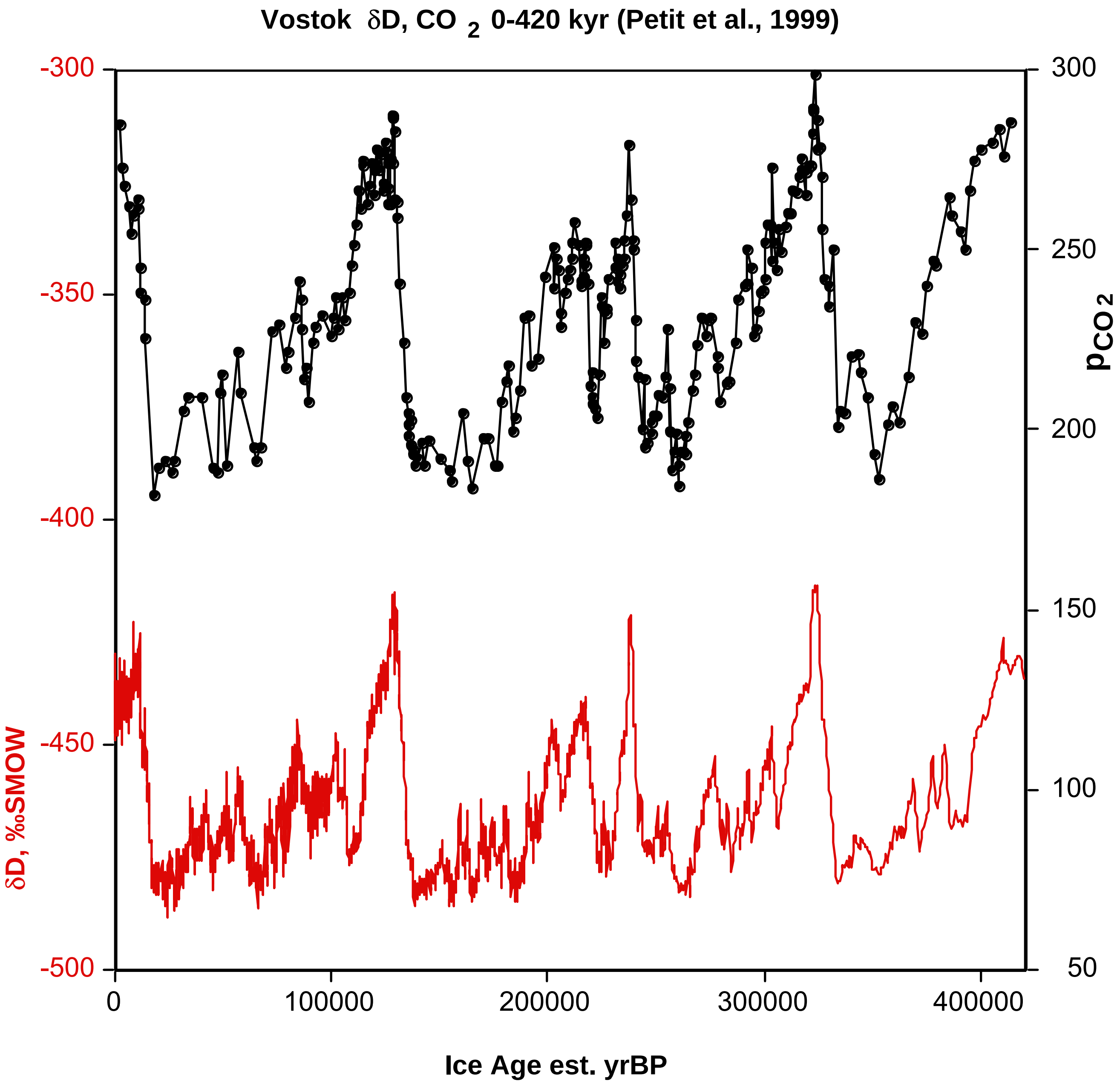
12.740 Paleoceanography
Spring 2008

ATMOSPHERIC CO_2, OCEAN CHEMISTRY, AND MECHANISMS OF CLIMATE CHANGE

I. Recall: Ice core evidence for changes in atmospheric CO_2

A. Pre-anthropogenic p_{CO2} was about 280 ppmV

B. Glacial p_{CO2} was about 190 ppmV. Five Antarctic ice cores give same number. Greenland cores agree tolerably well, but their high dust loading and reaction with CO_2 leads to some problems.



Data from Petit et al. (1999)

C. In the early 1980's, it seemed that the Dye 3 Greenland ice core showed relatively large, rapid (few hundred year) fluctuations in CO_2 during glacial stadial/interstadial fluctuations. These were not observed in the high resolution Byrd Antarctic ice core, and it is now thought that these apparent high CO_2 events were artifacts due to melt layers or interactions with dust.

D. So why did atmospheric CO_2 change with the glacial/interglacial cycles? Is the CO_2 change a chicken or an egg in the progression of climate change?

1. Many ideas have been proposed; almost an equal number have been disposed (or is it deposed?). Speaking informally, it is as if theories on glacial/interglacial carbon dioxide are radioactive with two year half-lives.
2. Despite this situation, there is much to be learned about CO2 in the ocean from those ideas, so a historical examination of them is still worthwhile.

II. CO_2 digression

A. Two useful <u>conservative</u> quantities (properties that mix linearly) are:

1. $\mathbf{\Sigma CO_2 = [CO_2(aq)] + [HCO_3^-] + [CO_3^=]}$
2. **Alkalinity** $\mathbf{= [HCO_3^-] + 2[CO_3^=]}$

$$\mathbf{+ [B(OH)_4^-] + [OH^-] - [H^+] + (etc...)}$$

a. "Alkalinity" is a device for employing a special form of the charge balance equation which divides ions into those that have acid-base reactions and those that don't:

e.g., in a system consisting of a solution of NaCl, $MgSO_4$, $NaCO_3$, and $NaHCO_3$:

$$[Na^+] + 2[Mg^{++}] - 2[SO_4^=] = [HCO_3^-] + 2[CO_3^=] + [OH^-] - [H^+] = \text{Alkalinity}$$

b. Adding or removing CO_2 from a water sample does not change the alkalinity (convince yourself of this!)

C. A common simplification is that of Broecker:

$$[CO_3^=] = Alk - \Sigma CO_2$$

This approximation is conceptually simple but not accurate because of the neglect of significant contributions from borate and aqueous CO_2 . For example, for values of Alk and ΣCO_2 typical of pre-anthropogenic warm surface waters (Alk=2275, ΣCO_2=1900; pH=8.3; pCO_2=283) and cold deep waters (Alk=2375, ΣCO_2=2260; pH=7.9):

units: (µmol/kg)

	$[CO_2(aq)]$	$[HCO_3^-]$	$[CO_3^=]$	$Alk-\Sigma CO_2$	$[B(OH)_3]$	$[B(OH)_4^-]$
ws	8	1628	264	375	288	119
cd	27	2150	85	115	349	58

In deep waters one can estimate $\Delta CO_3^= \approx 0.6\ [Alk-CO_2]$ (i.e., about 40% of increased alkalinity converts $B(OH)_3$ to $B(OH)_4^-$)

D. Relevant equilibria ("apparent" thermodynamic constants). Because seawater is a "high ionic strength" solution (i.e., it is very salty), conventional thermodynamic constants (activity coefficients, etc.) are difficult to define because of strong ionic interactions. But because the composition of seawater (for major ions) is constant save for variations in total salt content, we can adopt "apparent constants" which incorporate the activity coefficients and ion interactions into the "apparent" constant (denoted by '):

i. $CO_2\ (gas) = CO_2\ (aq)$

$$\alpha_s' = \frac{CO_2\ (aq)}{P_{CO_2}} \approx 10^{-1.5}$$

ii. $CO_2(aq) + H_2O = H^+ + HCO_3^-$

$$K_1' = \frac{[H^+]\,[HCO_3^-]}{[CO_2(aq)]} \approx 10^{-6.0}$$

iii. $HCO_3^- = H^+ + CO_3^=$

$$K_2' = \frac{[H^+]\,[CO_3^=]}{[HCO_3^-]} \approx 10^{-9.1}$$

iv. $B(OH)_3 + H_2O = B(OH)_4^- + H^+$

$$K_B' = \frac{[H^+]\ [B(OH)_4^-]}{[B(OH)_3]} \approx 10^{-8.7}$$

These apparent constants are functions of temperature, salinity, and pressure.

E. Once the system of equations relevant to a problem have been set up (and these may include mass balance, alkalinity, or other constraints), they are solved generally by computer, where the underlying method involves substituting terms to create a single polynomial equation with [H+] as the only variable. This equation is then solved with Newton-Rapson or similar method. For the range of values appropriate for seawater, simplifications can be made that reduce this system of equations to a cubic polynomial with an exact solution.D. By expressing all species in terms of $[H^+]$, then combining into a single equation in [H+]), it can be shown that

$$pH = f(\frac{Alk}{\Sigma CO_2},(T,S,P))$$

Assuming deviations within the range of values likely to be found in the ocean, the relationship can be expressed as a simple cubic equation which has an exact solution. Since the relative amount of the various CO_2 species is a function of the pH, we can compute the absolute amount of each species as f(pH)*ΣCO_2; or directly as f(Alk, ΣCO_2). The best formulation for CO_2 system calculations *under natural conditions* is to solve the cubic equation for the hydrogen ion where Alk, ΣCO_2, and borate are taken into account:

1. Let **A = Alk/ΣCO_2** and **B = $\Sigma B/\Sigma CO_2$**, let **$[H^+]$** = the activity of hydrogen ion, and let K_1', K_2', and K_B' be the apparent constants in seawater at the appropriate temperature, pressure, and salinity; then:
2. $$\begin{aligned} \mathbf{0} = {} & [H^+]^3 A \\ & + [H^+]^2 [K_1'(A-1) + K_B'(A-B)] \\ & + [H^+] [K_1'K_B'(A-B-1) + K_1'K_2'(A-2)] \\ & + [K_1'K_2'K_B'(A-B-2)] \end{aligned}$$

E. A quick approximate solution to the carbonate system can be obtained by combining the equations for K_2' and K_B':

$$[B(OH)_4^-] / [CO_3^=] = (K_B'/K_2') ([B(OH)_3]/[HCO_3^-]$$

and noting that the ratio $[B(OH_3)/[HCO_3]^- \bullet \frac{1}{6}$ does not vary much throughout the ocean, (and $(K_B'/K_2') \bullet 3$), so:

$$[B(OH)_4^-] \bullet [CO_3^=] / 2$$

and hence (noting that CO_2(aq) is small and so are its variations (17±10):

$CO_3^= \bullet (Alk - \Sigma CO_2 + 17) / 1.5$ (17 is the approximate aqueous CO_2)

$HCO_3^- \bullet \Sigma CO_2 - CO_3^= - 17$ “ “ “

$[H+] \bullet K_2' [HCO_3^-] / [CO_3^=]$

$[CO_2(aq)] \bullet [H+] [HCO_3^-] / K_1'$

$p_{CO2} \bullet [CO_2(aq)] / \alpha_s'$

F. Carbon Isotope Fractionation: equilibrium carbon isotope fractionation between CO_2 system species is a function of temperature. Kinetic lags are important.

$\delta^{13}C$ and gas exchange

A. Temperature-dependent equilibrium: fixing the carbon isotope composition of the atmosphere and allowing seawater to equilibrate:

	25°C	0°C
gaseous CO_2	-6.4	-6.4
aqueous CO_2	-7.6	-7.7
HCO_3^-	+1.5	+4.4
$CO_3^=$	-0.5	+0.8
($CaCO_3$)	+3.0	+0.0
ΣCO_2	+1.3	+4.1

These isotope fractionation factors can be incorporated into the apparent equilibrium constants and then you can treat $^{13}CO_2$ as a completely independent chemical system (apart from the pH control which is set by $^{12}CO_2$).

I. CO_2 gas exchange

CO_2 exchange between the ocean and atmosphere

Stagnant film model:

D (~$10^{-5} cm^2/sec$; depends on gas)
z_{film} (~30 µm; depends on wind conditions).

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                                          gas partial pressure -->
        well-mixed air                   equilibrium with air
     ~~~~~~~~~~~~~~~~~~~~~~                   |
                                         _____|_______________________
     stagnant film of water             |      \
                                        |       \
                                        |        \
     ~.~.~.~.~.~.~.~.~.~.~.             |........\...............
                                      z |        |
                                        |        |
    well-mixed surface ocean            |        |surface
                                        |        |ocean
                                        |        |conc'n
                                        |        |
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$$\text{Flux} = D \frac{C_m - C_o}{z_{film}}$$

where C_m = concentration of dissolved gas in (interior) mixed layer of ocean
C_o = concentration of dissolved gas at surface of ocean (equilibrium with atm)
z_{film} = thickness of stagnant film
D = diffusion coefficient of dissolved gas

1. Piston Velocity concept. If we look at the dimensions of the above equation, it has dimensions of distance per time. One can think of this process *as if* imaginary pistons were moving through the water column and simultaneously pushing gas in and out of the ocean. This "piston" has a velocity magnitude of about 2000 m/yr!

2. For gases like oxygen and nitrogen, which equilibrate entirely between the gas phase and the dissolved aqueous form, gas exchange is very effective and surface waters are almost at equilibrium. For carbon dioxide however, where the dissolved aqueous gas equilibrates with the bicarbonate and carbonate ions which occur at much higher concentrations, gas exchange takes much longer and surface waters are usually out of equilibrium with the atmosphere - sometimes by up to a factor of two.

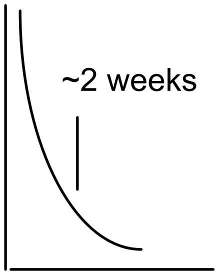
3. Rate of exchange of CO_2 between ocean and atmosphere. Speaking in round terms, we can calculate the average rate at which CO_2 moves across the sea surface:

$$\underbrace{2000\ \text{m/yr}}_{\text{piston vel.}} * \underbrace{10^{-5}\ \text{moles/kg}}_{\text{aq. } CO_2 \text{ conc.}} * \underbrace{1000\ \text{kg/m}^3}_{\text{conversion factor}} = 20\ \text{moles/m}^2\text{/yr}$$

Given that the upper 75 m of the water column (mixed layer) underneath a square meter contains 150 moles of carbon, full equilibration for carbon isotopes (e.g. ^{13}C, ^{14}C) can take some time (years). pCO_2 equilibration takes less time however, because the pH shift induced by gas exchange shifts the water towards equilibrium (e.g., if water is supersaturated with respect to atmosphere, CO_2 is lost and pH of seawater rises and some aqueous CO_2 is lost to the bicarbonate pool. Hence p_{CO_2} is moved towards equilibrium both by loss of aqueous CO_2 to atmosphere and by loss of aqueous CO_2 to bicarbonate pool (this is related to the Revelle Factor).

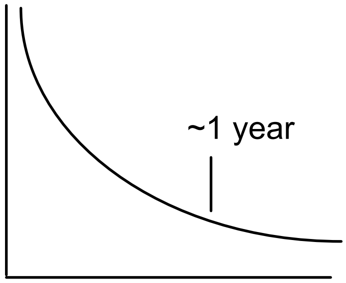
4. One square meter of the the upper 100m of the ocean (10^5kg) contains 200 moles of carbon. 0.5% of this carbon is as dissolved CO_2, and the Revelle Factor is ~10, so about 200*0.005*10 = 10 moles of CO_2 needs to be transferred to equilibrate the mixed layer with the atmosphere. Since the gas exchange rate is 20 moles/m^2/yr, the mixed layer of the ocean can equilibrate with the atmosphere on a time scale of about a half-year (note however that ^{13}C and ^{14}C will take longer to equilibrate because the <u>total</u> carbon dioxide must exchange to fully equilibrate the isotopes, i.e., 200/20 = 10 years). Hence the "average" anthropogenic CO_2 molecule has plenty of time to equilibrate with the mixed-layer.

Simple Gas Exchange
(e.g. O2, Ar)



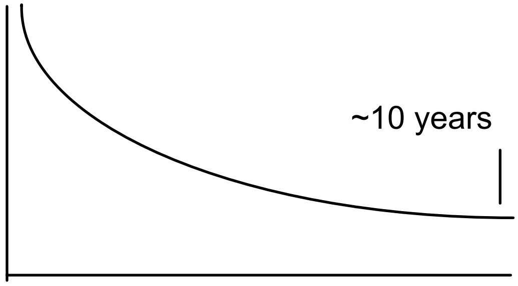
(depth of mixed layer divided by piston velocity - i.e. total gas content divided by gas flux)

pCO2 equilibration



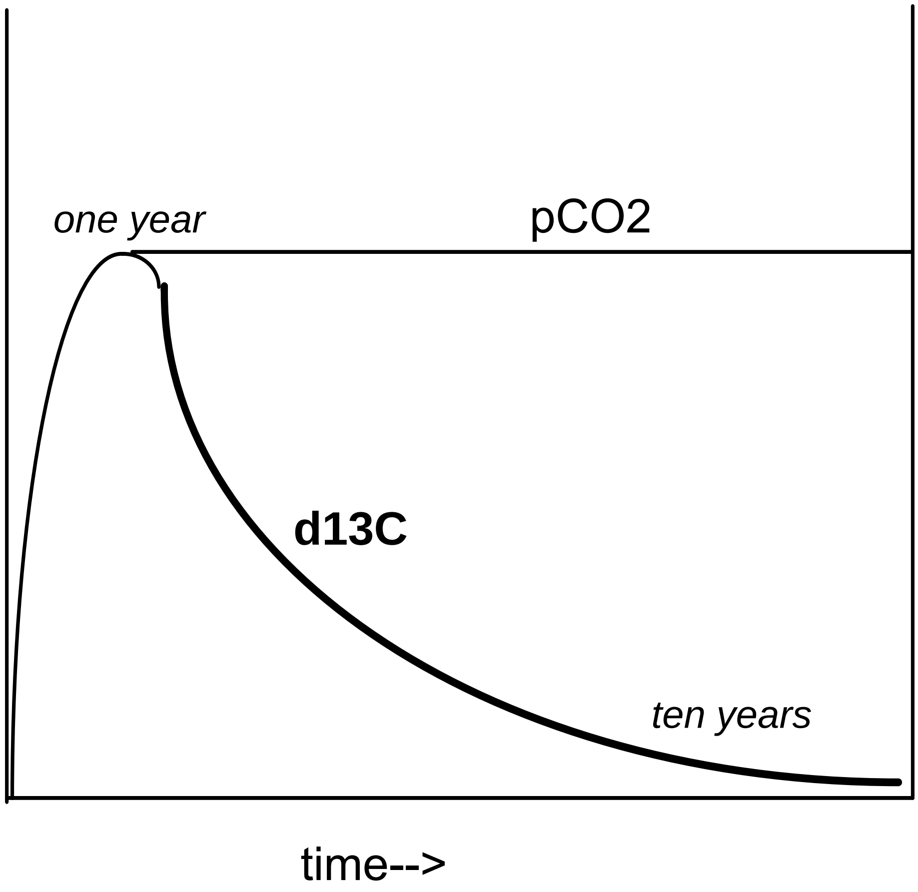
(change in TCO2 required to change pCO2 in seawater is divided by gas flux: e.g. for a 3% increase in pCO2, CO2(aq) rises by 3% and TCO2 rises by 0.3%; but because TCO2 is ~200x CO2(aq), it then takes 200*0.3/3=20x longer

carbon isotope equilibration
(C13, C14)

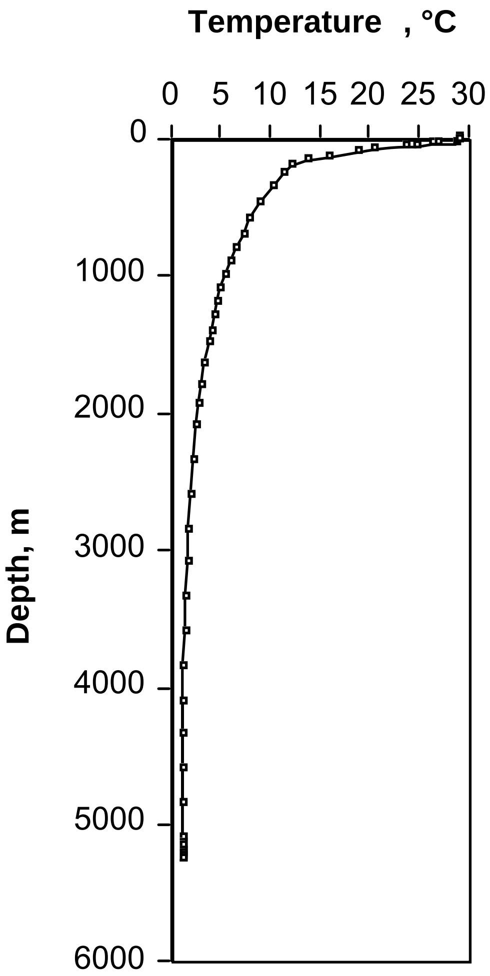


(total dissolved carbon dioxide divided by CO2 gas flux,
~20 moles/m2/yr)

Kinetic-isotope disequilibrium (Lynch-Stieglitz et al., 1995): Imagine a mixed layer system which is in equilibrium for carbon isotope ratio, but below equilibrium for p_{CO_2}. Gas exchange will drive the mixed layer into equilibrium in one year's time; but in doing so, it will shift the mixed layer towards the lighter isotope (because it is the light CO_2(aq) species which is involved in gas exchange). After about 10 years, the system comes back into isotopic equilibrium.



H. CO_2 and the oceans



1.. **The solubility pump:** CO_2 is more soluble in cold waters than in warm waters. If alkalinity were uniform throughout the ocean and if both cold and warm surface waters equilibrated their p_{CO2} with the atmosphere, then cold surface waters would have a higher dissolved carbon dioxide content than warm surface waters. As these cold surface waters circulate into the deep interior of the ocean, then deep waters will have more CO_2 than warm surface waters.

2. The biological pump**:** organisms remove carbon and nutrient elements from the surface ocean (which is equilibrated with atmospheric oxygen; note oxygen solubility is a function of temperature); the debris from these organisms sinks and decomposes, releasing carbon and nutrient elements into the deep water and consuming oxygen.

(Classical) Redfield Ratio:

$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2 \text{ -> } 106CO_2 + 16HNO_3 + H_3PO_4$

This reaction represents elemental stoichiometries observed in ocean water samples and plankton. It considers marine organic matter as if it were a mixture of carbohydrates (CH_2O), proteins (containing NH_3), and phospholipids and nucleic acids (H_3PO_4 bearing). In reality, a broad mixture of compounds occur, and the stoichiometry of O_2:C in particular $\Delta O_2/\Delta C$ in deep ocean waters implies a higher value (~165, because of more hydrocarbon-like functional groups):

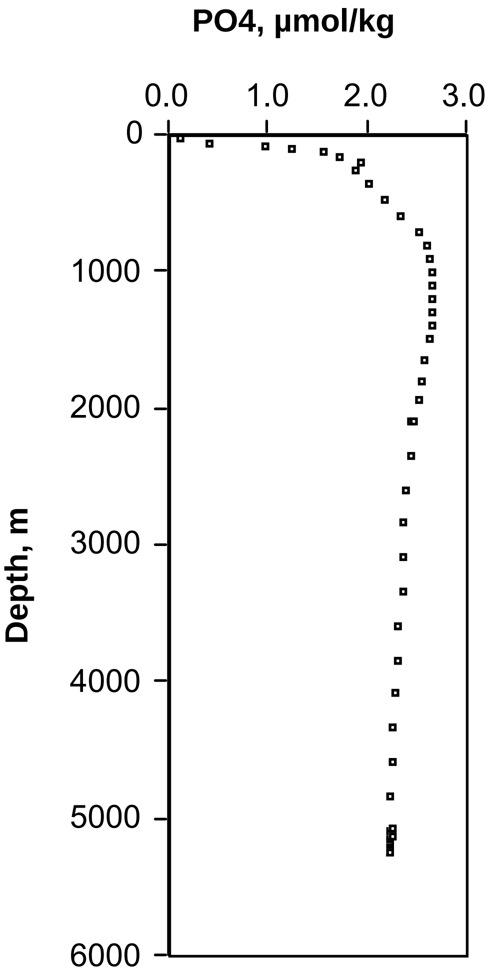
$$(CH_2O)_{111}(CH_4)_{11}(NH_3)_{16}(H_3PO_4) + 165\ O_2 = 122\ CO_2 + 16\ HNO_3 + 149\ H_2O + H_3PO_4$$

Note the production of nitric and phosphoric acid in this process; this acid creates changes in alkalinity. Once you acknowledge this process, you also need to take into account another effect that reduces the acid effect on alkalinity by about 1/3: the presence of ion-exchanged carboxyl groups:

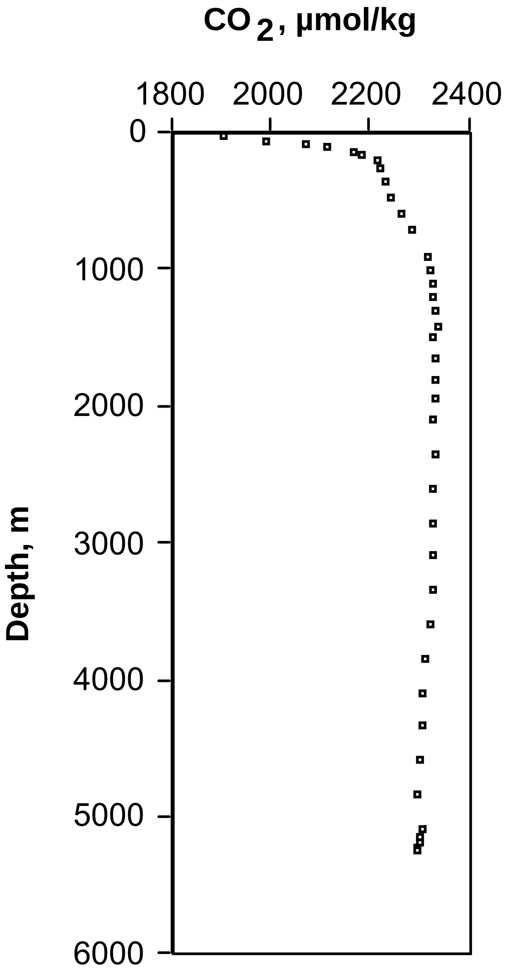
$$\begin{aligned}(CH_2O)_{102}(CH_4)_{14}(HCOO\text{-}Na+)_6(NH_3)_{16}(H_3PO_4) + 165\ O_2 \\ = 122\ CO_2 + 16\ HNO_3 + 146\ H_2O + H_3PO_4 + 6\ NaOH\end{aligned}$$

There is intense debate on whether the C:P and N:P stoichiometries are fundamental to marine ecosystems, or whether there is some plasticity (e.g., could N:P = 25?). (There is less debate on variable C:N ratios than for C:P).

We should also note that some organisms precipitate inorganic shells out of calcium carbonate (CaCO3) and silica ($SiO_2 \cdot nH_2O$). For example for every 106 organic carbon atoms converted to organic matter, about 22 CaCO3 molecules are precipitated (ocean-wide average).



3. **The Salt Pump:** Evaporation-precipitation cycle will change the p_{CO_2} of a surface water significantly because:
   - a. pH ≈ constant (so $CO_2(aq)/\Sigma CO_2$ = constant)
   - b. ΣCO_2 goes up (linearly with salinity)
   - c. Revelle factor of 10 for change in p_{CO_2} relative to ΣCO_2
   - d. CO2 is less soluble in saltier water.
4. Total dissolved carbon dioxide distribution (combination of all pumps, but mainly due to ~$^1/_3$ solubility pump and ~$^2/_3$ biological pump)



II. Broecker (1982) interpretation of G/I p_{CO_2} and oceanic $\delta^{13}C$ evidence

A. Considers various mechanisms which might change p_{CO_2}. Must involve the ocean, because it is dominant reservoir with which atmosphere communicates on ~20,000 year time scale. Salinity change (due to ice buildup) makes small difference, as does temperature change (if you accept the CLIMAP T estimates); these latter cancel each other out.

B. Consider surface water as deep water which has warmed up, had its P removed by organisms
(and accompanying removal of 106 CH_2O : 21 $CaCO_3$: 16 NH_3 : 1 P)

$$\mathbf{CO_2(surface) = CO_2(deep) - (\overset{\overset{\text{organic C}}{\downarrow}}{106} + \overset{\overset{CaCO_3}{\downarrow}}{21}) * P(deep)}$$

$$\mathbf{Alk(surface) = Alk(deep) - (\overset{\overset{CaCO_3}{\downarrow}}{2*21} - \overset{\overset{NH_3\text{oxidation}}{\downarrow}}{16}) * P(deep)}$$

Surface ΣCO_2 = 2260 - 2.2*(106+27) = 1967
Surface Alk = 2375 - 2.2*(54-16) = 2291

Interglacial two-box ocean:

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 ATMOSPHERE                          pCO2=324
 __|_|_________________________________________________________
|SURFACE OCEAN                                                 |
|                                                              |
| T=22   S=34.7   P=0    ALK=2291   ΣCO2=1967   δ13C=2.2       |
|______________________________________________________________|
  ↑ |              ↙
  | |              ↙  CH20:CaCO3:NH3:P=106:27:16:1;δ13C=-20
  | |_____________↙_____________________________________________
|DEEP OCEAN       ↙                                             |
|                                                               |
| T= 1   S=34.7   P=2.2  ALK=2375   ΣCO2=2260   δ13C=0.0        |
|                                                               |
|                    [CO3=]= 85                                 |
|                                                               |
|                                                               |
|                                                               |
|_______________________________________________________________|
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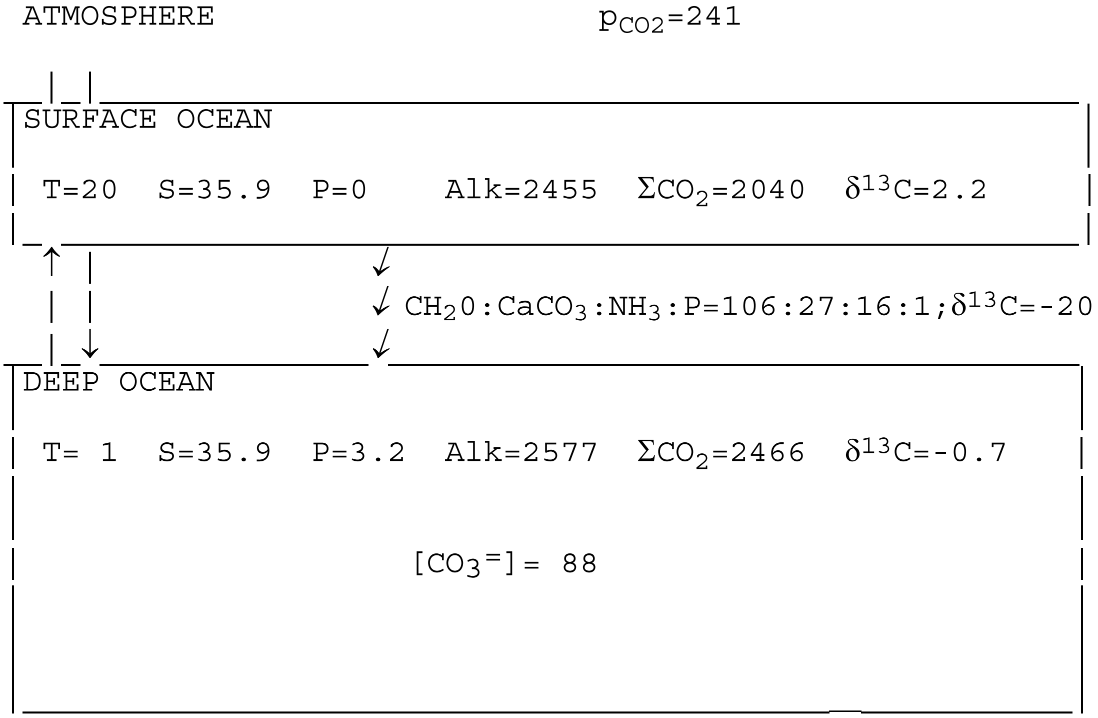
Proposed Glacial two-box ocean (add "Redfield" carbon from continental shelves):

Surface ΣCO_2 = 2466 - 3.2*(106+27) = 2040
Surface Alk = 2577 - 3.2*(54-16) = 2455



- (Assumes that marine organic matter from continental shelf is oxidized and put into ocean, and that sedimentary $CaCO_3$ dissolves to keep $[CO_3^{=}]$ of deep ocean is approximately constant)

C. Comparison to data

1. At the time, the calculated deep-sea $\delta^{13}C$ change was similar to the -0.7 permil suggested by Shackleton (1977) [although we now know that the change is less, about -0.3 to -0.4 ‰]
2. Planktonic (surface) $\delta^{13}C$ does not change in model; this result was consistent with evidence available at the time [but data for planktonics had a relatively large scatter which raises some concerns].
3. One major problem with this model is that it would deplete the deep-sea of oxygen. This outcome clearly did not happen (as proven by the existence of glacial-age benthic foraminifera, which are aerobic organisms).

III. Shackleton et al. (1983) planktonic-benthic $\delta^{13}C$ record

A. Did detailed analysis of N. dutertrei and Uvigerina $\delta^{13}C$ in the same core (V19-30). Subtracted the two to get surface-deep $\delta^{13}C$ contrast, which determines atmospheric CO_2, according to Broecker model. Appears to confirm reduced CO_2 during glacials; however, it appears that CO_2 change occurs before that of sea level (as indicated by $\delta^{18}O$)

IV. Cd evidence:

A. It does not appear that deep ocean Cd did not increase (Boyle and Keigwin, 1985/6; Boyle, 1992); Broecker theory requires +40% increase in P.

B. Paired Cd-δ^{13}C evidence suggests that much of the global δ^{13}C change is due to P-free carbon (trees and soils).

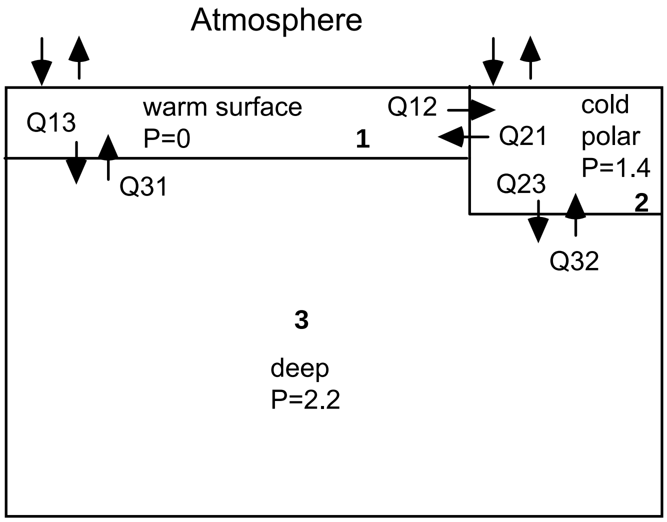
V. Pre-formed phosphate scenario (Toggweiler and Sarmiento, 1984,1985; Wenk and Siegenthaler, 1984,1985; Ennever and McElroy, 1984,1985)

A. One unrealistic feature of the two-box ocean is that not all of the phosphorus is removed before water that upwells at high latitudes is cooled and returned to the deep sea as bottom. About $^1/_3$ of all deep ocean phosphorus arrives advectively rather than by particulate transfer. In effect, this makes the deep ocean "leaky" with respect to CO_2, so that atmospheric CO_2 levels are higher than they would be in the absence of this "leak". Factors that change the "leakiness" of the deep ocean carbon dioxide can change atmospheric CO_2

B. Another unrealistic feature of the two-box ocean is that warm surface waters do not fill up most of the deep ocean; instead, cold surface waters at high latitudes sink to fill up most of the ocean. This aspect brings more oxygen into the deep sea.

C. So it is more realistic to have the deep ocean in communication with a cold surface ocean which contains residual phosphorus.

D. Consider a three-box ocean with a cold polar outcrop



1. Definition of pre-formed phosphate: PFP = P - r AOU(T)

where $r = \Delta O_2:\Delta P$ "Redfield ratio"
and AOU = Apparent oxygen utilization (equil. sol. - observed O_2)

2. Calculation of magnitude of CO2 changes for a given PFP change.

3. Ways to change pre-formed phosphate:

a. Change relative exchange rates of warm surface and deep ocean with cold polar.

b. More biological productivity in cold polar surface waters (?why? Martin iron hypothesis).

c. Change nutrient content of thermocline and hence upwell water of different nutrient content at high latitudes.

D. Advantages/Disadvantages of this theory:

1. Advantage: can produce rapid CO_2 changes
2. Advantage: consistent with benthic-planktonic $\delta^{13}C$ evidence
3. Disadvantage: doesn't solve oxygen problem
4. Disadvantage: there is no evidence that PFP changes! (high latitude planktonic Cd does not change, and planktonic $\delta^{13}C$ actually gets more negative)

E. Multi-box steady-state ocean modeling using linear matrix methods: Ocean Box Modeling.

VI. Coral Reef hypotheses

A. Basic premise is that $CaCO_3$ precipitation leads to release of CO_2: $Ca^{++} + 2HCO_3^- = CO_2 + CaCO_3$, and that a rise in sea-level will increase the growth opportunities for corals.

B. Keir-Berger w/"Worthington's Lid": this effect is enhanced by formation of a meltwater lid that keeps much of the released CO_2 in the mixed layer/atmosphere (hence coral growth rates don't have to be especially high). Snag: no evidence that deep ocean ventilation rates were cut off during deglaciation (recall: benthic-planktonic ^{14}C difference).

C. Opdyke version (Holocene coral growth rates greater than input from weathering). Coral growth rates are not likely to be this high, and the continuation of this phenomenom for 10,000 years would drive the deep ocean into a state of intense carbonate undersaturation.

VII. Nutrient deepening/alkalinity response model (Boyle, 1988).

A. Recall that one of the results of the paleo-deep water studies is that glacial P and $\delta^{13}C$ distributions change to move nutrients from the upper ocean into the deepest parts of the ocean. Since CO_2 is a weak acid, this movement of CO_2 into the deep ocean will make the deep ocean more corrosive to $CaCO_3$ (i.e., deep $[CO_3^=]$ will go down).

B. As Broecker (1982) pointed out, if weathering input and deep-sea biological carbonate production remains constant, then in order to maintain the CCD/lysocline at the same position, the deep $[CO_3^=]$ must remain approximately constant. If there is more CO_2 in deep waters, then to keep $[CO_3^=]$ constant, then the alkalinity will have to rise. This is achieved by dissolving some of the $CaCO_3$ on the seafloor: $CO_2 + CaCO_3 = Ca^{++} + 2HCO_3^-$. Note that this reaction increases the alkalinity of the whole ocean by two μeq/kg for every μmol/kg of CO_2 added from dissolution. Hence the ratio of $Alk/\Sigma CO_2$ in the whole ocean increases, pH rises, and pCO_2 drops.

C. A complication of this model is that CO_2 may not be transferred vertically independently of alkalinity; in some scenarios, the $[CO_3^=]$ response is small (e.g. versions that increase vertical mixing between the surface and intermediate depth ocean) while in others it is much larger (e.g., an increase in the fraction of organic matter that decomposes in the deep ocean as opposed to the intermediate depth ocean).

D. The state of this idea: (1) it doesn't appear that the whole ocean nutrient-deepening is quantitatively large enough to account for more than a fraction of p_{CO_2} drop, even give given the most sensitive scenario (Boyle, 1992), and (2) the $[CO_3^{=}]$ = constant constraint may not be the best way to simulate the lysocline/CCD response; using a more explicit model of carbonate dissolution on the seafloor reduces the effectiveness of this mechanism at changing p_{CO_2} (Emerson and Archer, 1993).

VIII. Rain Ratio Model

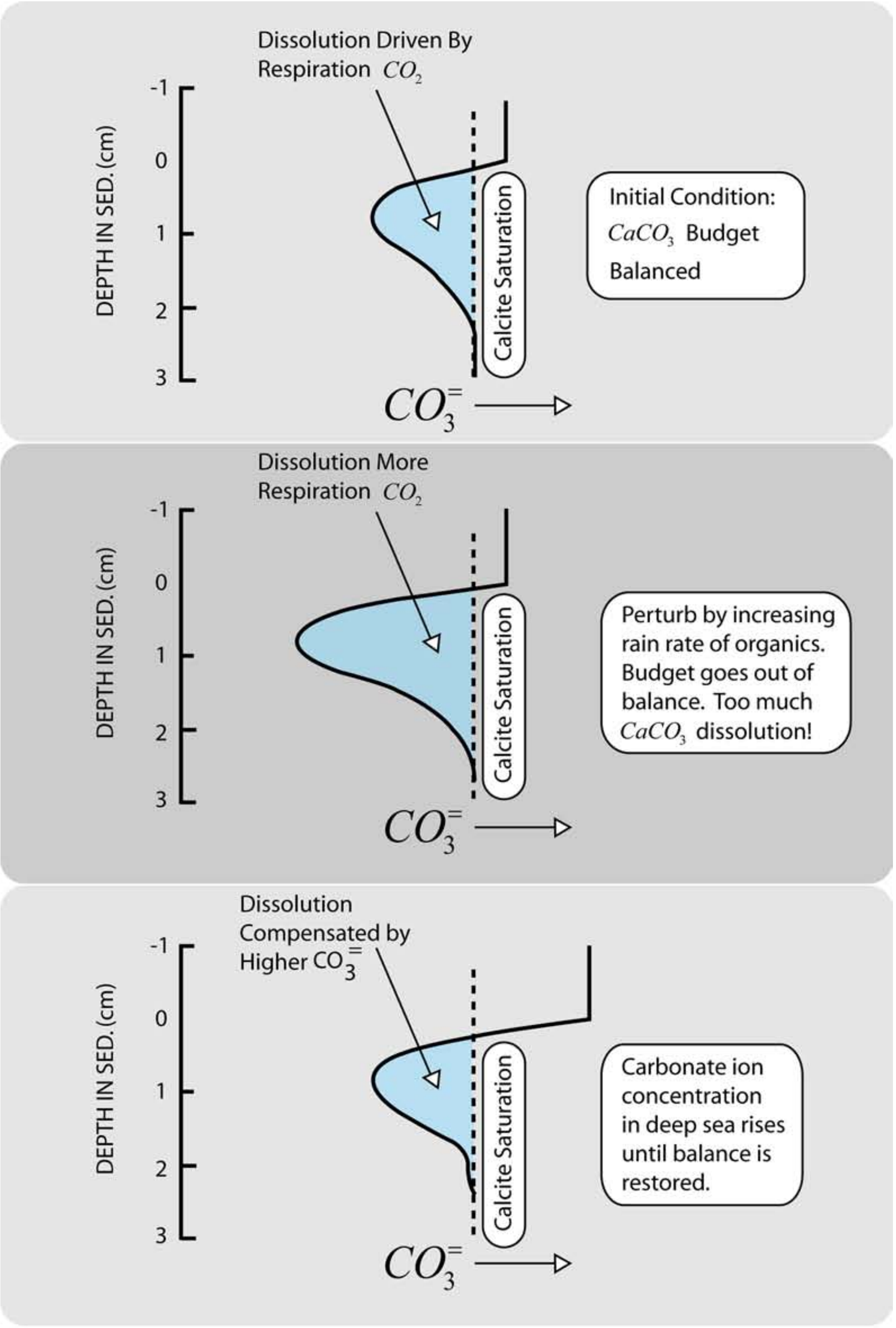
A. Exists in various incarnations. What the ideas have in common is noting that there is a "rain ratio" of CH_2O:$CaCO_3$, and that this ratio may have changed between glacial and interglacial times (e.g. Keir and Berger, 1985).

B. Early versions of this idea sprang from the idea that "diatoms are more efficient at reducing surface water p_{CO_2} than coccolithophorids". At face value, this notion seems subtly obvious: diatoms remove only CO_2 (as CH_2O) while coccolithophorids remove both CO_2 and $CaCO_3$. But because coccolithophorids remove two units of alkalinity for every $CaCO_3$ removed, they lower the pH and hence create a higher p_{CO_2} for a given ΣCO_2 level. However, as we saw earlier, reducing the low-latitude $CaCO_3$: CH_2O rain ratio by a factor of two in the Toggweiler-Sarmiento 3-box ocean model had a significant response (280->271 ppmV), but not enough to account for glacial p_{CO_2} lowering. Even lowering the ratio by a factor of 4 in that model - placing the rain rate precariously close to the point at which carbonate isn't being deposited as fast as it is being weathered - only gives an additional 12 ppmV. The reason for this lack of response is that a mass-conserving ocean will often take CO_2 that is removed in one part of the ocean pop back up in another part of the ocean, cancelling the apparent effectiveness of the original change. In this case, the upwelling of deep water to the high latitude ocean counters the direct effect of the low-latitude rain ratio change. Let this serve as a warning about purely qualitative ideas about mechanisms controlling p_{CO_2}.

C. In a more subtle variation on this theme, it is noted that currently about 5 times more calcium carbonate is being formed by organisms than is coming in from rivers, hence 80% of the biogenic flux is dissolved. If the rain ratio is reduced by a factor of 50% (biogenic = 2.5xinput, only 60% of the biogenic flux needs to be dissolved. Hence the $[CO_3^{=}]$ concentration of the deep ocean can be higher, leading to higher oceanic alkalinity and hence lower p_{CO_2}.

D. Archer/Maier-Reimer O-GCM w/CO_2 chemistry:

1.Model is an ocean GCM including carbon cycle chemistry and a $CaCO_3$ dissolution model for the seafloor, holding ocean circulation constant. Key characteristic of dissolution model is a major role for *in-situ* organic carbon degradation in $CaCO_3$ dissolution. In the model, the CH_2O:$CaCO_3$ rain ratio is varied slightly, and it is found that the degree of *in-situ* dissolution increases greatly - so much so, that most of the deep ocean is supersaturated with respect to $CaCO_3$! Hence, the balance between input and output of $CaCO_3$ is mediated by a balance between the extent of supersaturation and the extent of *in-situ* organic carbon degradation (higher supersaturation leads to lower $CaCO_3$ dissolution, higher *in-situ* organic degradation leads to more $CaCO_3$ dissolution; for a given organic degradation the deep ocean supersaturation moves to the point where dissolution is sufficient to compensate for excess of production over input. Notable in model is the relatively small change in rain ratio necessary to create large p_{CO_2} changes.



The Archer-Maier-Reimer scenario for the cause of the low atmospheric CO_2 content during glacial time (Archer and Maier-Reimer, in press). An increased rain rate of organic matter raises the amount of respiration CO_2 released to sediment pore waters. This increase causes the rate of $CaCO_3$ dissolution to exceed that required for material balance. As a result, the CO_3^{2-} ion content of the sea rises, eventually compensating for the excess dissolution. This rise in ocean CO_3^{2-} content drives down the atmosphere's CO_2 content.

Figure by MIT OpenCourseWare. Adapted from source: Broecker (Glacial World According to Wally) concept from Archer and Maier-Reimer.

2. Model predicts large pH increase in deep ocean. This may be verifiable by boron isotope paleo-pH method.
3. One caution: the published version of this paper relies on a version of the calcium carbonate dissolution kinetics that assumes that the dissolution rate varies as the 4th power of the undersaturation. More recent evidence discussed by Hales (••••)

suggests that this formulation is in error and that dissolution rate is linear with undersaturation. It would be interesting to know how sensitive this model is to changing this assumption.

4. One major flaw of this model is that it predicts that essentially the whole ocean floor (including the deep Pacific) should be covered by calcium carbonate during glacial times. This is not observed.

IX. R. Keeling "sea ice/gas exchange mechanism: proposes that LGM sea ice cover over the Antarctic prevented the CO2 "leak" in the Southern Ocean. Problem: sea ice cover must be extremely efficient (>95%) for this mechanism to work.

X. Nitrate as a limiting nutrient: the idea and its development

A. McElroy et al. proposed that instead of changes in oceanic phosphorus, nitrate changes could control glacial/interglacial CO_2 cycles. The reason for an increase in nitrogen in the glacial ocean would be a decrease in denitrification (perhaps due to lower sea-level, although other causes may also produce this effect). Because nitrate has a residence time of about 10^4 years (compared to 10^5 years for P), it is easier to change the oceanic N value on G/I timescales.

B. This idea was initially discounted on two grounds:

1. Redfield argued that P, not N, is the limiting nutrient in seawater because it is only supplied and lost through geological interactions (dissolution from rocks, loss to sedimentation). Nitrogen, on the other hand, is dominantly fixed biologically (nitrogen fixers), and if the supply of N is not sufficient, the ecological balance would be shifted towards nitrogen fixers, and the nitrate supply would “catch up” with the available phosphorus.
2. Altabet and Curry showed that it did not appear that the isotopic composition of oceanic nitrogen changed on G/I timescales. This was taken as evidence against a large decrease in denitrification during glacial times, because water column denitrification is accompanied by a large isotopic fractionation. However, recent studies by Brandes and Devol (1997) indicate that continental shelf sedimentary denitrification does not produce an isotope shift.

C. This idea has been recently revived (in somewhat modified form) given the following arguments:

1. Falkowski has argued that the Redfield argument is wrong because it does not take into account another limiting nutrient: iron. Redfield derived his arguments from terrestrial studies (Hutchinson), where Fe is not limiting. However, in the ocean in many environments, iron is limiting – in some cases to all marine life, and perhaps almost everywhere with respect to nitrogen fixation. Nitrogen fixation is an iron-intensive biochemical process. Hence nitrate, not phosphate might be the limiting nutrient.
2. It is not clear that a reduction in denitrification will necessarily be reflected in a change in the isotopic composition of oceanic nitrate. Studies by Devol and Brandes show that continental margin sediments – where nitrate is completely depleted at

some depth in the sediment due to denitrification – do not evidence any isotopic fractionation in nitrate because the nitrate is completely consumed within the sediments. Although a very small isotope fractionation may remain – due to the difference in the diffusion of $15NO_3^-$ (63 amu) compared to $14NO_3^-$ - (62 amu) – the large isotope fractionation due to denitrication has little effect.

D. Studies of the nitrogen isotope composition of continental margin sediments off of Mexico (Ganeshram et al., 1995) and in the Arabian Sea (Altabet et al., 1995) show lighter nitrogen; this is interpreted as implying less efficient glacial water column denitrification in these environments.

E. Denitrication today appears to occur roughly equally on continental shelves and in the low-oxygen zones of the Eastern Tropical Pacifical Pacific. If both of these sinks was diminished, and the supply of fixed nitrogen enhanced by the greater iron supply in the dusty glacial atmosphere, then the nitrate content of the ocean may well have been higher. The fly in this ointment: how will we ever establish that this happened (paleo-nitrate indicators being in limited supply).

F. Studies of the nitrogen isotopic composition of Antarctic sediments and diatoms (suggesting somewhat more efficient nitrate utilization) have also revived the polar nutrient hypothesis to some extent.

XI. Toggweiler "change in mode of Southern Ocean deepwater formation" model (personal communication, 2002). Premise is that in the ocean today, AABW formation occurs on the continental shelf after nearly complete equilibration of the surface water with atmosphere (hence CO_2 is "lost" from ocean to atmosphere). He proposes that during the last glacial maximum, deepwater formation proceeded by deep ocean convection (short-lived uniform column of high density water from surface to bottom) where gas exchange equilibration cannot occur - hence sealing off the ocean CO_2 "leak" and reducing atmospheric CO_2.

XII. Oceanic Si reorganization (Brzezinski et al. 2002): Argue that higher glacial Southern Ocean iron leads to lower (1:1 compared to 4:1 today) $Si(OH)_4$:N ratios in glacial Antarctic phytoplankton (because diatoms make thinner shells when they are iron-replete: Hutchins and Bruland, 1998). This leads to more $Si(OH)_4$ in sinking Antarctic water masses and hence more Si in the low latitude ocean: hence leading to more diatoms relative to coccolithophores in the low latitude ocean, weakening the carbonate pump and increasing the depth of organic matter remineralization (diatoms sink faster than other forms of organic matter). Taken all together, these factors are estimated to lower CO_2 by as much as 60 ppm.

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