

# CARBONATE DISSOLUTION UNDER RISING ATMOSPHERIC CO<sub>2</sub> AND OCEAN ACIDIFICATION

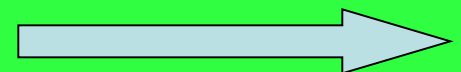
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“The major goal of the workshop is to make significant progress toward specific implementation strategies that address gaps and unknowns about ocean acidification” and “not start from scratch and rehash basic information that has been discussed at previous workshops”, The Steering Committee.



But just so we do not forget



One of the first modern recognitions of the fact that carbon dioxide (CO<sub>2</sub>) added to the atmosphere by fossil fuel combustion will lead to absorption of this gas by the ocean *and* the acidification of seawater was a 1971 paper by Broecker, Li and Peng published in *Impingement of Man on The Sea* (Carbon dioxide—man's unseen artifact, 1971, Donald W. Hood, Ed., John Wiley & Sons, Inc, pp. 287-324).

I calculate that if we burn  
the whole conventional  
fossil fuel reserves of 5000  
Gt carbon, 11.7 g  
CaCO<sub>3</sub>/cm<sup>2</sup> of sea floor,  
equivalent to the upper  
58.3 cm of sediment,  
would need to be dissolved  
to neutralize the added  
acidity.

# 11

## Carbon Dioxide—Man's Unseen Artifact

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WALLACE S. BROECKER, YUAN-HUI LI, and TSUNG-HUNG PENG, *Lamont-Doherty Geological Observatory of Columbia University, Palisades, New York*

During the past century man has recovered 10<sup>11</sup> tons of coal, 10<sup>11</sup> barrels of petroleum, and 10<sup>12</sup> m<sup>3</sup> of natural gas from the sedimentary rocks which mantle the earth's surface. The carbon in these fuels has been delivered via combustion to the atmosphere as CO<sub>2</sub> gas. During the coming century an order of magnitude greater of fuel will be required to meet our energy demands. As a consequence, sometime during the first half of the next century the CO<sub>2</sub> content of our air will reach a level twice as high as it is today.

Fortunately CO<sub>2</sub> is not toxic. Our medical well-being is not endangered. Instead we must worry about the effect on our climate. The CO<sub>2</sub> and H<sub>2</sub>O in our atmosphere trap outgoing infrared light. Because of this impediment to loss of energy our planet maintains a temperature considerably warmer than would exist in the absence of these gases. By adding more CO<sub>2</sub> to the atmosphere man will shift the balance in the earth's radiation budget. In order to maintain equilibrium between incoming and outgoing energy some change in cloudiness, water vapor content, and temperature will take place. As a result climate will gradually change. Whether these changes will be beneficial, harmful, or of little consequence to the various nations of the earth is a matter of immense concern to man.

In order to evaluate the situation we must know (a) the amounts of CO<sub>2</sub> which have been and will be produced, (b) the fraction of this CO<sub>2</sub> which has and will remain in the atmosphere, and (c) the manner in which

Furthermore, in 1973 Bacastow and Keeling in a paper entitled “Atmospheric carbon dioxide and radiocarbon in the natural carbon cycle: Changes for A. D. 1700 to 2070 as deduced from a geochemical model” (In *Carbon in the Biosphere*, George M. Woodwell and Erene V. Pecan, Eds., U. S. Atomic Energy Commission Technical Information Center, Office of Information Services, pp. 86-135) recognized that as anthropogenic CO<sub>2</sub> is added to the atmosphere the **“ocean surface water will become progressively more acid”**.

## ATMOSPHERIC CARBON DIOXIDE AND RADIOCARBON IN THE NATURAL CARBON CYCLE: II. CHANGES FROM A. D. 1700 TO 2070 AS DEDUCED FROM A GEOCHEMICAL MODEL

ROBERT BACASTOW and CHARLES D. KEELING

Scripps Institution of Oceanography, University of California at San Diego,  
La Jolla, California

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### ABSTRACT

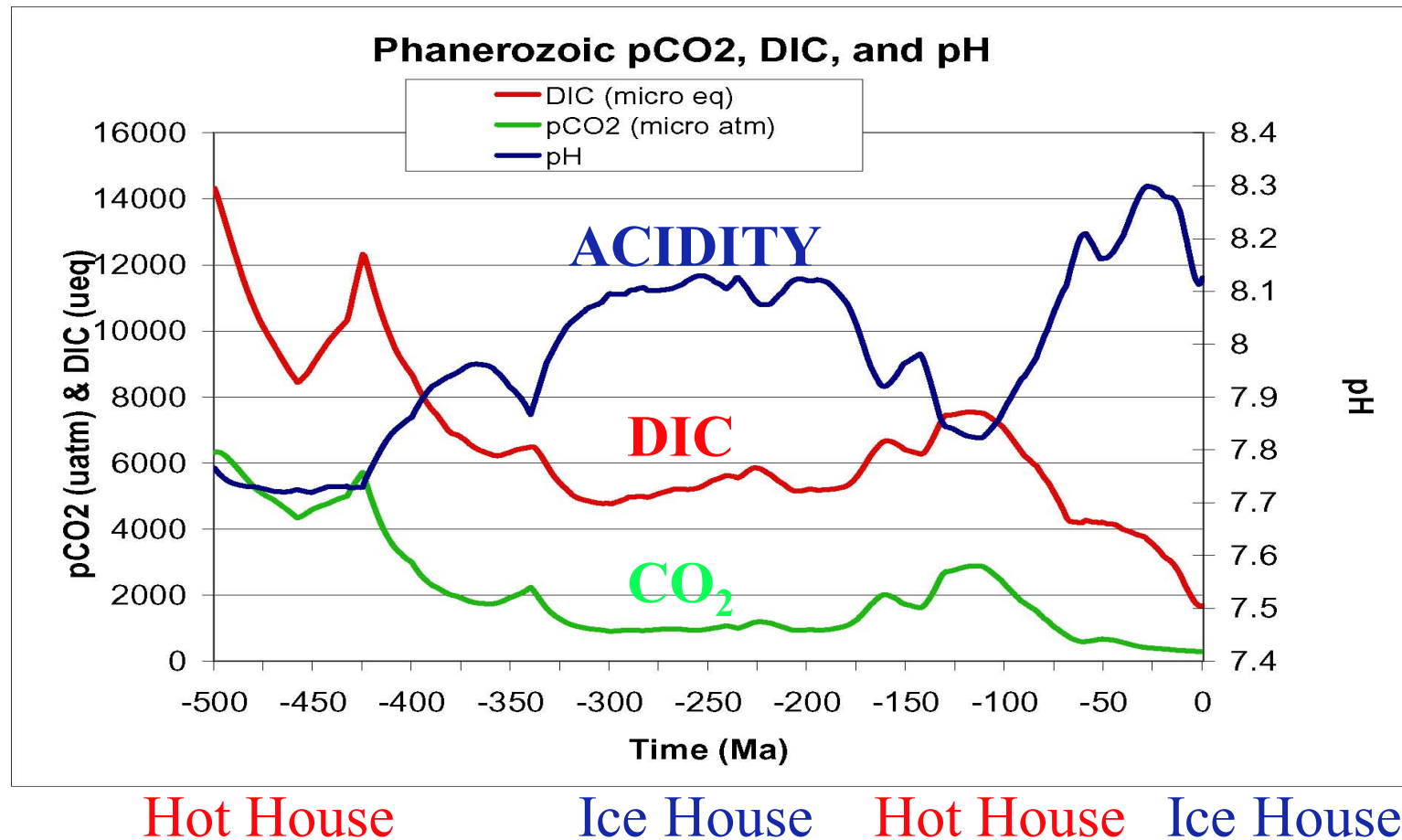
A nonlinear geochemical model of the interaction of atmospheric CO<sub>2</sub> with the oceans and land biota has been constructed to predict future changes in atmospheric CO<sub>2</sub> concentration in the next century. If production of CO<sub>2</sub> from fossil fuels continues, the perturbations from preindustrial times may become so large that a linear model is unrealistic, especially because it fails to take into account that ocean surface water will become progressively more acid and less able to absorb each new increment of industrial CO<sub>2</sub>. On the assumption that industrial CO<sub>2</sub> production continues to increase at the rate of the past 20 years and that the ultimate increase in biomass of the land biota is no more than twice the present biomass, the atmospheric CO<sub>2</sub> concentration will reach a value six to eight times the preindustrial value in 100 years.

When the radiocarbon concentration in dated wood and the recent atmospheric increase in CO<sub>2</sub> are compared in the context of the model, it appears that the land biomass has increased 1 to 3% since the beginning of the industrial era. This calculation takes account of the actual year to year variations in industrial CO<sub>2</sub> production and the heliomagnetic variation in radiocarbon production in the stratosphere. The inferred biomass increase, presumably owing to CO<sub>2</sub> fertilization, is too small to be verified by direct observation and is not considered to be established. On the other hand, the trend in atmospheric CO<sub>2</sub> apparently rules out any large recent change in biomass.

Combustion of fossil fuels (coal, petroleum, and natural gas) is adding increasing amounts of carbon dioxide (CO<sub>2</sub>) to the atmosphere each year. The fate of this CO<sub>2</sub> attracts interest because a sustained increase might modify the earth's climate through the “greenhouse” effect<sup>1</sup> and because, from the effects of this input, we may learn more about the earth's carbon cycle.

We have constructed a geochemical model of the natural reservoirs into which industrial CO<sub>2</sub> can mix. Our first objective is to predict the CO<sub>2</sub> concentration in the atmosphere during the next century, when atmospheric

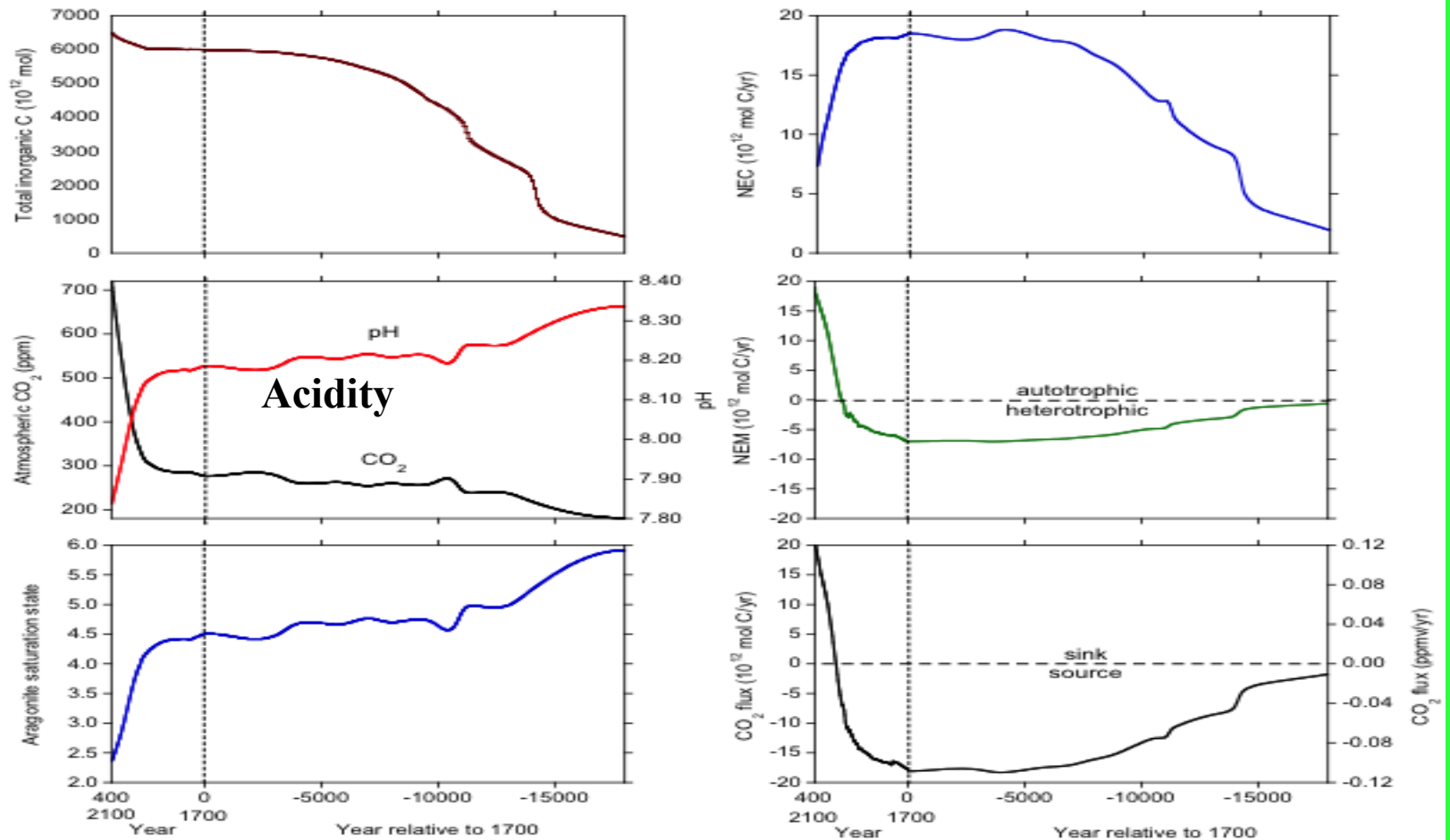
**500 million years of long-term changes in atmospheric CO<sub>2</sub>, ocean pH and dissolved inorganic carbon, and climate driven by plate tectonics (balance of uptake of CO<sub>2</sub> in weathering vs volcanic release of CO<sub>2</sub>) and plant evolution**



Adapted from Mackenzie, Arvidson and Guidry interactive cycles model, 2007

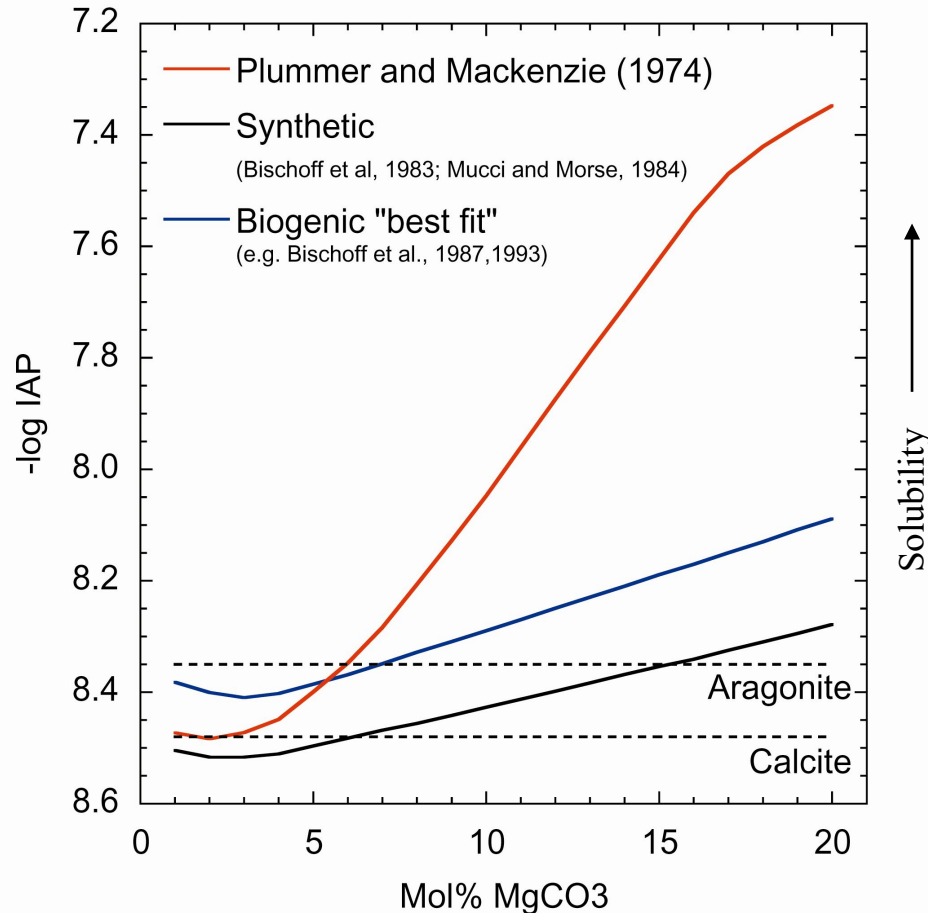


# Last Glacial Maximum (LGM) to Year 2100



Computed using Shallow-water Ocean Carbonate Model, SOCM;  
Andersson, Mackenzie and Lerman (Mackenzie and Lerman, 2006)

# Carbonate Mineral Solubility



- **Solubility** - important in order to predict response to rising  $p\text{CO}_2$  and ocean acidification

- **Associated with substantial controversy!**

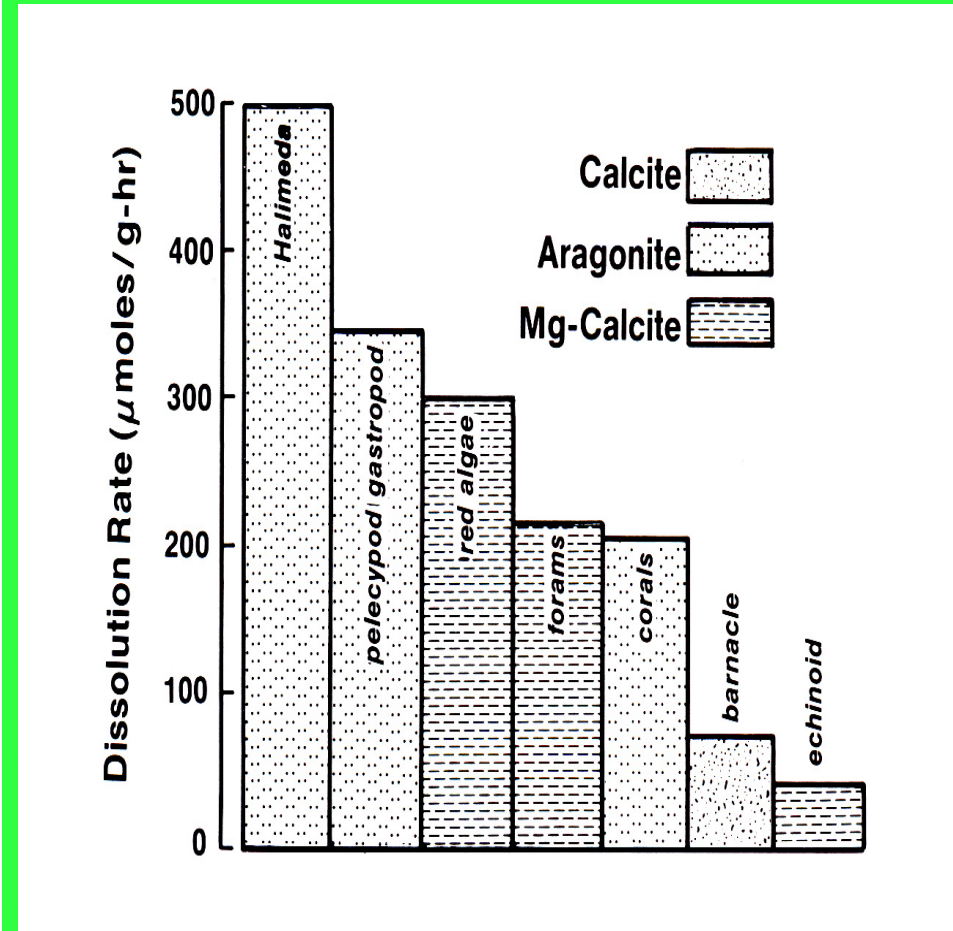
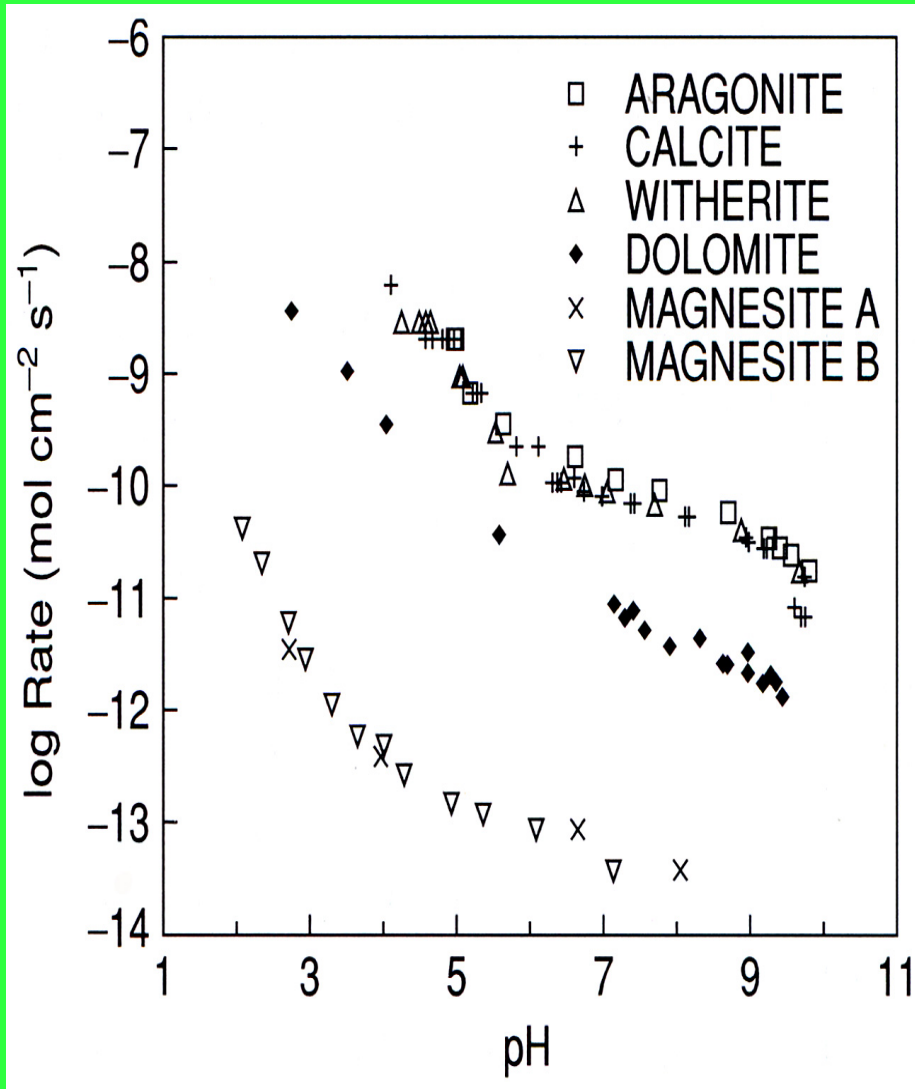
- Dissolve incongruently
- No true equilibrium
- Treated as a one-component phase

- **Large range of solubilities for biogenic Mg-calcite of similar Mg content**

- Impurities, inclusion of other ions ( $\text{H}_2\text{O}$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ ), cation and anion positional disordering
- Different preparation of material

- **Synthetic Mg-calcite solubility** – only “true” relationship as a function of  $\text{MgCO}_3$  content

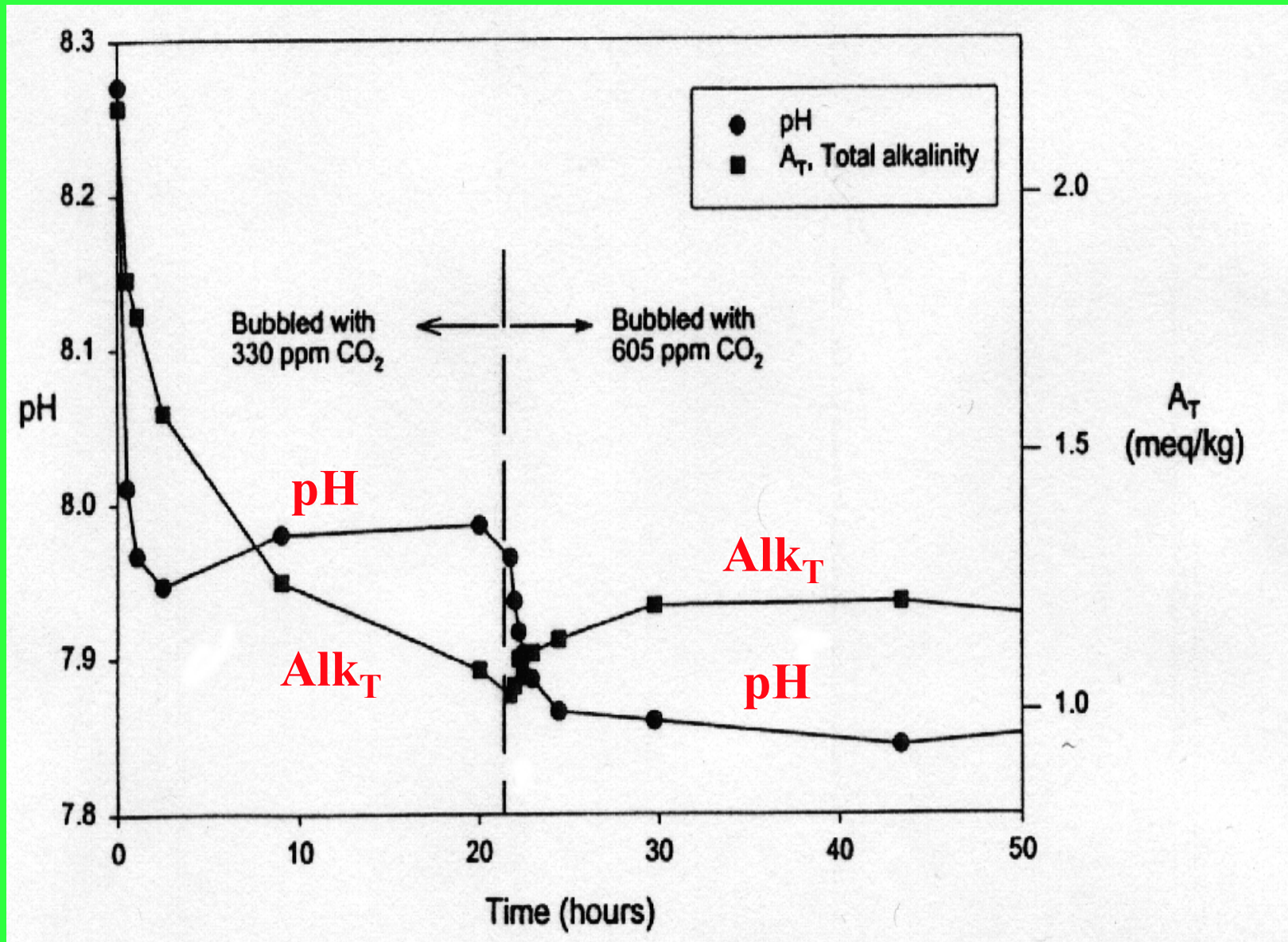
# Dissolution Rates of Major Carbonate Minerals



Biogenic phases in undersaturated seawater (Walter, 1985)

In aqueous solution as a function of pH (Chou, Garrels and Wollast, 1989)

# Simple kinetic experiment illustrating that carbonate sediment under increased $p\text{CO}_2$ dissolves rapidly



Tribble and Mackenzie, 1998

# RECOMMENDATIONS

**There is a very strong need for fundamental work on dissolution of carbonates under different CO<sub>2</sub> and T conditions. This would involve field experiments and laboratory work on solubility and kinetics.**

**1. Reevaluation of existing experimental data on the solubility behavior of Mg-calcites in seawater and design of new experiments to obtain the stoichiometric constants as a function of a range of CO<sub>2</sub> and T levels--use of flow through reactor?**

**2. Reevaluation of existing kinetic behavior for all carbonate minerals in seawater and experiments done under higher CO<sub>2</sub> and a range of T conditions to obtain rates and mechanisms--use of flow through reactor?**

**3. Field experiments should be designed to look at dissolution and precipitation rates of carbonate phases in different carbonate settings under different CO<sub>2</sub> and T conditions.**

**In both 1 and 2, natural phases should be used and the phase composition and structure characterized using modern analytical methods. In 3 modern analytical techniques should be used to quantify marine carbon chemistry and solid phases present and their reaction to CO<sub>2</sub> changes.**



# Models of $\text{CaCO}_3$ Budget for Global Ocean and Global Open Ocean

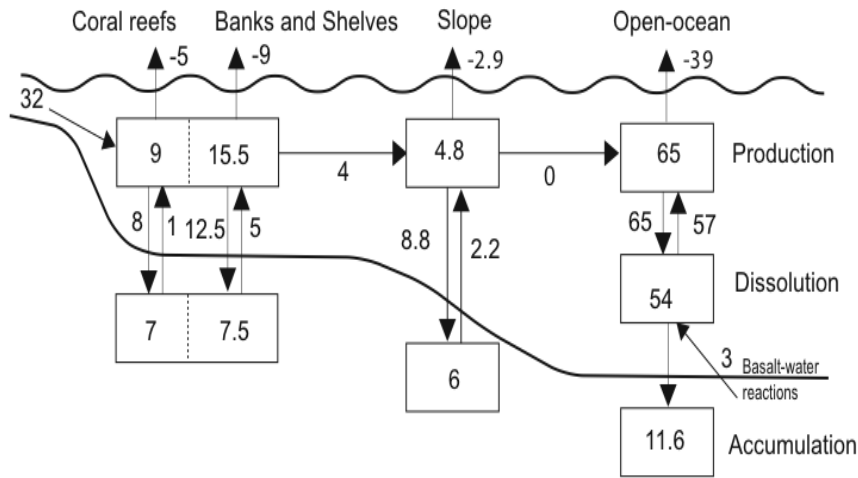
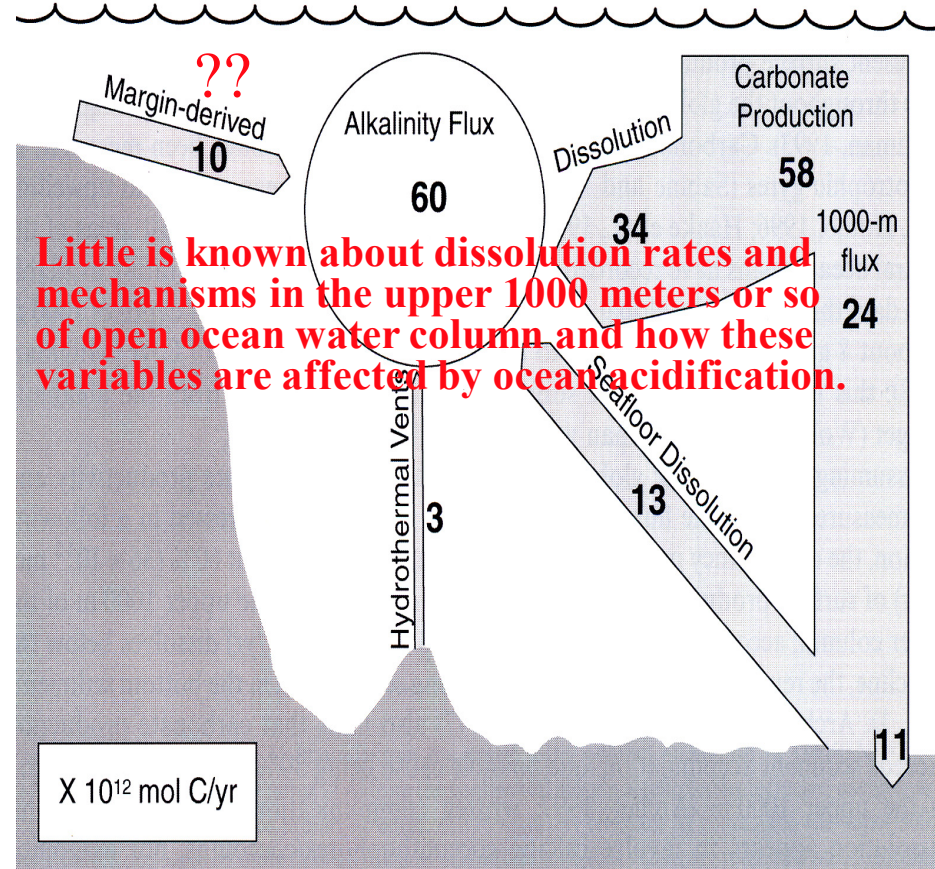


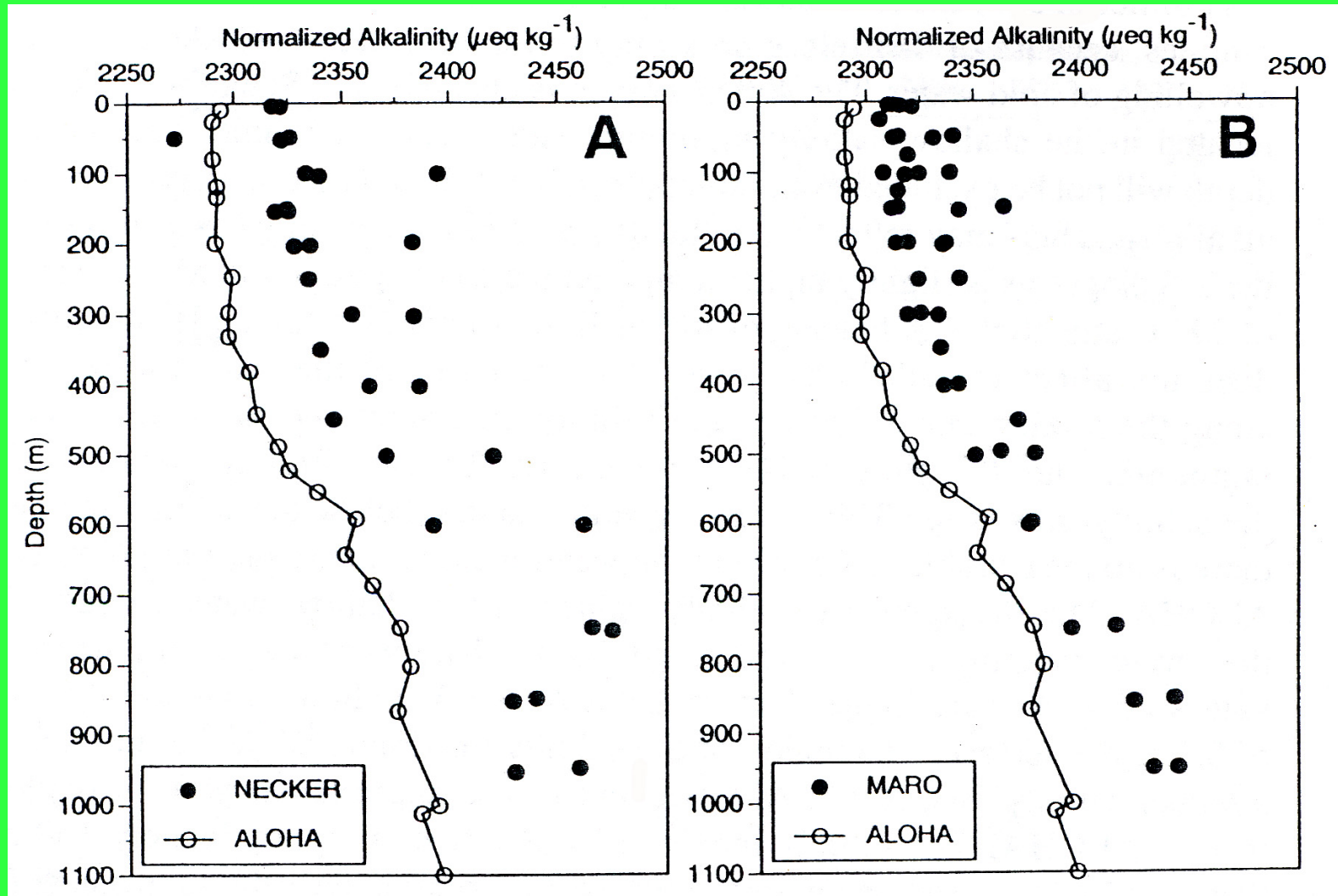
Figure 8-006. Mackenzie et al.

**Rivers add about half as much detrital  $\text{CaCO}_3$  to the ocean as is produced in the global coastal ocean! What happens to this? How much carbonate is there in “terrestrial” sediments?**



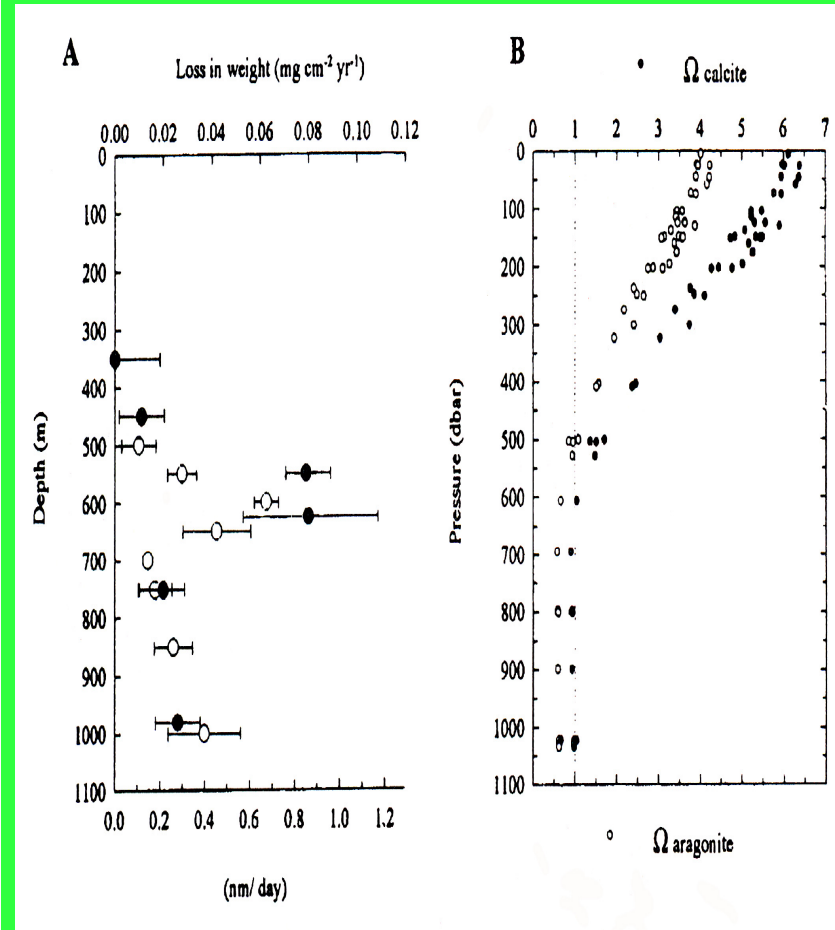
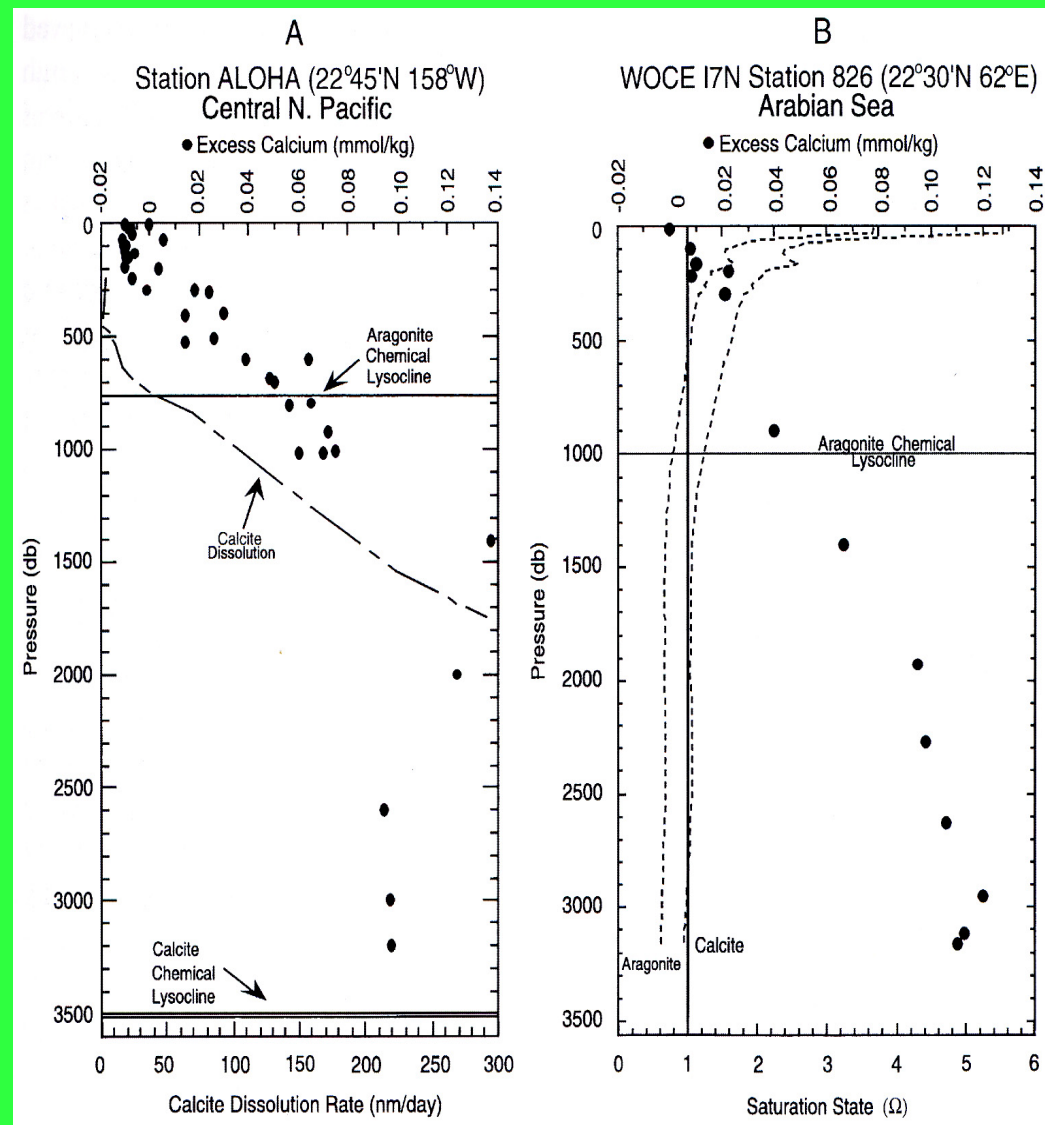
**From Mackenzie, Andersson, Lerman and Ver, 2004; Milliman, Troy, Balch, Adams, Li and Mackenzie, 1999. Global data are really poorly known and we all “chew” on the same old data with little new being added!**

**Alkalinity “halo” around Hawaiian islands produced from transport of biogenic high Mg-calcites offshore and their dissolution (How will ocean acidification and T affect this phenomenon and processes involved?)**



**Sabine and Mackenzie, 1993; also observed by John Morse around the Bahama Banks**

# Open ocean dissolution above the chemical lysocline: it occurs but what is the importance of different processes and how do they react to ocean acidification and increasing temperature?



From Troy, Li and Mackenzie, 1997; Milliman, Troy, Balch, Adams, Li and Mackenzie, 1999

## RECOMMENDATIONS

Peterson/Milliman-type carbonate substrate experiments traversing from coastal regions seaward using various carbonate minerals suspended at different depths. Surface morphology and evolution of surface roughness can be resolved by atomic force microscopy (AFM) and vertical scanning interferometry (VSI). Surface composition could be obtained from Auger or other surface spectroscopic techniques. Surface overgrowth mineralogy and structure potentially could be obtained with grazing incidence X-ray diffraction (see experimental approaches of Rolf Arvidson and Andreas Luttge at SMU). The key is to use each of these techniques or others in concert to produce an integrated quantitative result for investigating surface dissolution (or precipitation). One would also assess the dynamics of the marine carbon chemistry along the traverses. Other complementary data should be obtained.

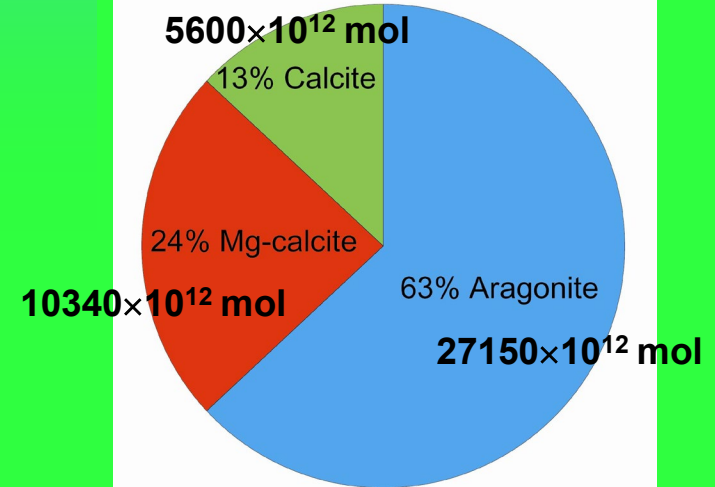
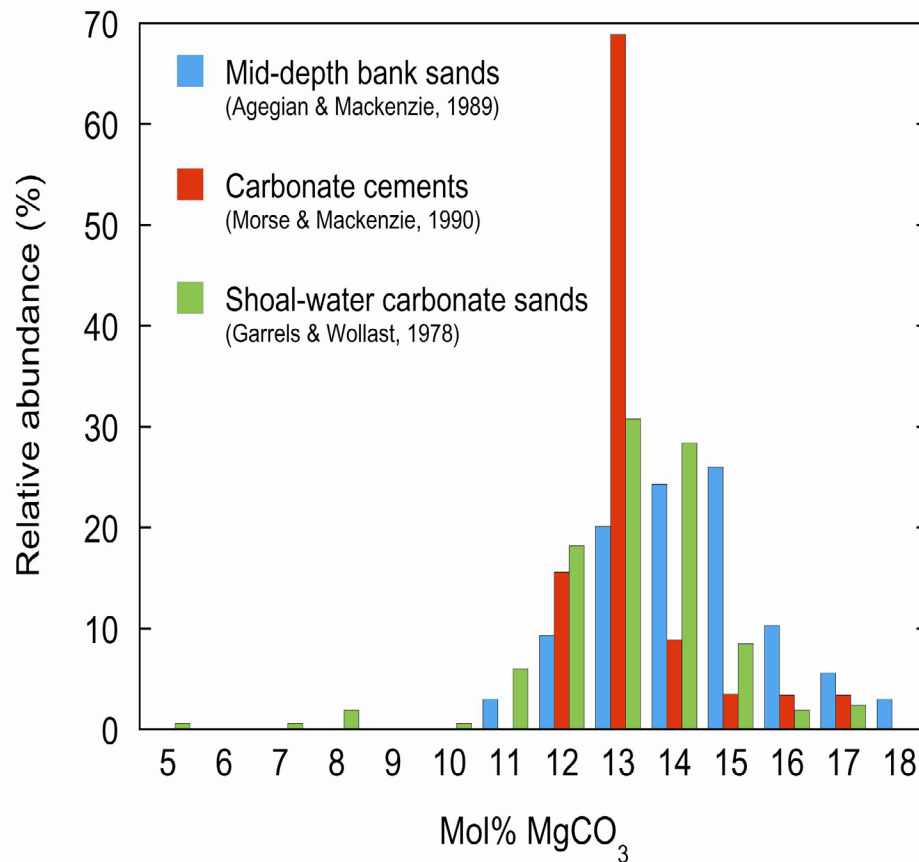
One possible location for tropical work would be Maunalua Bay or Kaneohe Bay in Hawaii (high island reef setting) seaward to the HOT site. The same could be done at Bermuda (low-island reef setting) and I also would select a temperate site [continental shelf of the western U.S. (?) where Steve Smith showed years ago the loss of significant benthic carbonate production by dissolution] and a high latitude, cool water carbonate site, perhaps the Skagerrak, Kattegat and Baltic Sea areas of “undersaturation” in which Alexandersson did his classic work. This could be done in cooperation with European colleagues. As with WOCE legs, repeat traverses would be necessary.



# Shallow water carbonate sediments

- major reservoir that can rapidly react to rising  $p\text{CO}_2$  and decreasing carbonate saturation state  $\Omega$

Reactive carbonate sediments on centennial time scales

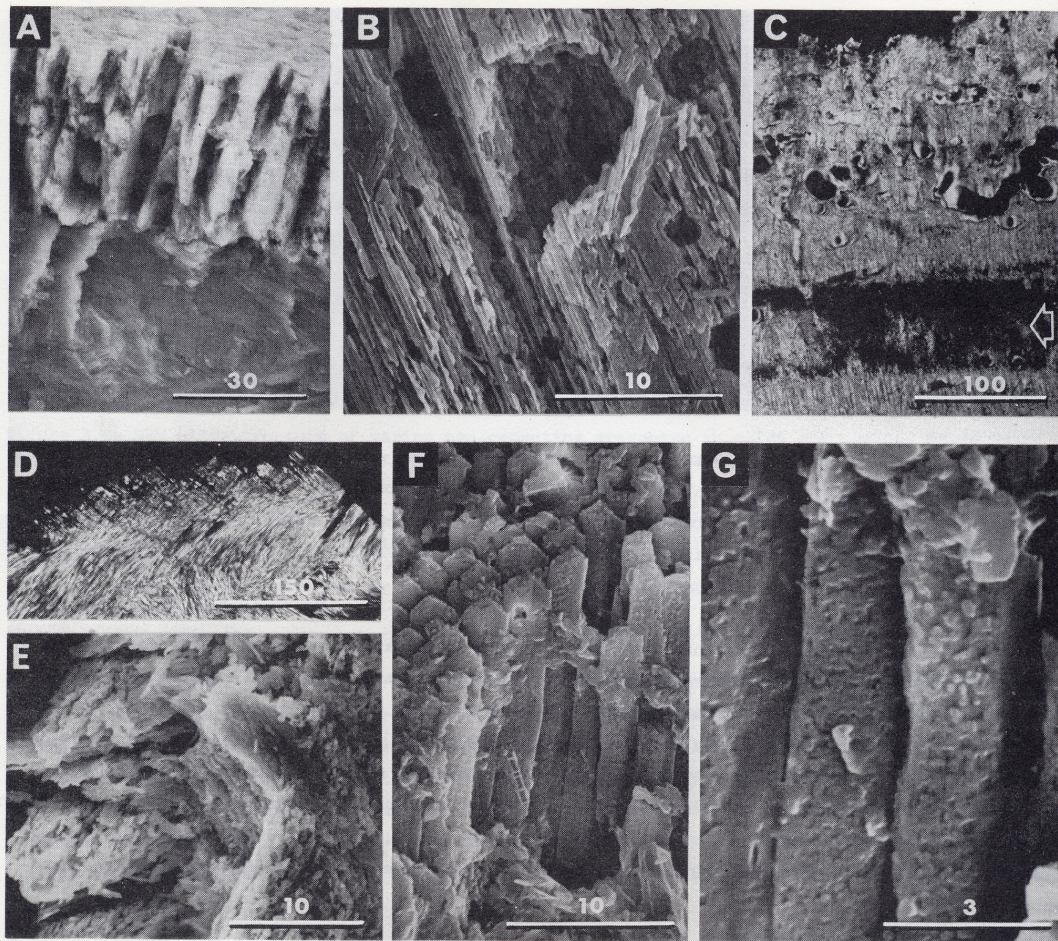


Morse, Andersson and Mackenzie, 2006

- Calcite-rhombohedral, stable
- Aragonite-orthorhombic, metastable
- Mg-calcite-rhombohedral, metastable,  $\text{Ca}^{2+}$  replaced by  $\text{Mg}^{2+}$

Biogenic Mg-calcite content: 4-30 mole%  $\text{MgCO}_3$

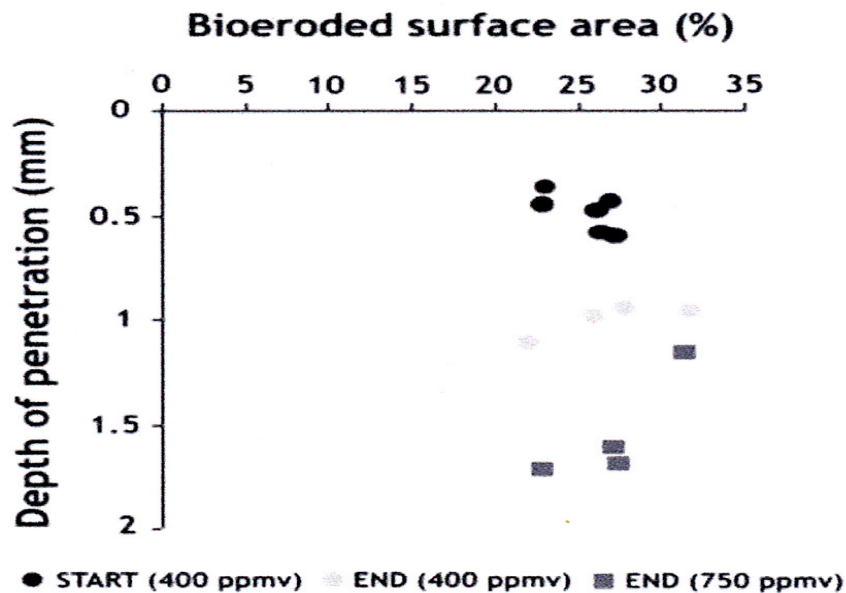
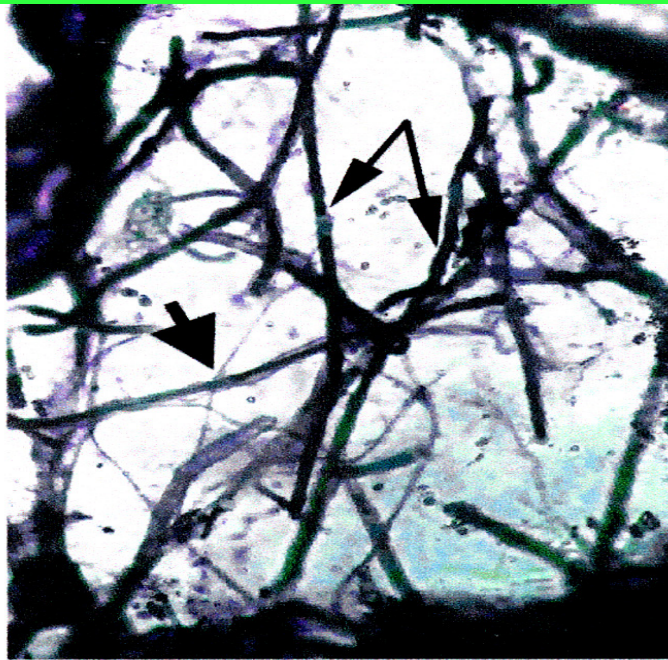




**Figure 4.**--- Shallow-marine dissolution of skeletal carbonate fragments. Scale bars in  $\mu\text{m}$ . (A) SEM, fractured pelecypod shell, Hovs Hallar, Kattegat. External surface up. Two shell layers with different internal organization show different response to the leaching process. Both layers are cross-lamellar, and both are probably aragonitic. (B) SEM, fractured mollusk shell, Hovs Hallar, Kattegat. Cross-lamellar aragonite fabric, partly dissolved. The borings were formed prior to the leaching. The area shown is not representative for the whole shell; rather, it represents preferential attack, as shown in C. (C) Mollusk shell, Kristineberg, Skagerrak. Thin section, crossed pols. External surface is up. The fragment is heavily bored but there is no secondary micrite in the borings. The arrow points to a dark band of preferentially leached fabric, a typical example of selective leaching of the particle interior. (D) Unidentified fragment, Grebbestad, Skagerrak. Thin section, crossed polarizers. High external surface relief, caused by leaching. (E) SEM, mollusk shell, Hovs Hallar, Kattegat. Natural external surface of leached cross-lamellar aragonite fabric. (F) SEM, *Mytilus* shell, Grebbestad, Skagerrak. Natural external surface of prismatic calcite fragment. The grain was very brittle, but still coherent and with a bluish tinge. (G) SEM, same specimen as in F. The detailed etch pattern of calcite fibers; a pattern which is related to the arrangement of small granules in the fibers.

**Endolithic boring and dissolution of skeletal carbonates, Kattegat, Skagerrak and Baltic seas (several papers by Alexandersson in the 1970s showing dissolution and endolithic boring features in aragonite, calcite and Mg-calcite skeletons and tests under “undersaturated” conditions).**





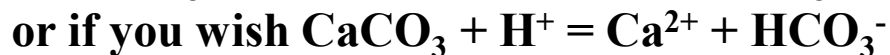
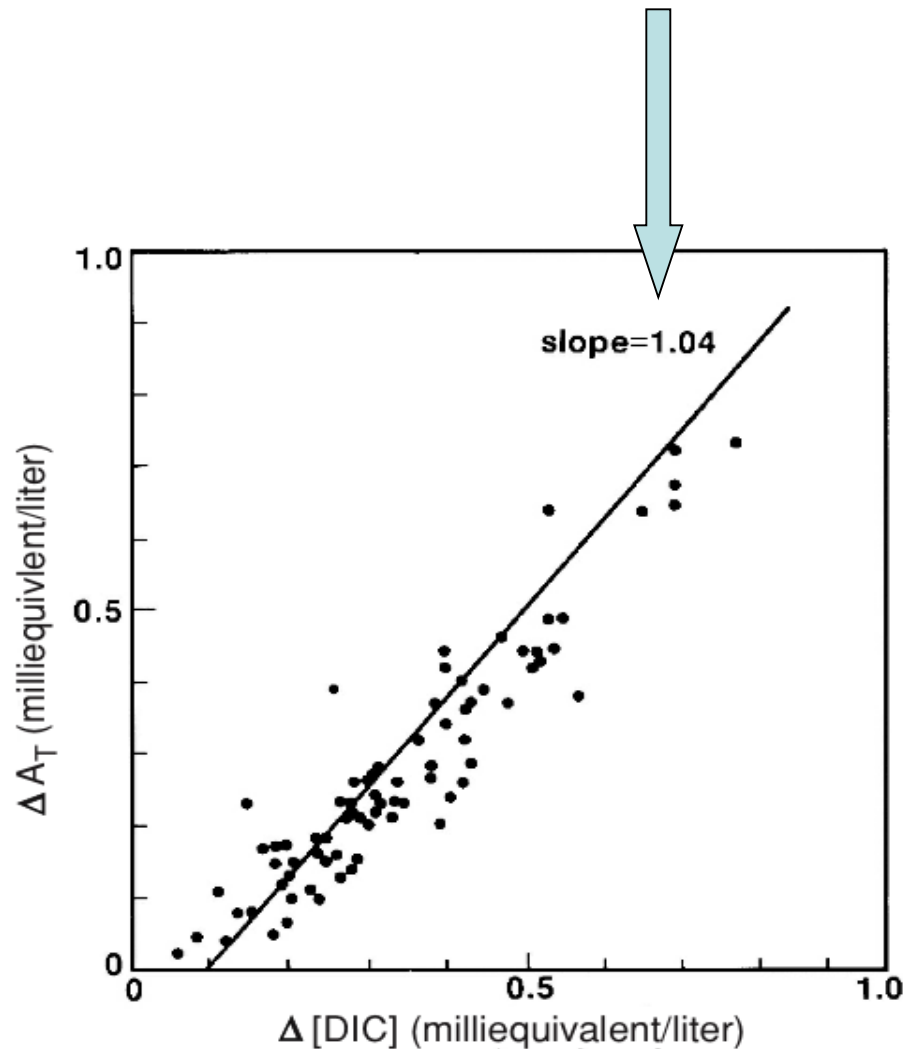
**Epiphyte borings in carbonate substrate illustrating potential for enhancing carbonate dissolution rates. The bioeroded surface appears to increase with higher CO<sub>2</sub> levels.**

**Courtesy of Tribollet, unpublished**

## Oxic environment and respiration

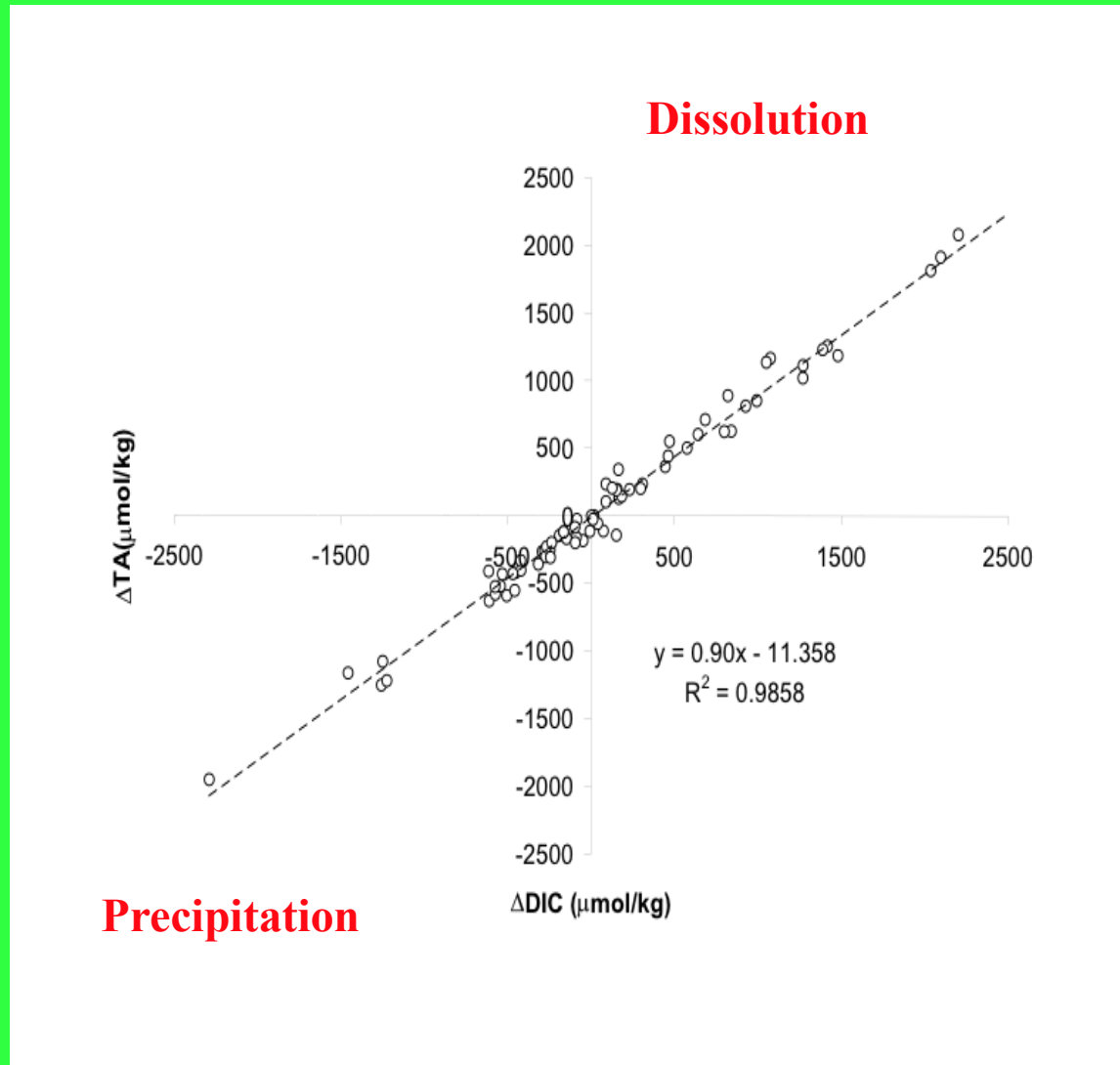
Increase in total alkalinity and DIC over that observed in overlying waters Gulf of Calvi, Corsica, resulting in dissolution in red algal *Lithothamnium* sp.-rich sediments of 75% of the carbonate initially deposited. (Moulin, Jordens and Wollast, 1985)

Similar results were observed in reef frameworks (Sansone, Tribble, Buddemeier and Andrews, 1990; Tribble, 1990).



Protons may come from oxic respiration of organic matter or from activity of “boring” endoliths

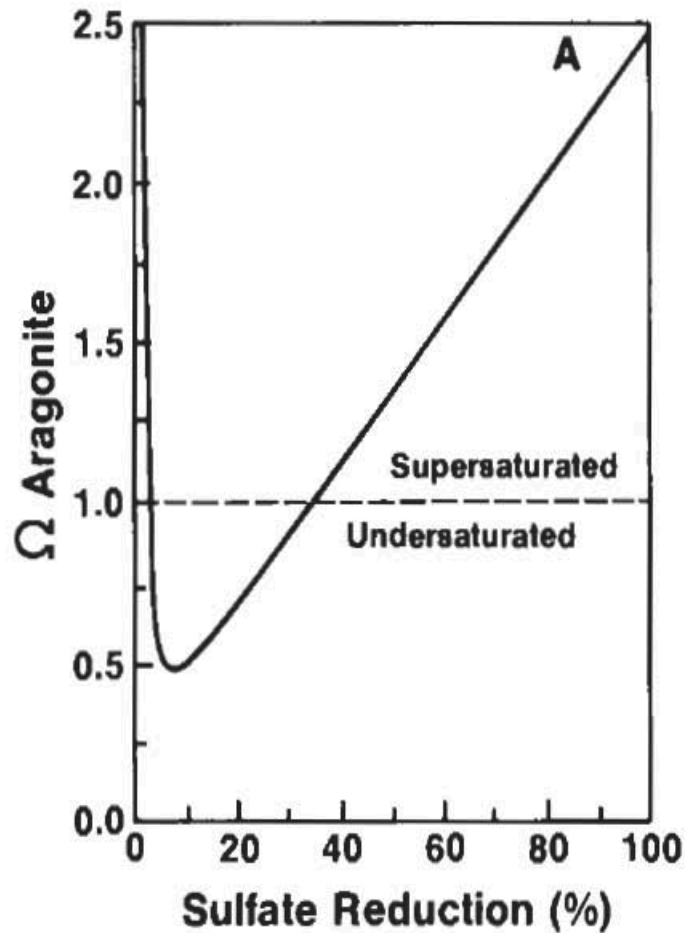
**Another example: diel changes in delta DIC versus delta TA from upper few centimeters of carbonate sediments, Bermuda. In this case one can see both dissolution and precipitation. Notice slope close to one as in Calvi Bay sediments.**



**From Andersson and Mackenzie, unpublished data**

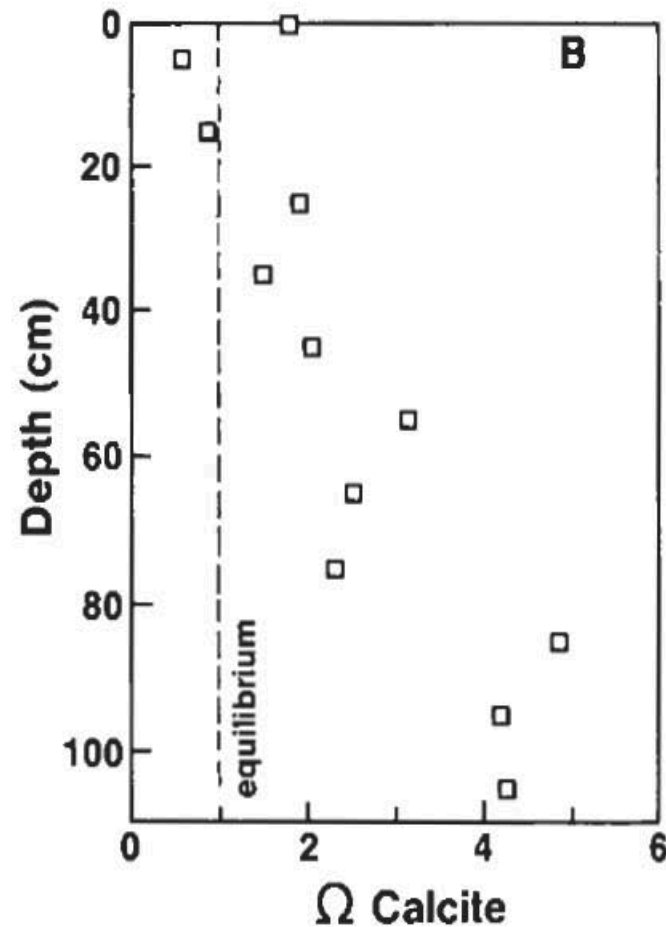
# Anoxic environment and sulfate reduction

## Model results



Ben Yaakov, 1973

## Observations, Mangrove Seawater Lake, Bermuda



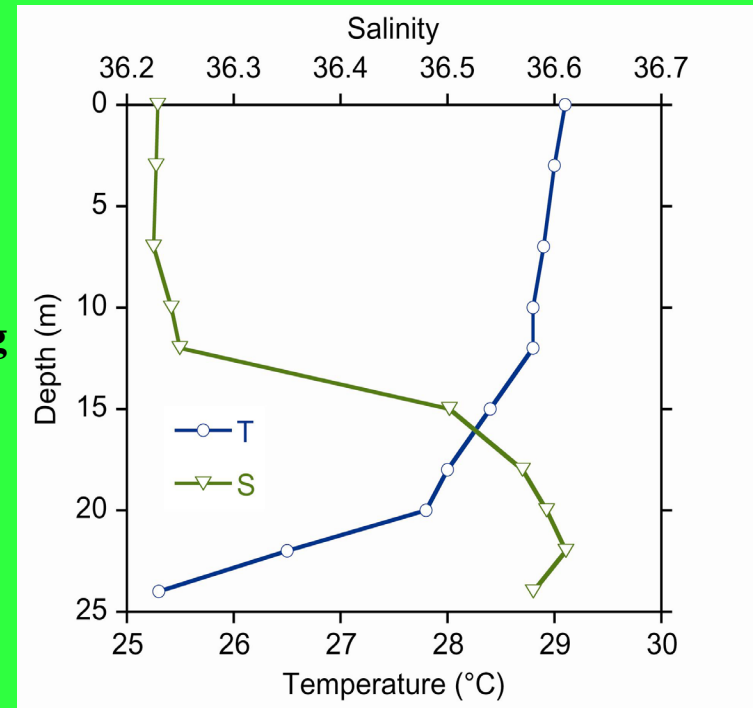
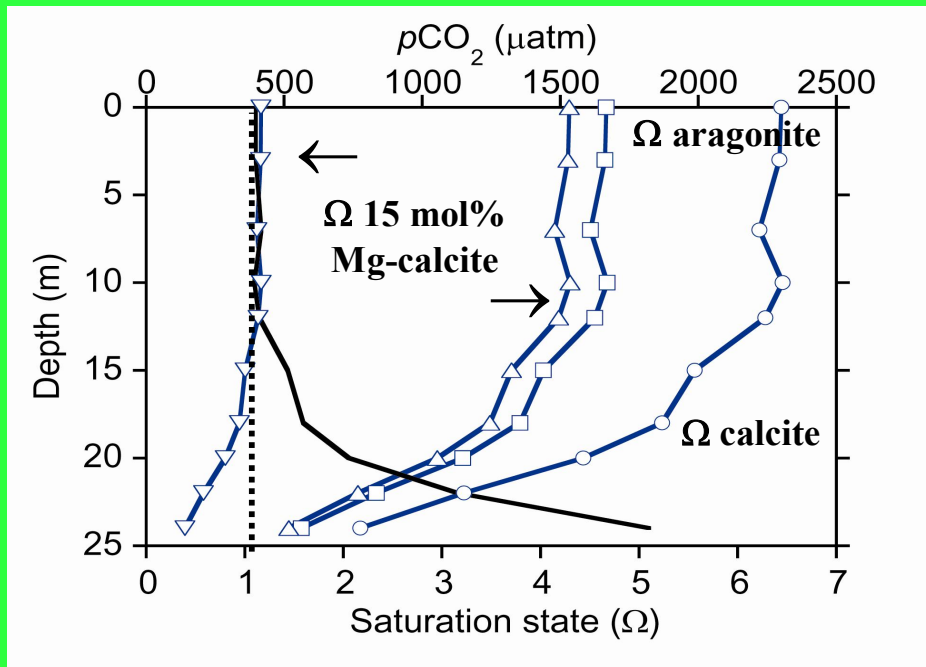
Mackenzie, Vink, Wollast and  
Chou, 1995



# Harrington Sound, Bermuda natural laboratory

(As you increase  $p\text{CO}_2$ , you will dissolve carbonate minerals in nature!)

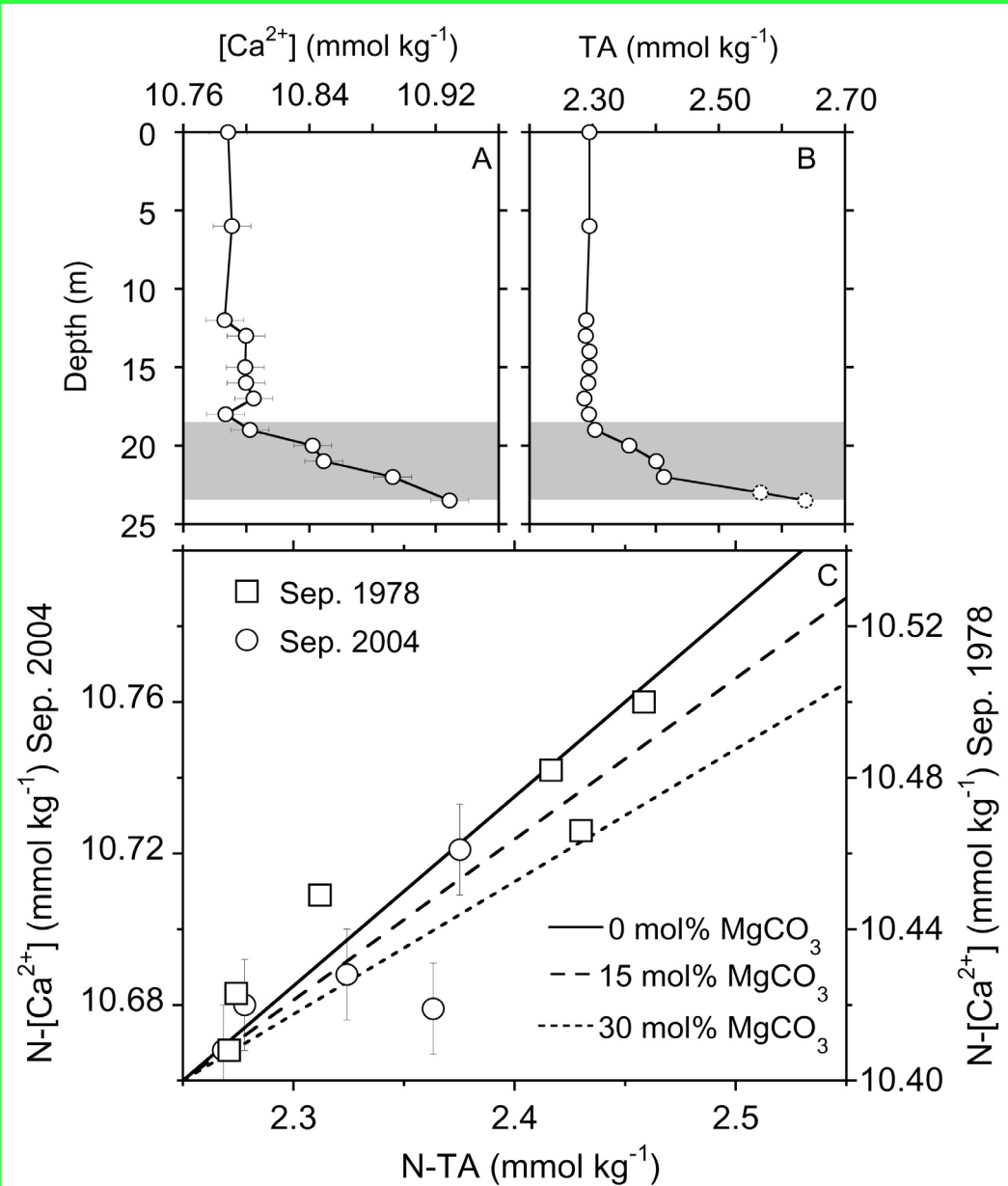
- Development of thermocline during summer
- Remineralization of organic matter drives  $p\text{CO}_2$  up and  $\Omega$  down
- Sediments: ~100% carbonate minerals
- Substantial production of high Mg-calcites in surrounding areas



Responses of Mg-calcites to elevated  $p\text{CO}_2$ : observations from Devil's Hole, Bermuda - "natural laboratory"

Andersson, Bates and Mackenzie, 2007

# Harrington Sound, Bermuda natural laboratory



- **Ca and TA – linear correlation**
- **Slope = 0.42 – average dissolving composition is ~16 mol% Mg-calcite (in agreement with Plummer and Mackenzie solubilities)**
- **Carbonate dissolution is ongoing in Devil's Hole**

# Shoal Water Carbonate Dissolution Rates

(Significant number of rate measurements but how do rates respond to increasing  $p\text{CO}_2$  and T?)

Location	Environment	Dissolution rate $\text{mmol m}^{-2} \text{ h}^{-1}$	Reference
Bahamas	Ooithic sand	0.01	Burdige et al., 2002
Bahamas	Seagrass	0.04	"
Bermuda	Carbonate sediments	0.14-1.6	Andersson et al., 2006
Biosphere 2	Hi Mg-calcite sediments	0.2	Langdon et al., 2002
Florida	Patch reef, 10% coral cover	0.5	Yates and Halley, 2003
Florida	Patch reef, top	0.1	"
Florida	Seagrass	0.4	"
Florida	Sand bottom	0.3	"
Florida	Seagrass, red algae	0.4	Walter and Burton, 1990
Florida	Mangrove, red algae	0.8	"
Great Barrier Reef	Reef flat	4	Barnes and Devereux, 1984
Great Barrier Reef	Back reef zone	3	Kinsey, 1978
Hawaii	Patch reef, 22% coral cover	1.5	Yates and Halley, 2003
Hawaii	Patch reef, 10% coral cover	1.1	"
Hawaii	Coral rubble	1.2	"
Hawaii	Sand bottom	0.3	"
Monaco mesocosm	Sand community	0.8	Leclercq et al., 2002
Moorea	Sandy bottom reef flat and lagoon	0.8	Boucher et al., 1998
Reunion Island	Back reef zone	7	Conand et al., 1997

Range = 0.01-7.0  $\text{mmol m}^{-2} \text{ h}^{-1}$

Average = 1.25  $\text{mmol m}^{-2} \text{ h}^{-1}$

**75% of data: 0.1 to 1.5  $\text{mmol m}^{-2} \text{ h}^{-1}$**

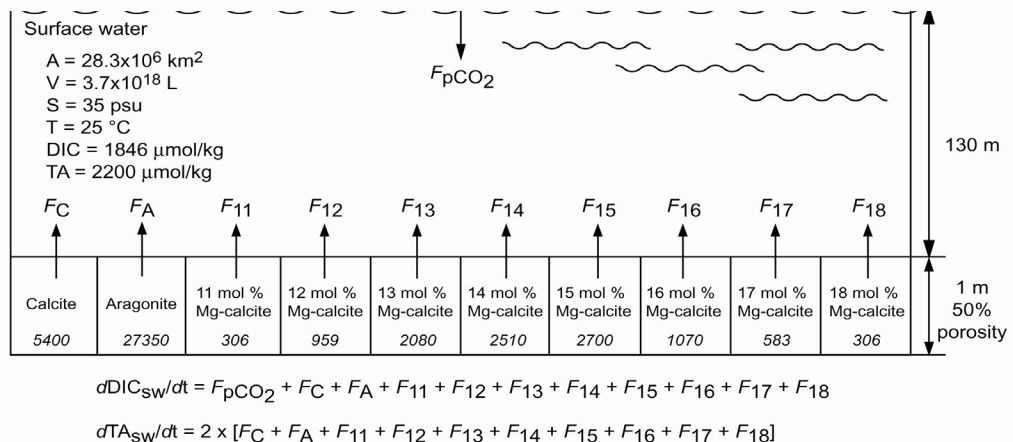
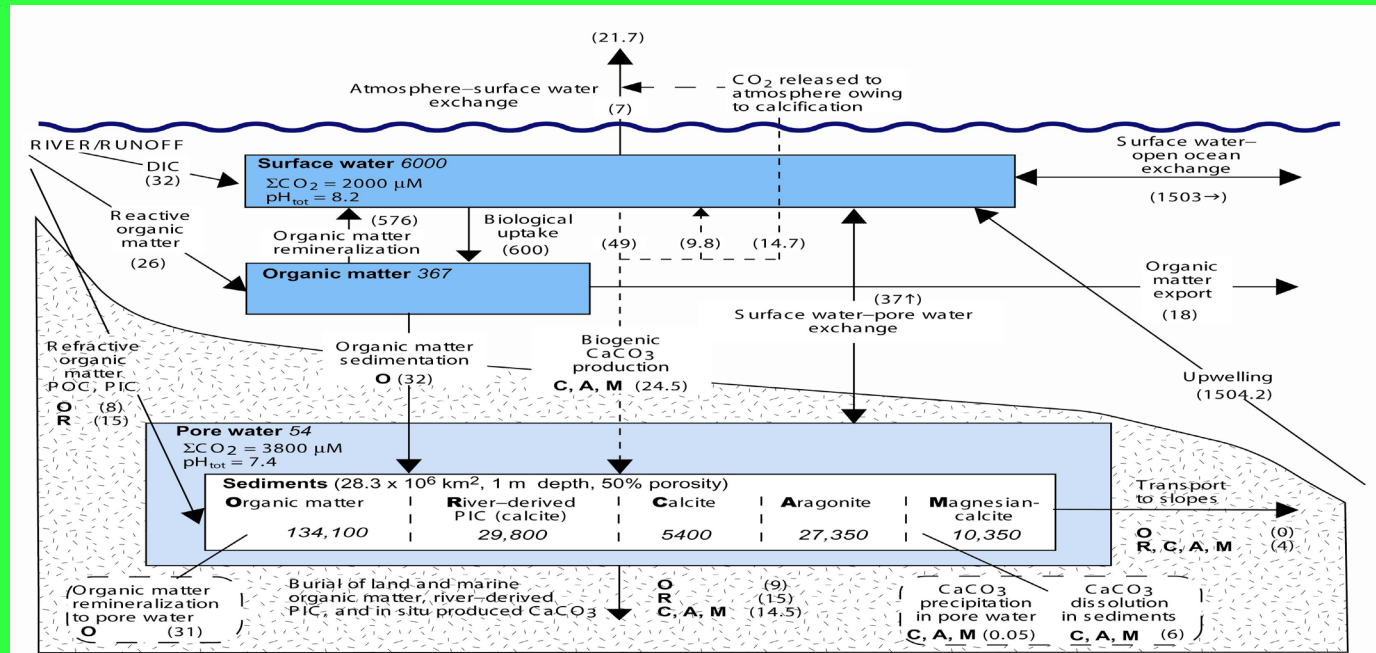
## RECOMMENDATIONS

- Need to quantify the contributions from different processes to total dissolution in shoal-water carbonate sediments, i. e., microbial remineralization of organic matter versus bioerosion owing to euendolithic communities of bioeroding cyanobacteria, algae and fungi communities, particularly because initial experiments show that the activity and dissolution rates of euendoliths are enhanced by higher CO<sub>2</sub> levels (Tribollet, Atkinson, Godinot and Cuet) *and* increasing amounts of “juicy” organic matter are being deposited in coastal environments, including coral reef areas, to be remineralized.
- Need to identify further and quantitatively where the processes of dissolution are taking place, water column, reef framework, sediments, or sediment-water interface and the effects of increased acidity and temperature on these processes. The rates of these processes to changing pCO<sub>2</sub> and T levels require evaluation.

**Final comment: there is a need for regionalized process-driven models linking atmosphere-ocean-sediments and in some cases atmospheric and land inputs of nutrients and acid components (S and N) to the ocean, especially coastal, to predict quantitatively the biological and dissolution effects of rising atmospheric CO<sub>2</sub> and ocean acidification on coral, cool water, and other carbonate ecosystems, including the carbonates found in terrestrial marine sediments.**

## Example: Shallow-water Ocean Carbonate Model (SOCM) (Andersson, Mackenzie and Lerman)

- Includes land and atmospheric inputs
- Rate constants for carbonate dissolution and production
- CO<sub>2</sub>-carbonic acid system chemistry
- Physical mixing
- Reactive mineral reservoirs
- Exchange with open ocean



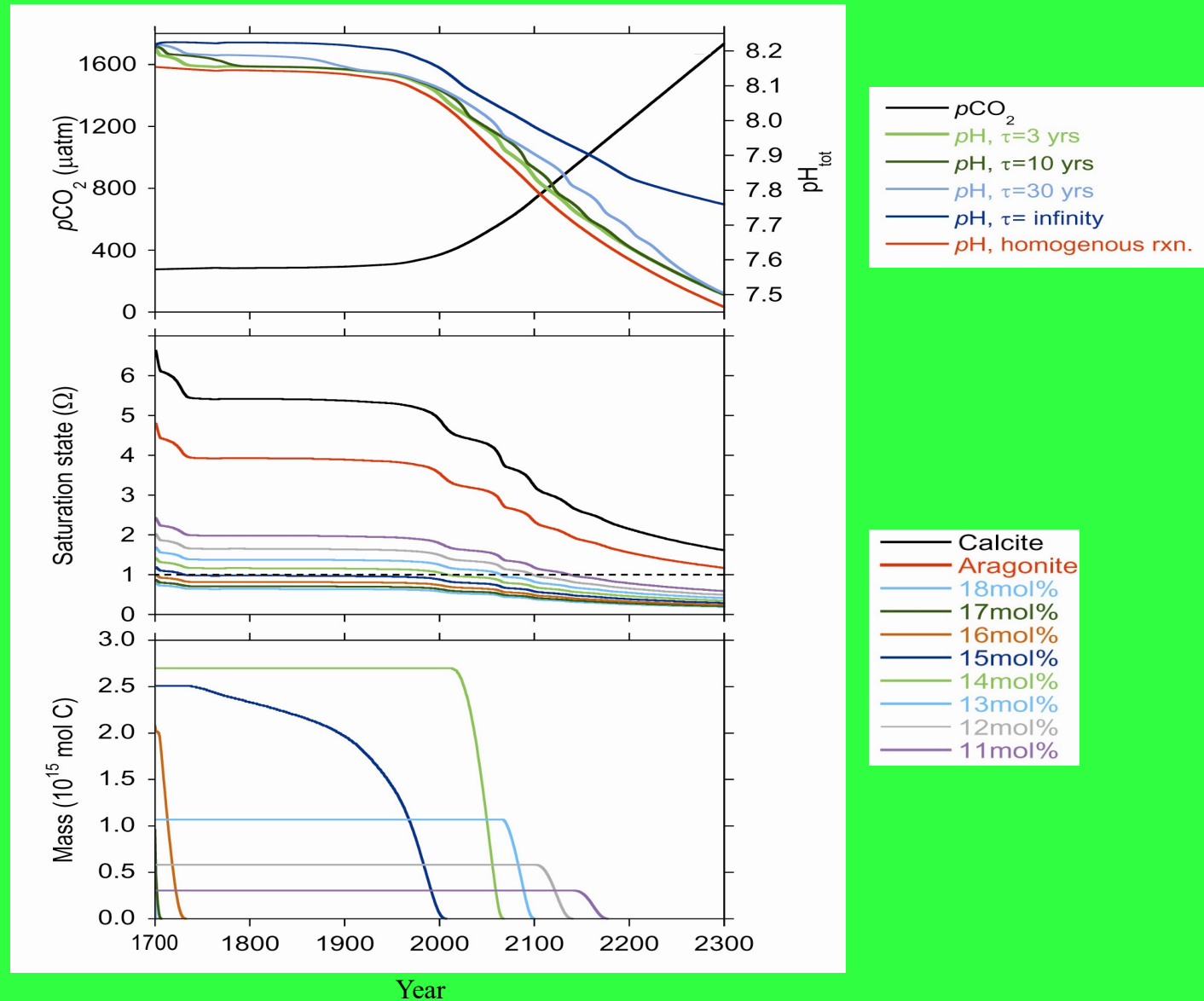


# Example Model results (Morse, Andersson and Mackenzie, 2006)

-open system (mixing,  $\tau = 3$  yrs)

- $p\text{CO}_2$ : 280 - 1,700  $\mu\text{atm}$  (observed  $p\text{CO}_2$ , IPCC IS92a, linear extrapolation)

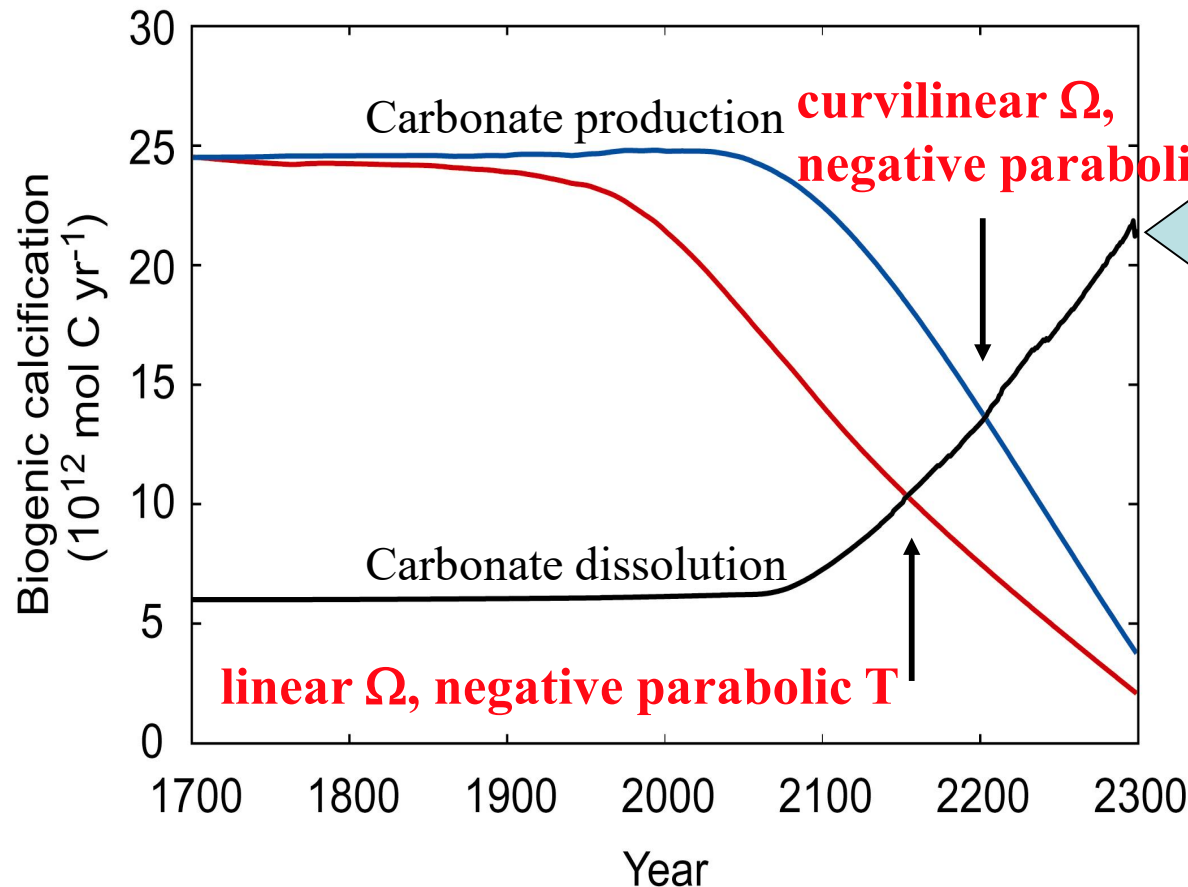
-Plummer & Mackenzie solubilities



# Future consequences of ocean acidification

## Shallow-water Ocean Carbonate Model-SOCM

(Andersson, Mackenzie and Lerman, 2003; 2005; 2006)



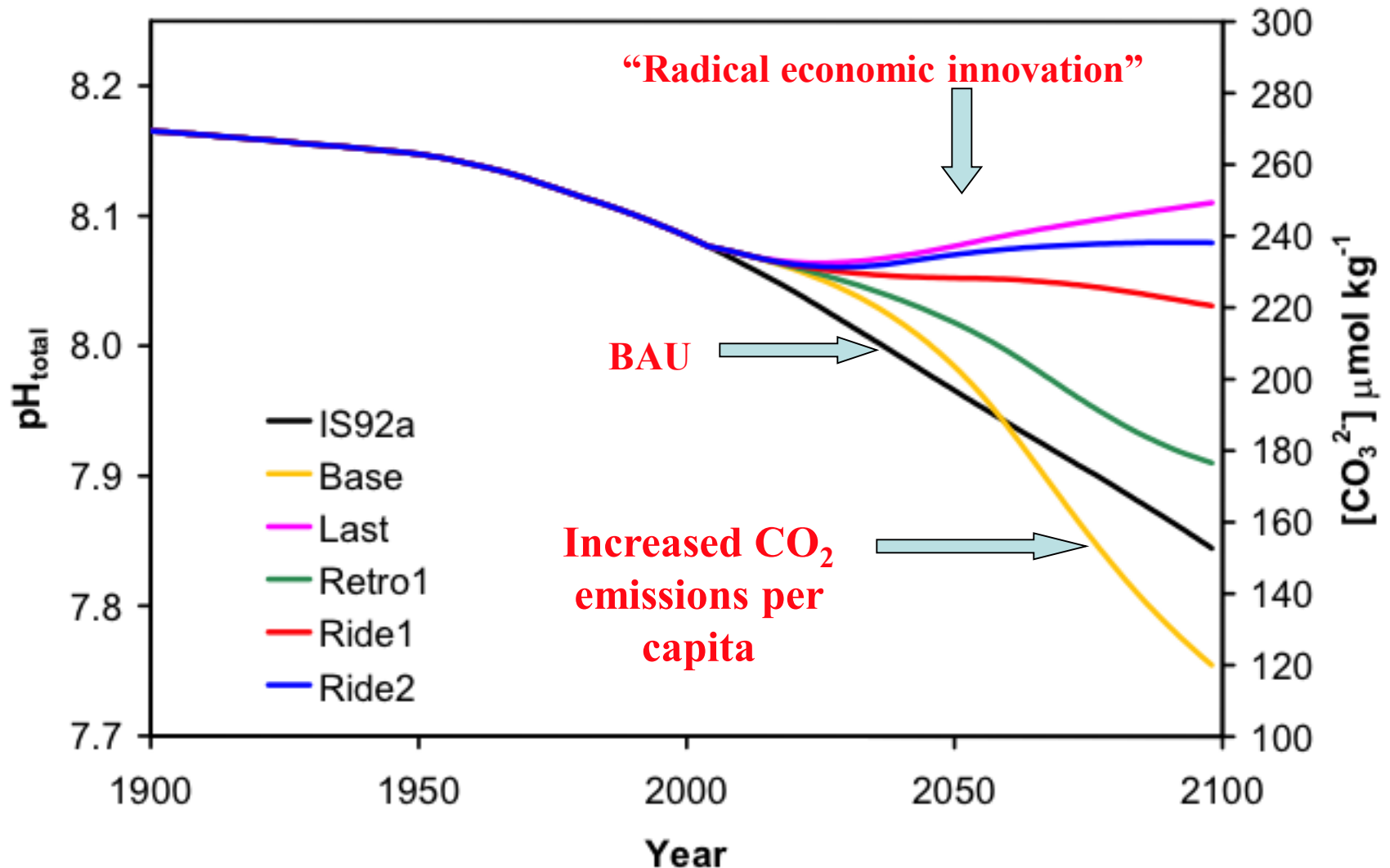
$22 \times 10^{12} \text{ mol C yr}^{-1}$   
(could easily be higher)

$p\text{CO}_2 \sim 1700 \mu\text{atm}$

Assuming BAU  
 $\text{CO}_2$  emission  
scenario

- Biogenic carbonate production could be exceeded by carbonate dissolution by the year 2150 (could easily be earlier).

# pH and $\text{CO}_3^{2-}$ changes due to rising atmospheric $\text{CO}_2$ under more recent social-economic scenarios of $\text{CO}_2$ emissions



Grossman, Mackenzie and Andersson, 2007

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## Carbon in the Geobiosphere – Earth's Outer Shell –

by

Fred T. Mackenzie and Abraham Lerman

Carbon and carbon dioxide always played an important role in the geobiosphere that is part of the Earth's outer shell and surface environment. The book's eleven chapters cover the fundamentals of the biogeochemical behavior of carbon near the Earth's surface, in the atmosphere, minerals, waters, air-sea exchange, and inorganic and biological processes fractionating the carbon isotopes, and its role in the evolution of inorganic and biogenic sediments, ocean water, the coupling to nutrient nitrogen and phosphorus cycles, and the future of the carbon cycle in the Anthropocene.

This book is mainly a reference text for Earth and environmental scientists; it presents an overview of the origins and behavior of the carbon cycle and atmospheric carbon dioxide, and the human effects on them. The book can also be used for a one-semester course at an intermediate to advanced level addressing the behavior of the carbon and related cycles.

*Mackenzie and Lerman's book is the culmination of two splendid careers dedicated to understanding the carbon cycle. It's everything you always wanted to know about carbon biogeochemistry past, present, and future.*

Lee R. Kump, Department of Geosciences,  
Pennsylvania State University, USA

*Majestic in scope; this text builds from fundamentals to front-line research, showing the pivotal role of the carbon cycle in earth system science.*

Rob Raiswell, University of Leeds, UK

*Using skills honed from decades of leadership in the field, Mackenzie and Lerman ably guide us along the pathways of carbon cycling in Earth's outer layers. This is an essential journey for anyone interested in the origin and evolution of life and its fate under human influence.*

Tim Lyons, University of California, Riverside, USA



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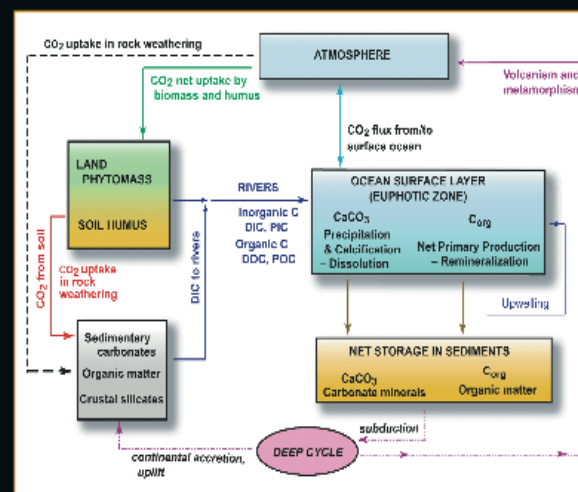
Mackenzie and  
Lerman

Carbon in the Geobiosphere – Earth's Outer Shell –



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