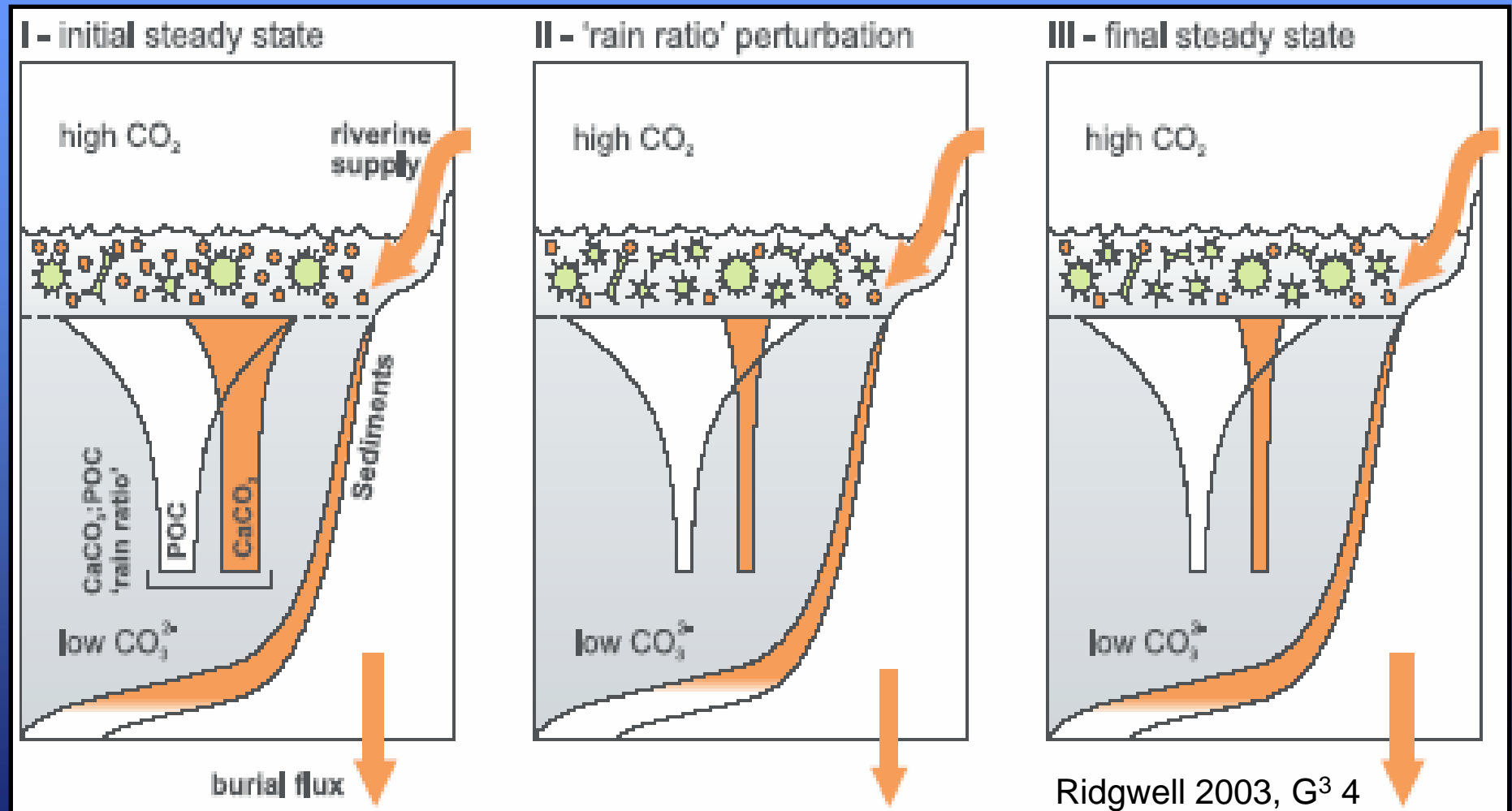


$\Delta[\text{CO}_3^{2-}]_A$ in $\mu\text{mol kg}^{-1}$

- Surface undersaturation ($\Delta[\text{CO}_3^{2-}]_A < 0$)
 - Southern Ocean
 - Subarctic Pacific
- Shoaling of the aragonite saturation horizon ($\Delta[\text{CO}_3^{2-}]_A = 0$)
 - Southern Ocean (by ~1000 m)
 - North Atlantic (by ~3000 m)

Orr et al., (submitted)

Effect of reduced CaCO_3 production and export may be counteracted by decreasing POC export ("ballasting effect")



The long term burial of organic C in the ocean is only $\sim 0.15 \text{ PgC yr}^{-1}$, but annual mixed layer export is $\sim 7 \text{ PgC yr}^{-1}$

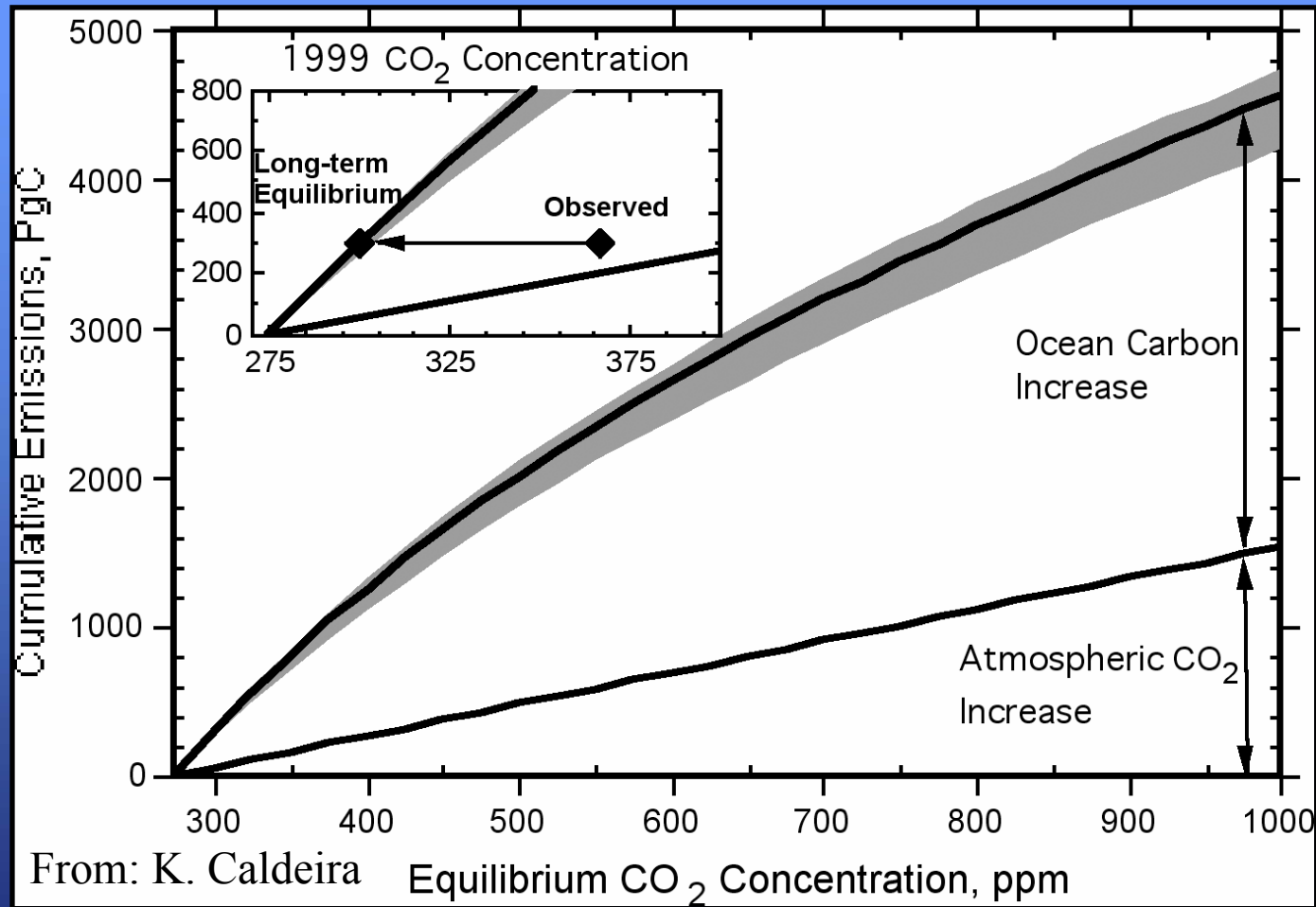
There is ~65 Million Pg C stored as CaCO_3 in ocean sediments



Dissolution of these sediments provides a huge potential for CO_2 uptake

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CH_4 hydrate release	Increased greenhouse forcing	Positive

Models predict that on millennial time-scales 65-70% of the emissions would end up in the ocean (no CaCO_3 compensation)



Dissolution of CaCO_3 sediments increases this number to 80-85%

The depth of carbonate dissolution affects the timing and magnitude of the atmospheric CO_2 signal

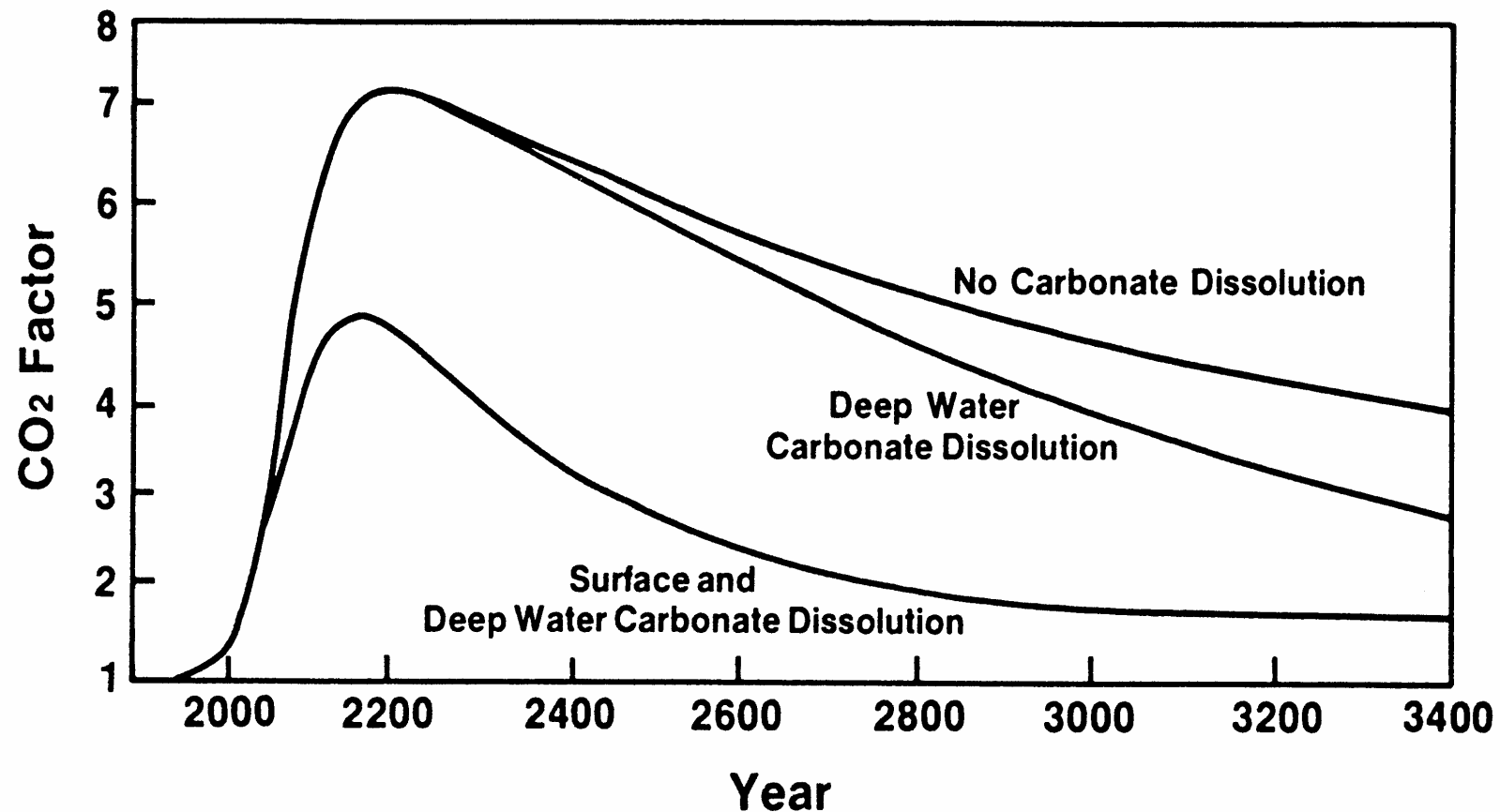
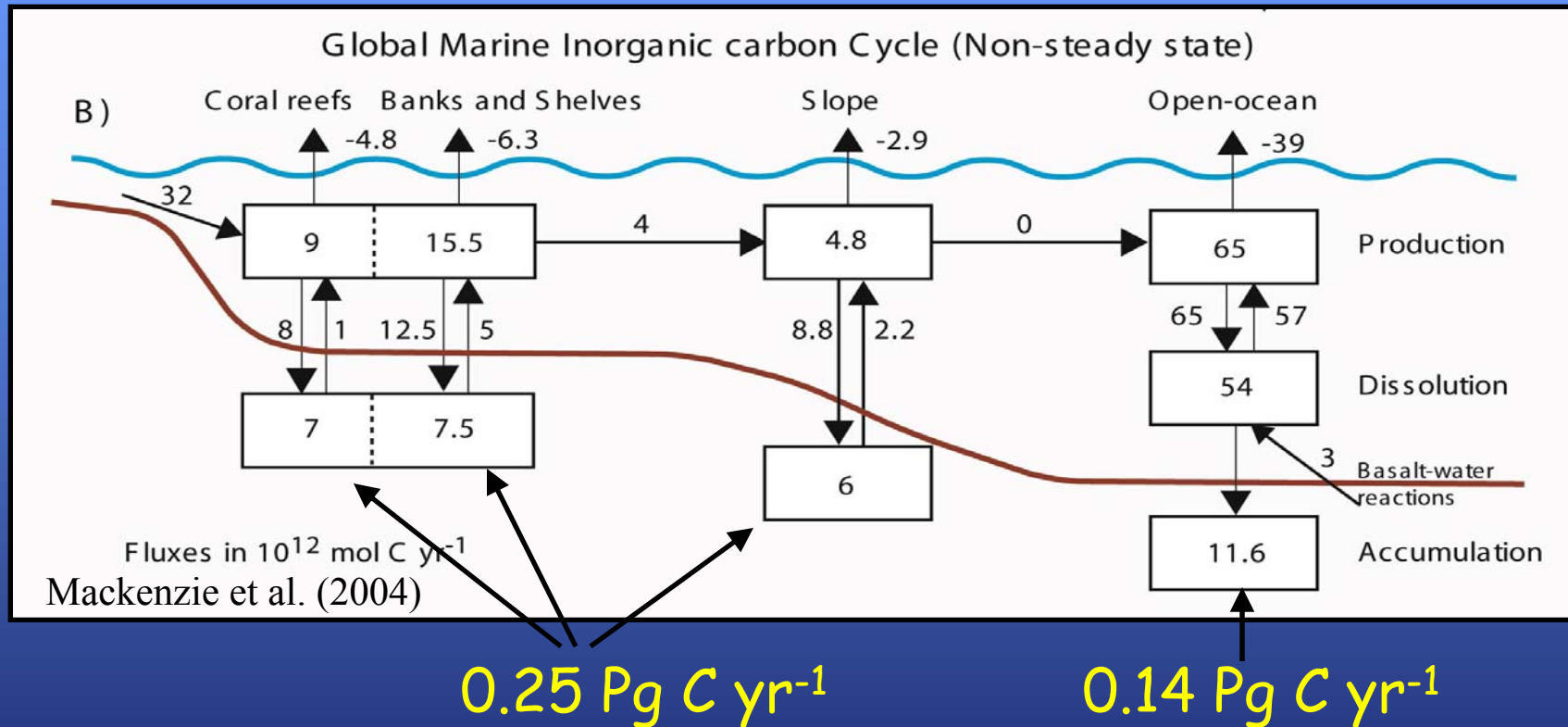
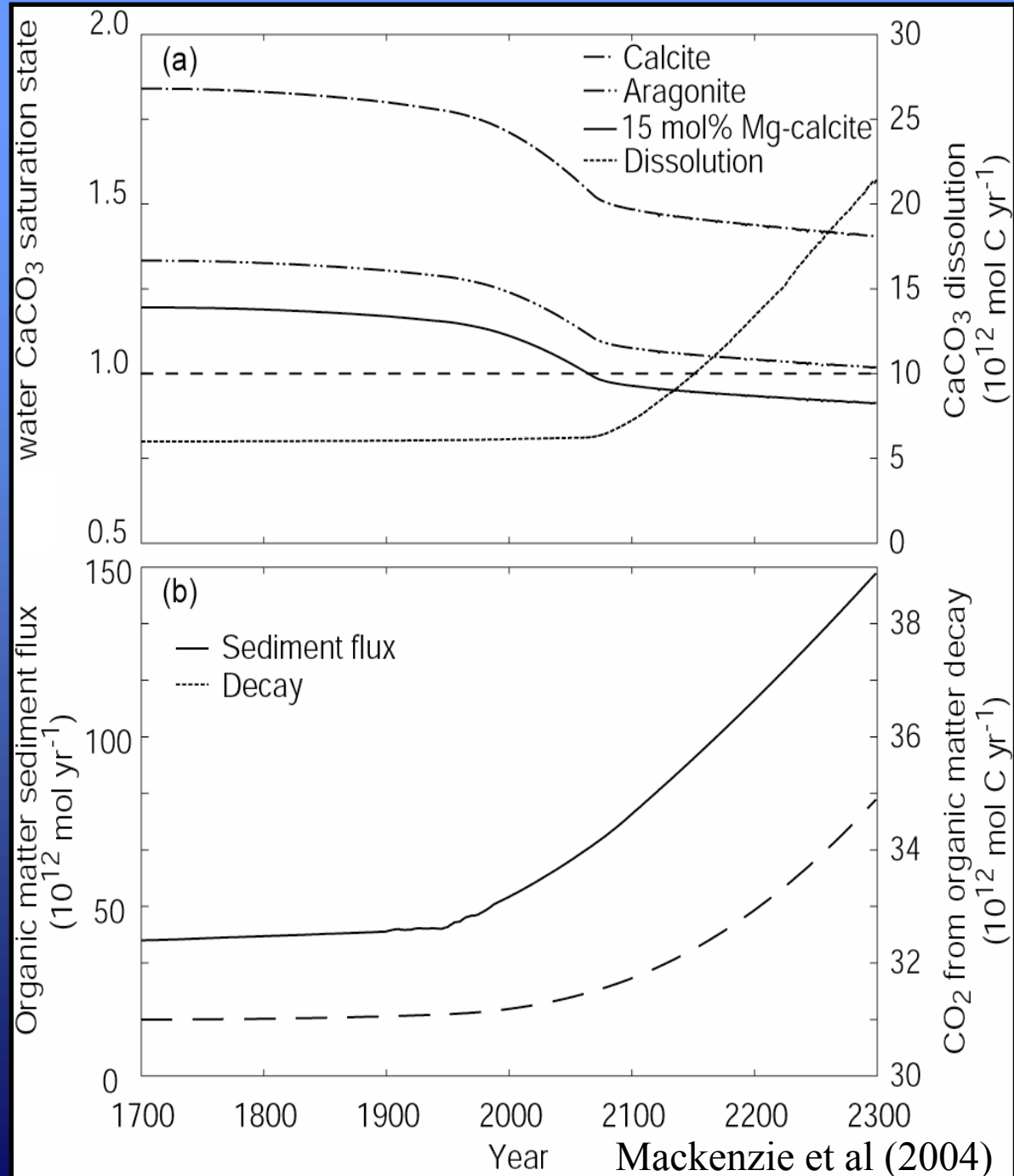


Figure 9.18. Graph illustrating that once CO_2 enters the atmosphere because of human activities, the return to original conditions takes a long time, regardless of whether or not CaCO_3 minerals are dissolved. (After Bacastrow and Keeling, 1979.)

The majority of CaCO_3 sediments are found on shelves and slopes



64% of Modern CaCO_3 accumulation is occurring on shelves and slopes

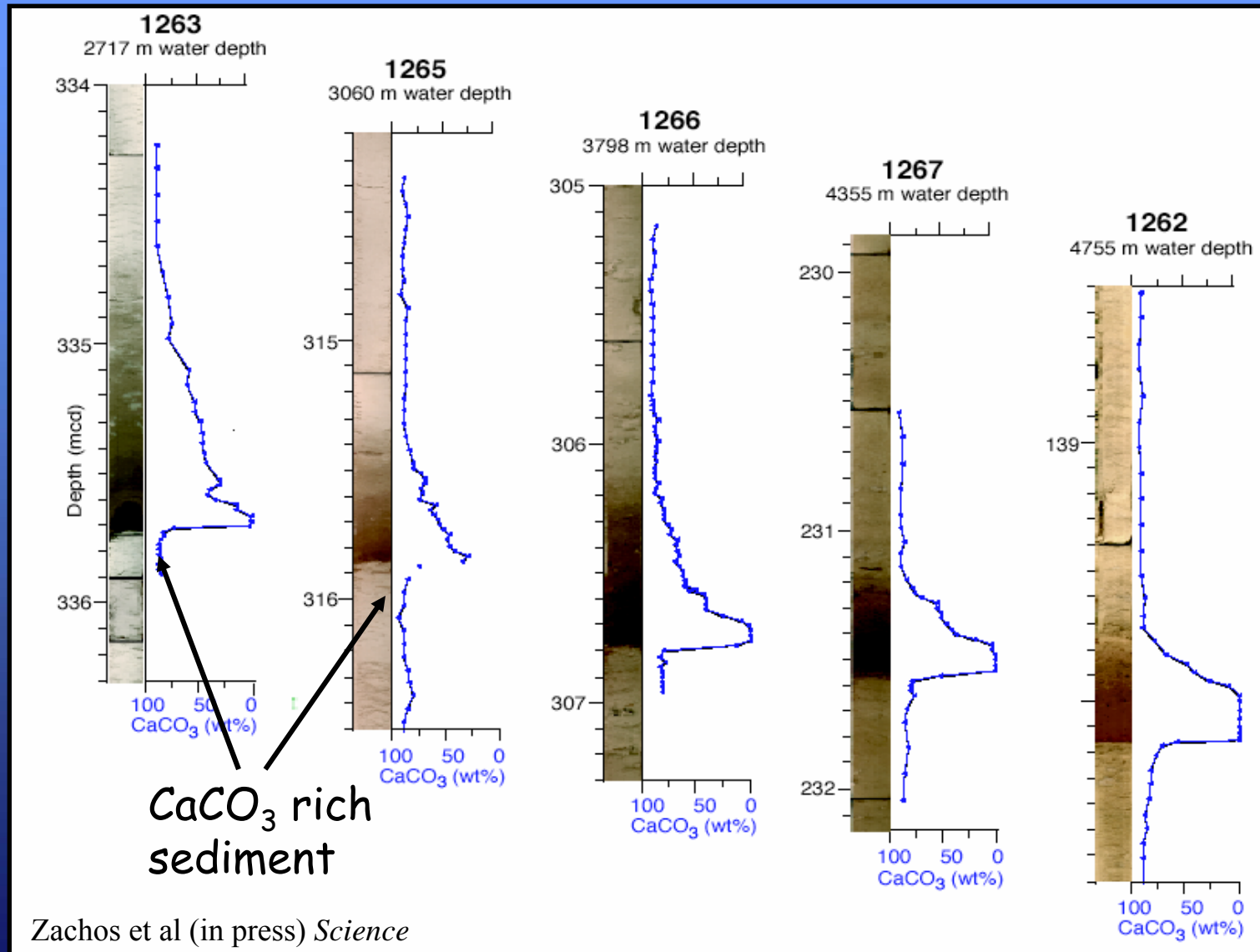


Pore water CaCO_3 dissolution flux increases in shallow sediments because of lower saturation states and increased organic matter oxidation

Organic matter oxidation in sediments increases as ocean temperatures increase

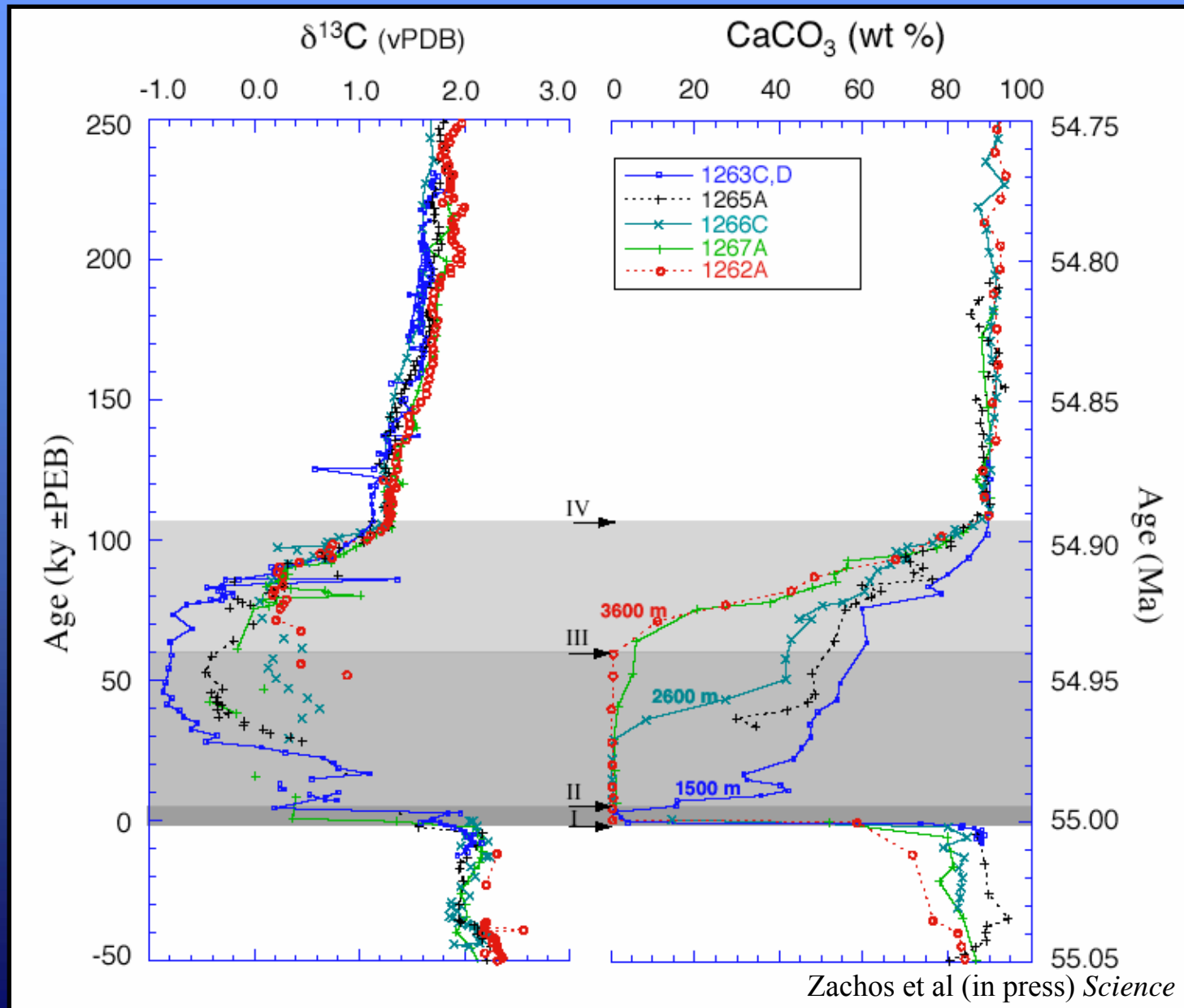
Big dissolution event at Paleocene-Eocene Thermal Maximum

55Ma sea surface temperatures rose by $\sim 8^{\circ}\text{C}$ over a few thousand years



30-40% of deep sea benthic foraminifera went extinct

A commensurate change in ^{13}C suggests that there was a huge “burp” of methane into the atmosphere.



CONCLUSIONS

- 1) Many of the ocean carbon cycle and climate feedbacks are tied to the CaCO_3 cycle.
- 2) The CaCO_3 cycle is still poorly understood and needs to be studied with a particular emphasis on the magnitudes and timing.
- 3) We know from thermodynamics that ocean uptake efficiency will decrease, but the real bottle neck is in moving the CO_2 into the ocean interior, which is controlled by circulation.
- 4) There is general consensus that elevated CO_2 will reduce calcification and lead to shallower dissolution producing a negative feedback, but the related decrease in organic matter export may counteract some or all of this effect.
- 5) There is a potentially very large negative feedback associated with dissolving carbonate sediments. This has been thought to be a millennial time scale issue, but there is growing evidence that this dissolution may occur quickly.

Take home message:

We should not limit our vulnerability studies only to positive feedbacks, but we also need to understand potential negative feedbacks.



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