

^{AV}CO₂ and the Oceans: Carbon Balance, Temperature, and Acidification*

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Abstract

On various time scales, atmospheric CO₂ and CH₄, global temperature, marine carbon chemistry, and pH, and sea level change in a nearly synchronous manner, although there are time lags among the variables. In this presentation, we explore, mainly from modeling and observational results, the trends in these variables and the processes controlling them. During the long-term Hot Houses (Greenhouses) of the Phanerozoic, atmospheric CO₂ and CH₄ were relatively high, seawater Mg and Ca concentrations were low and high, respectively, relative to modern seawater; carbonate mineral saturation was elevated despite depressed pH (the calcite-dolomite seas); the planet was warm; and sea level high. The opposite was true for the Ice Houses of the Phanerozoic (the aragonite seas). The fundamental driver of these different states of the Earth system was plate tectonics and accompanying feedbacks in the system. During the Pleistocene Ice Age, relatively high atmospheric CO₂ and CH₄ levels, slightly basic and lower dissolved inorganic carbon oceans, warm temperatures, and high sea levels characterized interglacial stages. The contrary was true for the glacial stages. The different states of the Ice Age were mainly a result of initial changes in Milankovitch forcing abetted by feedbacks, including weathering, in the Earth system. In contrast to these natural changes in the carbon cycle, in the Anthropocene, atmospheric CO₂ and CH₄ levels have risen mainly because of human activities, such as the burning of fossil fuels and land use changes. In the late pre-industrial era, the global ocean was a source of CO₂ to the atmosphere because of net heterotrophy and production of carbonates but, except for the global coastal ocean, it is now a sink. As a result of rising atmospheric greenhouse gas concentrations and the enhanced greenhouse effect, the global mean surface temperature has increased almost 1°C since the 19th century. Much of the warming of the last four decades from this enhanced greenhouse effect has been soaked up by the ocean to be stored for years to decades before release. The ocean has also absorbed about one third of the total anthropogenic CO₂ emissions from human activities. A result of the uptake of anthropogenic CO₂ by the ocean has been its acidification. If current trends continue, future temperature changes and ocean acidification could have severe consequences for marine calcifying organisms and perhaps also other organism communities.

Selected References

Alexandersson, T., 1970, The Sedimentary Xenoliths from Surtsey; Marine Sediments Lithified on the Sea-Floor; A Preliminary Report: Surtsey Research Progress Report, v. 5/5, p. 83-89.

- Andersson, A.J., F.T. Mackenzie, and A. Lerman, 2006, Riverine nitrogen export from the continents to the coasts: *Global Biogeochemical Cycles*, v. 20/1, p. GB1S92. <http://dx.doi.org/10.1029/2005GB002506>
- Andersson, A.J., F.T. Mackenzie, and A. Lerman, 2005, Coastal ocean and carbonate systems in the high CO₂ world of the Anthropocene: *American Journal of Science*, v. 305/9, p. 875-918.
- Andersson, A.J., F.T. Mackenzie, and L.M. Ver, 2003, Solution of shallow-water carbonates: An insignificant buffer against rising atmospheric CO₂: *Geology: Geological Society of America*, v. 31/6, p. 513-516. DOI: 10.1130/0091-7613.
- Canadell, J.G., D.E. Pataki, R. Gifford, R.A. Houghton, Y. Luo, M.R. Raupach, P. Smith, W. Steffen, 2007, Saturation of the terrestrial carbon sink: *Global Change The IGBP Series*, v. 24; p. 59-78.
- Gattuso J P; M. Frankignoulle, I. Bourge, S. Romaine, R.W. Buddemeier, 1998, Effect of calcium carbonate saturation of seawater on coral calcification: *Global and Planetary Change*, v. 18/1-2, p. 37-46.
- MacKenzie, F.T. and A. Lerman, 2006, Carbon in the geobiosphere; Earth's outer shell: *Topics in Geobiology*, v. 25.
- MacKenzie, F.T., L.M. Ver, and A. Lerman, 2002, Century-scale nitrogen and phosphorus controls of the carbon cycle: *Chemical Geology*, v. 190/1-4, p. 13-32.
- Mackenzie, F.T.; C.R. Agegian Catherine, 1989, Biomineralization and tentative links to plate tectonics, p.11-27.
- Riebesell, U., A.T. Revill, D.G. Holdsworth, J.K. Volkman, 2000, The effects of varying CO₂ concentration on lipid composition and carbon isotope fractionation in *Emiliana huxleyi*: *Geochimica et Cosmochimica Acta*, v. 64/24, p. 4179-4192.
- Riebesell, U, I. Zondervan, B. Rost, P.D. Tortell, R.E. Zeebe, F.M.M. Morel, 2000, Reduced calcification of marine plankton in response to increased atmospheric CO₂ : *Nature London*, v. 407/6802, p. 364-367.
- Sabine, C.L., R.A. Feely, N. Gruber, R.M. Key, K. Lee, J.L. Bullister, R. Wanninkhof, C.S. Wong, D.W.R. Wallace, B. Tilbrook, F.J. Millero, T.H. Peng, A. Kozyr, T. Ono, and A.F. Rios, 2004, The oceanic sink for anthropogenic CO₂: *Science*, v. 305/5682, p. 367-371. DOI: 10.1126/science.1097403.
- Smith, T.M. and R.W. Reynolds, 2005, A Global Merged Land–Air–Sea Surface Temperature Reconstruction Based on Historical Observations (1880–1997): *Journal of Climate*, v. 18/12, p. 2021-2036. DOI: 10.1175/JCLI3362.1.

ALOHA EVERYONE

CO₂ AND THE OCEANS: CARBON BALANCE, TEMPERATURE, AND ACIDIFICATION

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OUTLINE OF PRESENTATION

**Because of time constraints, this presentation considers
only two major themes derived from our abstract:**

I. The Anthropogenic CO₂ Balance during the Anthropocene

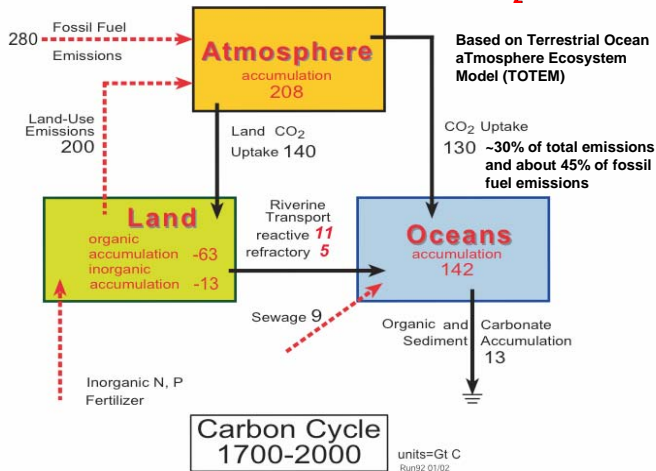
II. Acidification and Warming of Ocean Surface Waters

A. Record of Changes

**B. Some Consequences for Carbonate Ecosystems
(e.g., reefs)**

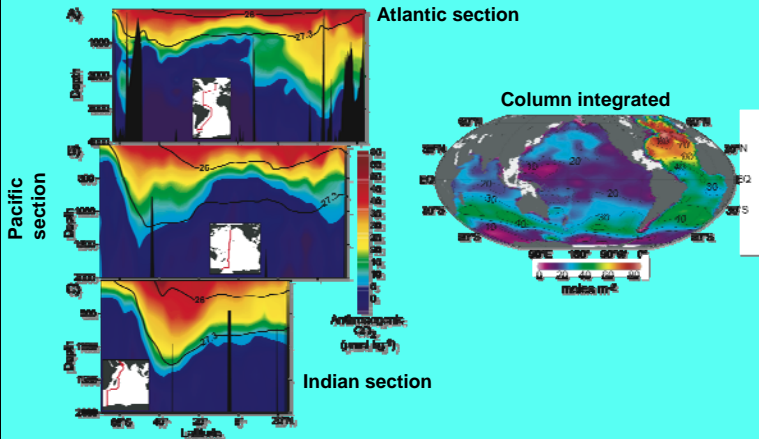
III. Final Statements

WHERE HAS ALL THE ANTHROPOGENIC CO₂ GONE?



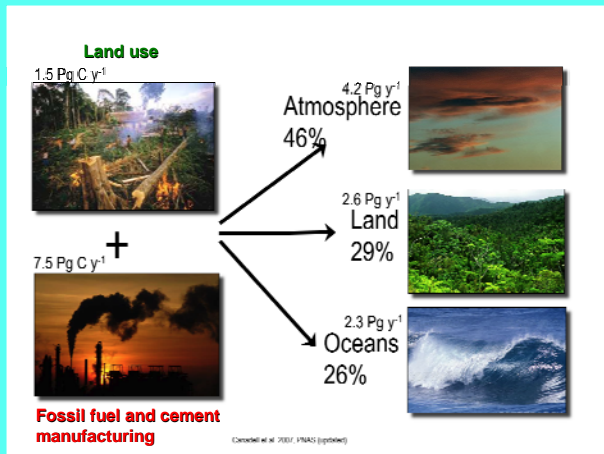
Agrees with observational inorganic carbon measurements of Sabine et al. (2004) for the period 1800 to 1994 for ocean uptake of anthropogenic CO₂ of 118 +/- 19 Gt C (Mackenzie, Ver and Lerman, 2002)

ANTHROPOGENIC 1800 to 1994 CO_2 PENETRATION INTO THE OCEAN BASED ON OBSERVATIONS

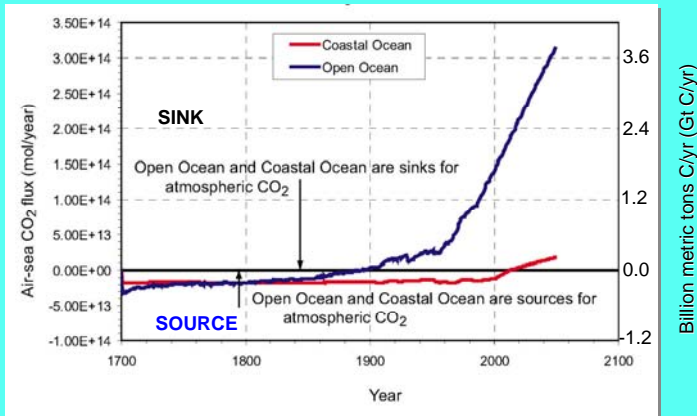


After Sabine et al., 2004

**MORE RECENTLY, WHERE HAS ALL THE ANTHROPOGENIC CO₂ GONE?
(average balance between 2000 and 2007)**



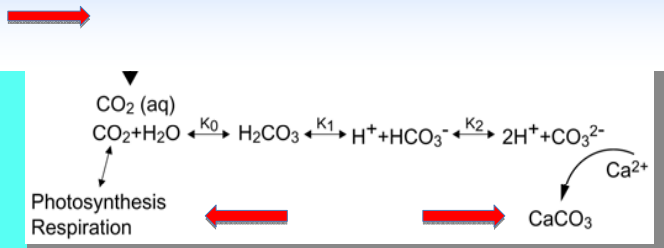
HISTORICAL AND FUTURE AIR-SEA EXCHANGE OF CO₂ FOR THE GLOBAL COASTAL AND OPEN OCEAN



Of all the fossil fuel, cement manufacturing, and land use CO₂ released since 1700, about 30% has gone into the ocean (Mackenzie et al., 2002), leading to its acidification.

Mackenzie and Lerman, unpublished

WHAT HAPPENS TO THE CO₂ THAT IS ADDED TO THE OCEAN?



• Net reaction of increasing CO₂: $\text{CO}_2 + \text{H}_2\text{O} + \text{CO}_3^{2-} \rightleftharpoons 2\text{HCO}_3^-$

⇒ ↓ pH – “ocean acidification”

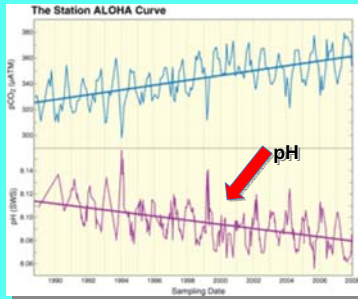
⇒ ↓ [CO₃²⁻]

⇒ ↓ carbonate saturation state (Ω)

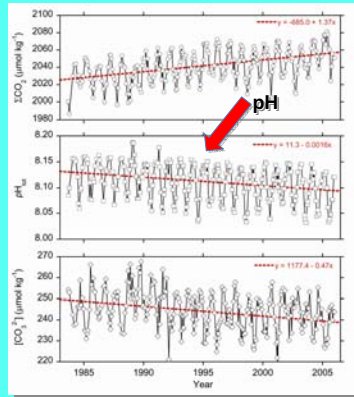
$$\Omega = \frac{\{\text{Ca}^{2+}\} \{\text{CO}_3^{2-}\}}{K_{\text{SP}}}$$

Presenter's Notes: As the atmospheric concentration of CO₂ increases, the flux of this gas into the surface ocean will also increase following Henry's law. Dissolved CO₂ reacts with water and form carbonic acid which dissociates into hydrogen ions, bicarbonate ions and carbonate ions, consequently lowering the pH of seawater, a process termed “ocean acidification”. However, the net reaction of this process, demonstrates how CO₂ combines with water and CO₃ ions to form bicarbonate, essentially titrating CO₃ ions out of solution. As a result, the CO₃ will decrease and consequently the saturation state, omega, with respect to carbonate minerals which is determined by the ion activity product of calcium and carbonate ions divided by the solubility product. As you will see later this may have implications for marine calcifying organisms which produce their shells and skeletons out of calcium carbonate.

CO₂ and pH of surface waters at hydrostation ALOHA north of the main Hawaiian Islands 1988-2008 and at hydrostation BATS east of Bermuda 1983-2008



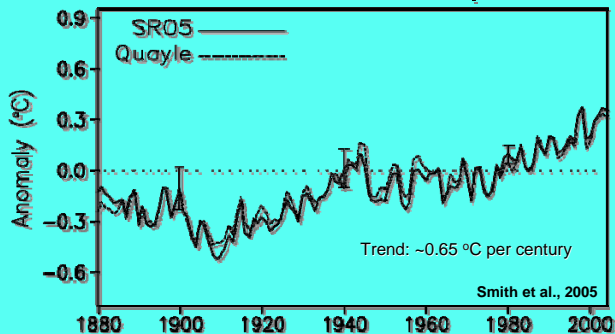
http://hahana.soest.hawaii.edu/hot/hot_jgofs.html



<http://bats.bios.edu>

ESTIMATED GLOBAL SEA SURFACE TEMPERATURE (SST) FROM 1880 to 2004

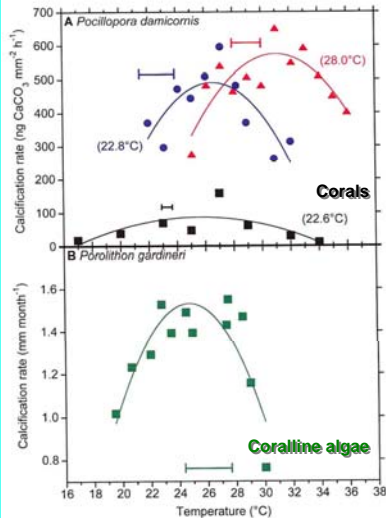
(baseline 1961-1990; satellite and *in situ* data)



Based on Thousands of CTD Profiles:

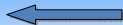
20-Year SST trend for HOTs is +0.4 °C per decade at 150 meters

22-Year SST trend for BATs is +0.25 °C per decade in mixed layer



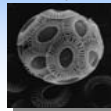
**IMPORTANT CORAL REEF
BUILDING, CEMENTING,
AND INFILLING CaCO₃
SKELETAL ORGANISMS
LIVE NEAR THEIR LETHAL
TEMPERATURE
THRESHOLD IN TERMS OF
MORBIDITY OR MORTALITY**

Decreasing pH and CaCO_3 Saturation State Lead to Decreasing Calcification and Production Rates of Various Calcifying Organisms



Decreasing pH, saturation state

Coccolithophoridae



<http://www.marinebiology.edu/>

Corals

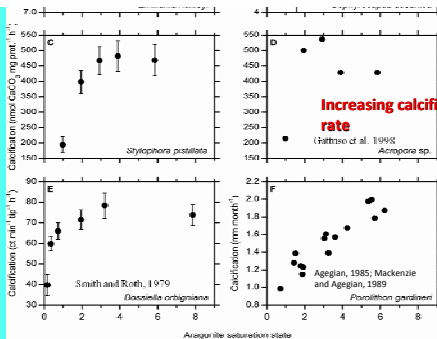


<http://www.coralreefecosystems.com/>

Coralline algae



<http://www.coralreefnetwork.com/>



Smith and Rolf, 1979; Mackenzie and Agegian, 1989; Gattuso et al., 1998; Riebesell et al., 2000

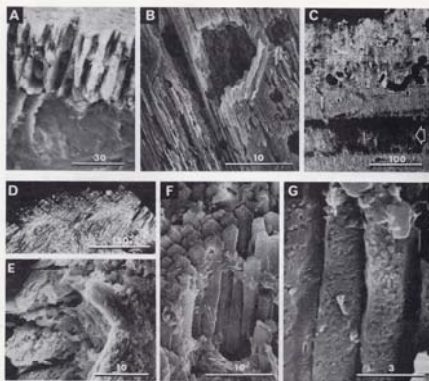


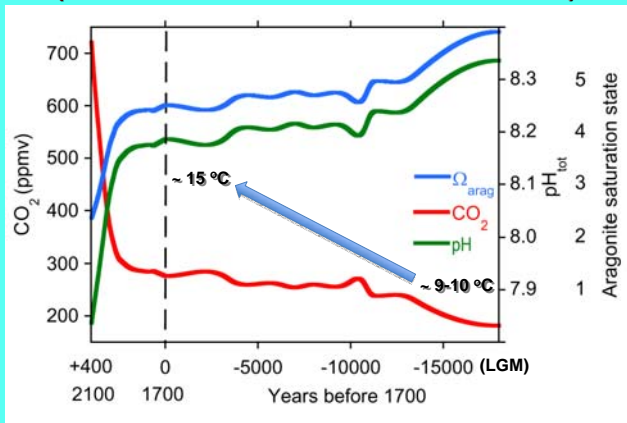
Figure 3.-- Shallow-marine dissolution of skeletal carbonate fragments. Scale bars in μm . (A) SEM, fractured galeaspid shell, Nova Hallar, Kattegat. External surface up. Two shell layers with different internal organization show different response to the leaching process. Both layers are cross-lamellar, and both are probably aragonite. (B) SEM, fractured mollusk shell, Nova 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 polars. External surface is up. The fragment is heavily bored but there is no secondary accretion to 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, Nova Hallar, Kattegat. Natural external surface of leached cross-lamellar aragonite fabric. (F) SEM, mollusk 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 stub pattern of calcite fibers; a pattern which is related to the arrangement of small granules in the fibers.

THE OTHER SIDE OF THE COIN: DISSOLUTION

Boring of microalgae and
fungi and solution of
calcium carbonate shells
under low pH conditions
in the Kattegat, Skagerrak
and Baltic seas

Alexandersson, 1970s

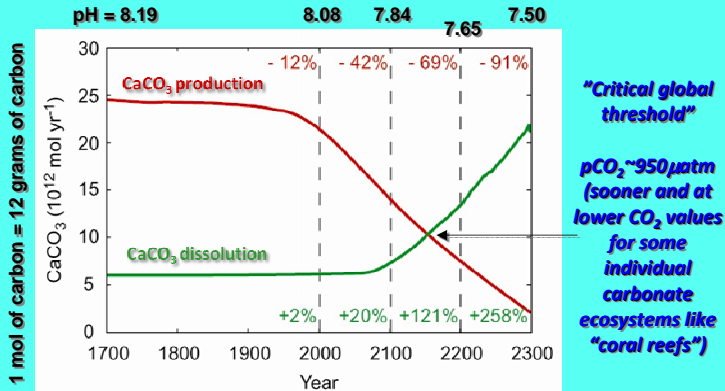
THE OCEAN: FROM MORE BASIC TO MORE ACIDIC (LAST GLACIAL MAXIMUM TO YEAR 2100)



Last Glacial Maximum to Year 2100 Atmospheric CO₂, Ocean Sea Surface pH, Saturation State, and Temperature under a Future Business as Usual CO₂ Emission Scenario

Lerman, Mackenzie and Andersson, in prep.; in Mackenzie and Lerman, 2006

DECREASING pH AND CaCO_3 SATURATION STATE AND INCREASING TEMPERATURE LEAD TO DISSOLUTION OF REEF AND OTHER CaCO_3 ECOSYSTEMS EXCEEDING PRODUCTION



Andersson, Mackenzie and Lerman., 2003, 2005, 2006

FINAL STATEMENTS AND CONCLUSIONS

- We have had acidic oceans in the past and without doubt rising atmospheric CO₂ levels due to fossil fuel burning and land use emissions of CO₂ to the atmosphere have led to, and will continue to lead to, lowering of the pH and carbonate saturation state of surface ocean waters as the ocean continuously absorbs the anthropogenic CO₂ emissions.
- Early this century the pH of surface seawater will begin to fall more quickly (acidity increases more rapidly). Cold and high latitude seawaters will go undersaturated first with respect to the CaCO₃ minerals that make up the skeletons of organisms bathed by these waters. Rises in SST and other stresses on reef systems only compound the problem of acidification (e.g., coral bleaching on reefs from increasing temperatures).
- There are considerable uncertainties in the ability of individual organism taxa to acclimate, adapt, or evolve and in ecosystem responses (including those of benthic and pelagic fisheries, marine food webs, microbial communities, biodiversity, etc.) to rising atmospheric CO₂ and temperature but the physics and chemistry involved with the uptake of CO₂ in the ocean and its acidification are well established.
- The only prevention of future changes in ocean pH is to reduce globally land use and fossil fuel CO₂ emissions to the atmosphere or to capture CO₂ from the air.

Degraded Reef



Healthy Reef



MAHALO FOR COMING AND FOR YOUR ATTENTION!