GREENHOUSE PUZZLES

KEELING'S WORLD
MARTIN'S WORLD
WALKER'S WORLD

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Preface

Our field suffers from a dearth of textbooks. Further, those that do exist are often prohibitively expensive and often somewhat out-of-date. Because of this, our students are forced to do much of their reading in specialized journal articles written for professionals.

This problem is related to the highly competitive and rapidly changing character of global change science. Researchers qualified to write textbooks are far too busy with proposals, reports, journal articles, workshops... to take out the immense amount of time it takes to put together a textbook. Books are often written over a period of years. The publisher then takes a year or two more to review, tune, proofread and print the book. By this time, the field has often advanced to the point where a revision is needed a few years after publication.

Recognizing these problems, we have tried to dream up some innovations to the process. *Tracers in the Sea* was self-published allowing the price to be held down by threefold. *The Glacial World According to Wally* and this book go a step further. They are designed to permit ease of continuing revision. No formal printing will be made. Rather, spiral-bound xerox copies are sold to interested users. The user is encouraged to xerox as many copies as he or she wishes.

The other advantage is that we, the authors, can produce these books with far less effort than were they to be formally printed. As new information appears, we can make revisions and put out updated versions.

Of course, this approach is not without its disadvantages. As the quality of reproduction of photographs is poor, we avoid using them. The rigor in proofreading is not up to publishing-house standards. But for a profession that does much of its reading in preprints, this is not a serious drawback.

The authors
September 1998

Part I

KEELING'S WORLD

IS CO_2 GREENING THE EARTH?

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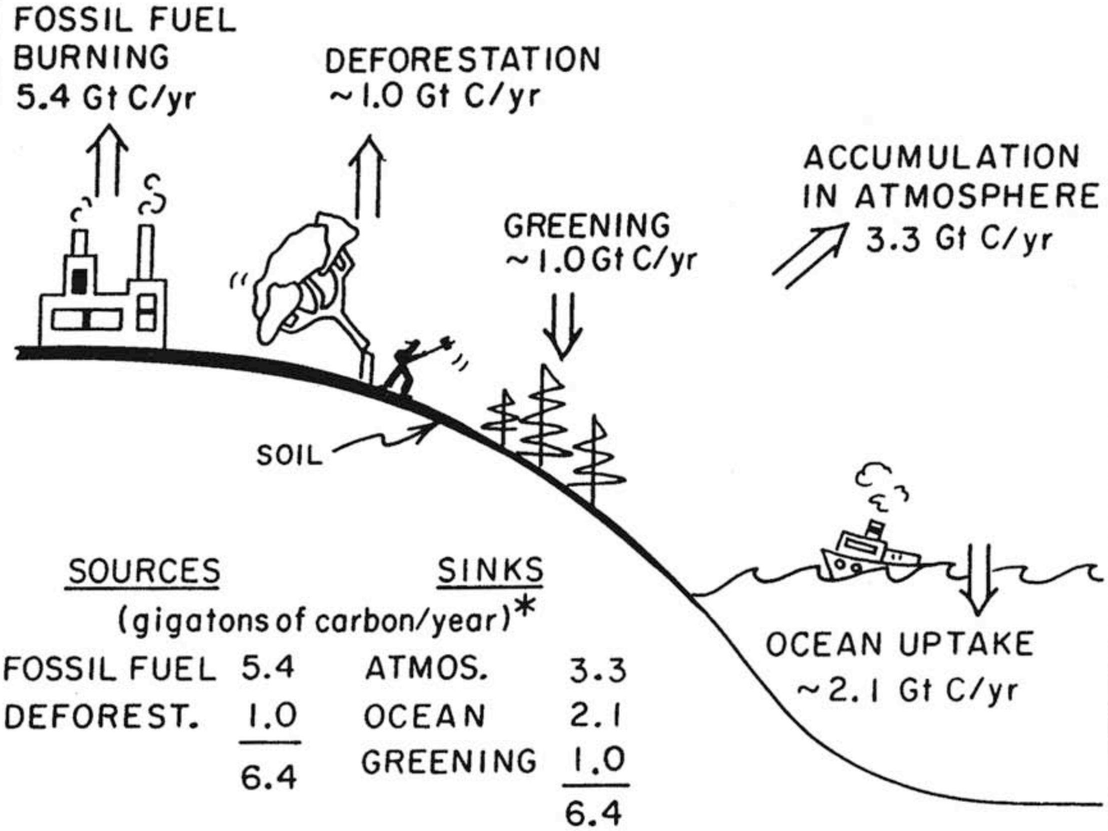
KEELING'S WORLD:
IS CO_2 GREENING THE EARTH?

This section's hero is Charles David Keeling. In the late 1950's, he had the wisdom to establish two stations for the continuous precise measurement of atmospheric carbon dioxide, one high on Hawaii's extinct volcano Mauna Loa and the other at the South Pole. The records from these stations provide the foundation upon which all studies of man's perturbation of the Earth's carbon cycle rest. Not only did Keeling have the foresight to establish these stations but also the tenacity to make sure that year in and year out they produced accurate results. Keeling took on this task as part of a career-long effort to understand the flux of CO_2 *gas through the atmosphere, into the ocean and into and out of the terrestrial biosphere. He was the first to realize the wealth of information contained in the spatial and seasonal texture of the atmosphere's* CO_2 *content. In addition to his direct scientific contribution, he fostered a secondary one. Son, Ralph, is doing for atmospheric* O_2 *all the kinds of things papa did for atmospheric* CO_2*.*

We know from the CO_2 content of air trapped in glacial ice that during the centuries prior to the Industrial Revolution, the CO_2 content of the Earth's atmosphere remained nearly constant. In other words, the world's carbon cycle remained close to steady state; removal of CO_2 through photosynthesis balanced its addition through respiration. But starting in the last century, activities of the expanding human population tipped the balance in favor of respiration. In response to the ever increasing demand for agricultural products, forests were cut and lands were tilled. These activities accelerated the oxidation of carbon stored in trees and in soil. In response to the expanding need for energy, engines fueled by coal, oil and natural gas proliferated. Organic matter which had survived for many tens of millions of years was recovered and burned. As a result of these activities, the CO_2 content of the atmosphere began a rise which steepened with each passing year. When this book was last revised, the CO_2 concentration was 30% higher than that for pre-industrial times

APROXIMATE EARTH CARBON BUDGET FOR THE 1980s; THE ANTHROPOGENIC PERTURBATION



SOURCES		SINKS	
(gigatons of carbon/year)*			
FOSSIL FUEL	5.4	ATMOS.	3.3
DEFOREST.	1.0	OCEAN	2.1
	6.4	GREENING	1.0
			6.4

FRAC. TO ATMOS. $\frac{3.3}{6.4} = .52$

FRAC. TO SEA $\frac{2.1}{6.4} = .33$

FRAC. TO CONT. $\frac{1.0}{6.4} = .15$

$\overline{1.00}$

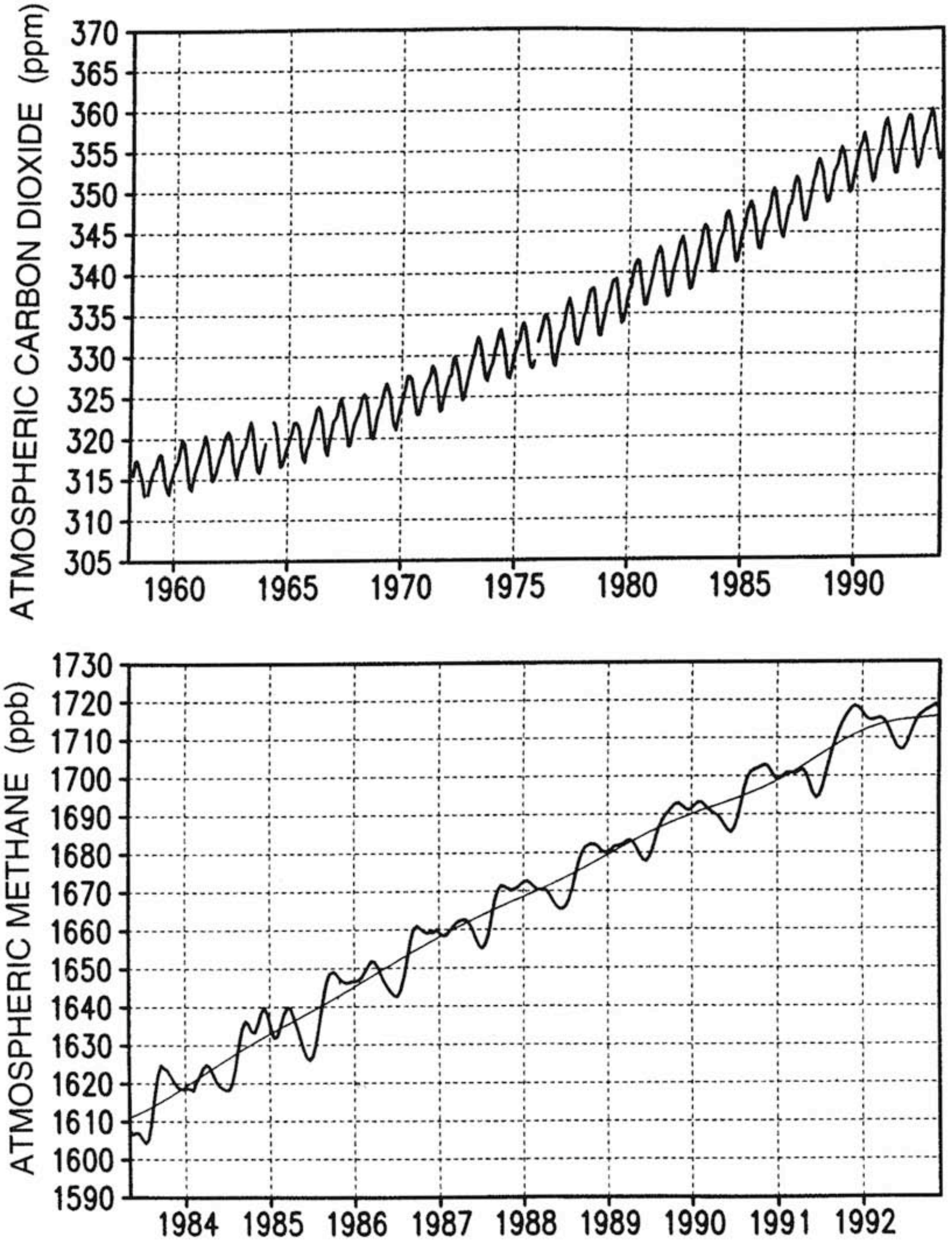
*1 Gt = 1×10^{15} grams = 1×10^{9} tons (in the year 1800, the CO_2 content was 280 parts per million ppm; as of 1997, it was 360 ppm).

This section's mystery is not that the atmosphere's CO_2 burden is rising, but rather that it is rising much more slowly than expected. The amount of excess CO_2 appearing in the atmosphere each year is just over one half that produced by fossil fuel burning. Nearly fifty percent has disappeared! The mismatch between CO_2 production and CO_2 buildup becomes even larger when the amount of CO_2 released as the result of forestry is taken into account. Although the magnitude of this activity remains poorly documented, during the last decade or so, an amount of CO_2 averaging about 25% that from coal, oil, and natural gas was released as the result of forest cutting. When this biosphere-derived CO_2 is included as a source term, the fraction of the CO_2 which remains airborne drops to only about 40% of the input. Where has the rest gone?

The most obvious hiding place is the ocean. Excess CO_2 in the atmosphere passes across the air-water interface and reacts with $CO_3^{=}$ ions dissolved in the sea to produce HCO_3^{-} ions. Were the atmosphere to be at chemical equilibrium with the entire ocean, about five sixths of the excess CO_2 would take up residence in the sea. Only one sixth would remain airborne. But it's not so simple; the sea mixes so slowly that only a small fraction of its capacity for CO_2 uptake is being utilized. Vast parts of the deep sea are accessible only on the time scale of hundreds of years. When this dynamic limitation is taken into account, it turns out that while the sea is an important hiding place, its uptake can account for only about one half the missing CO_2. Our mystery has to do with the fate of the remainder. Where has it gone?

The search for the so called "missing carbon sink" has been pursued for more than two decades. The conclusion is always the same. Only one reservoir, the organic matter which makes up the terrestrial biosphere, is big enough for the task. Somehow human activity must have increased the rate of photosynthesis. As a consequence, more carbon is being stored in tree trunks and soil humus. One might say, while the terrestrial

ANTHROPOGENIC INCREASES IN ATMOSPHERIC CO_2 AND CH_4

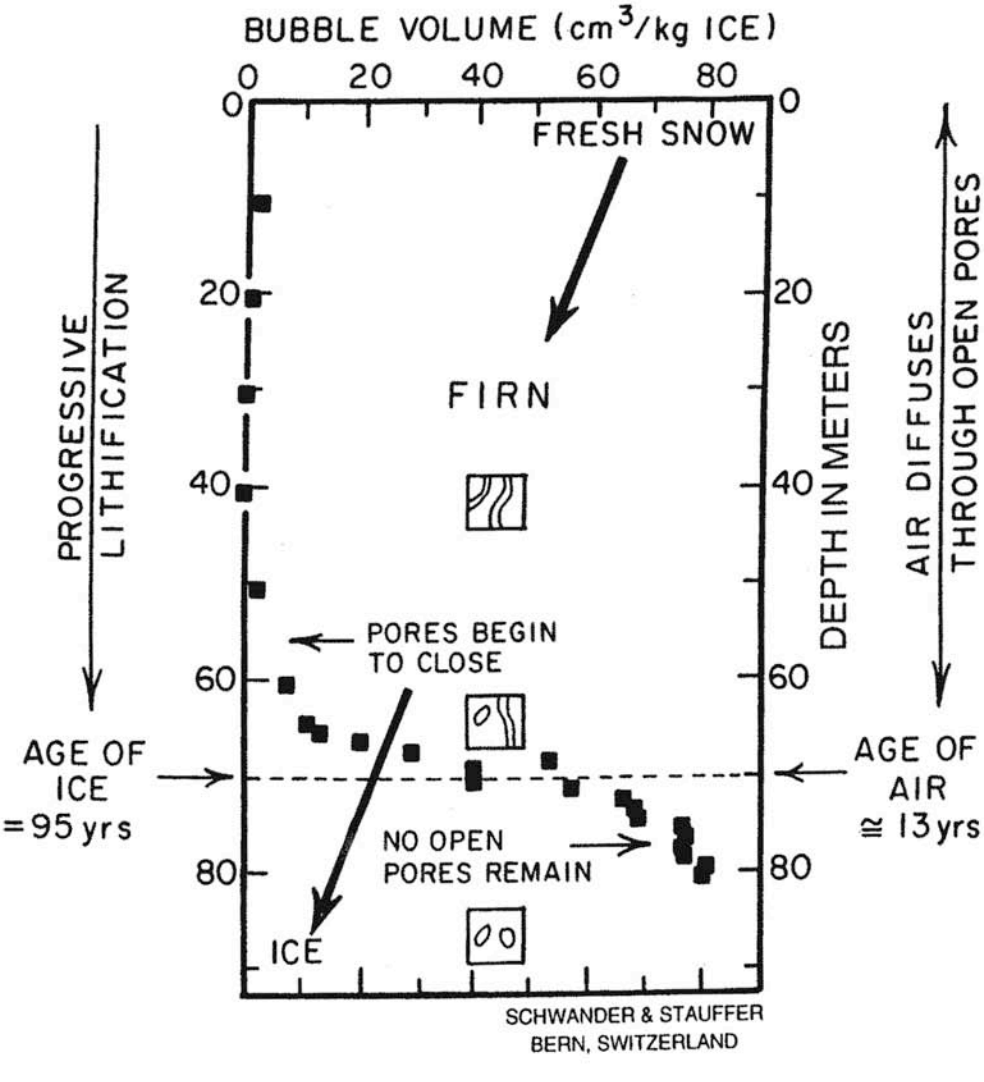


biosphere reservoirs is being trimmed around the edges, it is becoming more lush in the interior. Through our activities, we have been "greening", not just agricultural land but the entire planet. Actually, agricultural land is part of the problem, and not of the solution. First, as plants grown on agricultural land are harvested each year, no above ground storage of carbon occurs. More important, agricultural practice has been shown to drive down the humus content of soil. So, if the missing carbon is being packed away in wood and humus, this storage is occurring on lands we classify as uncultivated.

Two mechanisms have been identified which might propel a global greening. The first involves CO_2 itself. As carbon is the primary building block for plant matter, the increased abundance of CO_2 in the atmosphere might be expected to accelerate photosynthesis. More CO_2 flows into the factory allowing more organic matter to be manufactured. Indeed, experiments carried out in growth chambers suggest that, at least on the short term, a 30% increase in the CO_2 content of the air leads to growth enhancements averaging 10%. If CO_2 is driving an enhancement of this magnitude in the wild, then, each year more wood is being generated (leading to fatter forests) and more organics are being pumped into soils (leading to richer humus). The second mechanism involves nitrogen. Growth in most plant communities is often limited by the availability of this important nutrient. Farmers counter this deficiency by fertilizing their fields with ammonia or by allowing them to remain fallow so that plants with nitrogen-fixing root symbionts can generate natural fertilizer. The internal combustion engine extends nitrogen fertilization to the wilds. Atmospheric N_2 molecules are split at the high temperatures achieved in automobile engines producing nitrogen oxide gases. These gases become widely dispersed through the atmosphere before they are transformed to nitric acid molecules which dissolve in raindrops. This automobile-generated fertilizer allows more wood and soil humus to be generated. While a strong case can be made that extra carbon dioxide and fixed nitrogen are greening the planet, as we shall see, this greening process must be operating at maximum efficiency if it is to account for the

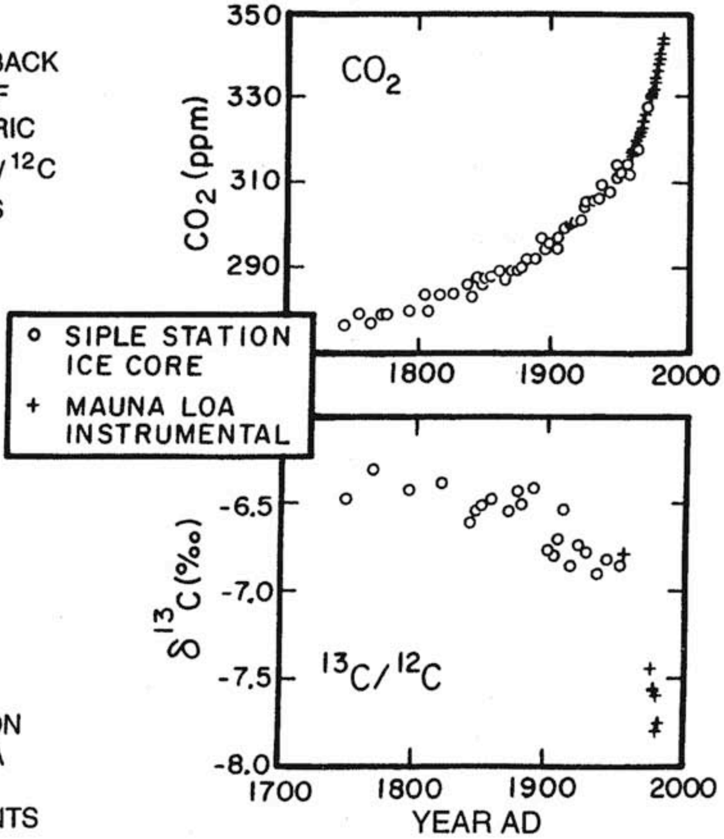
RELATIONSHIP BETWEEN AGE OF ICE AND AGE OF AIR TRAPPED IN BUBBLES IN ICE FOR SIPLE STATION ANTARCTICA

$T_{AIR} = T_{ICE} - 82$ YEARS



SCHWANDER & STAUFFER
BERN, SWITZERLAND

EXTENSION BACK
IN TIME OF
ATMOSPHERIC
CO_2 AND $^{13}C/^{12}C$
RECORDS

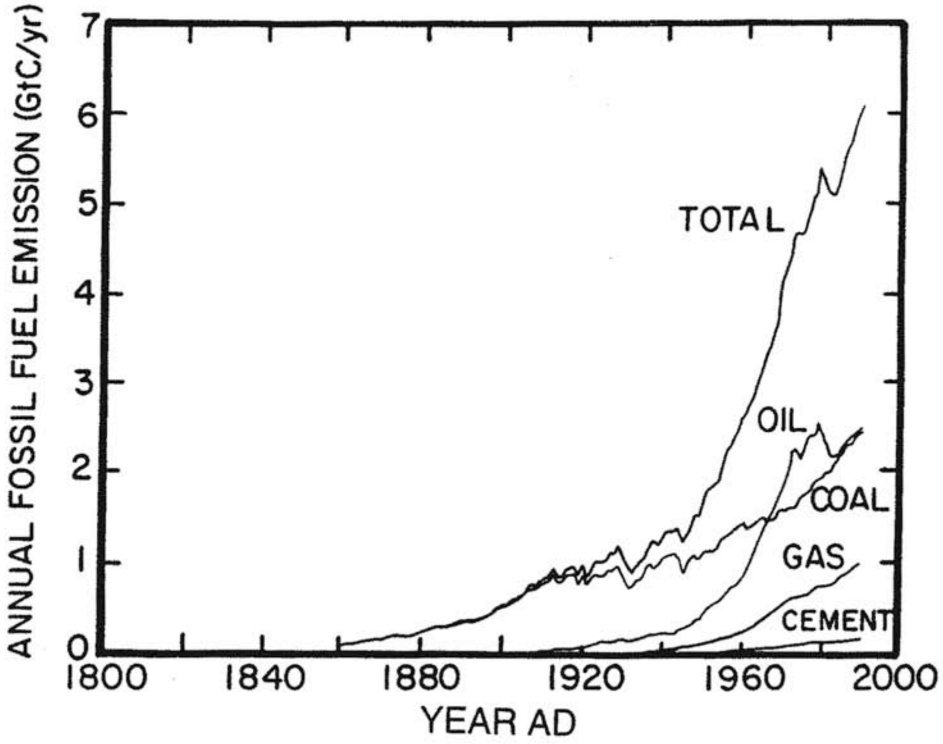


SIPLE STATION
ANTARCTICA
ICE CORE
MEASUREMENTS

Depth (m)	Ice Age (yr. AD)	Gas Age (yr. AD)	CO_2 (ppm)	$\delta^{13}C$ (‰)	
81.22	1871	1953	312.7	- 6.85	← ANNUAL LAYER 113
86.80	1861	1943	307.9	- 6.82	
90.77	1853	1935	306.6	- 6.91	
95.17	1845	1927	305.5	- 6.78	
98.80	1839	1921	301.6	- 6.74	
101.80	1833	1915	300.5	- 6.86	
105.25	1827	1909	299.2	- 6.54	
107.20	1823	1905	296.9	- 6.71	
108.80	1821	1903	294.8	- 6.80	
110.20	1817	1899	295.8	- 6.77	
116.82	1805	1887	292.3	- 6.42	
121.80	1796	1878	290.3	- 6.51	
123.80	1792	1874	289.5	- 6.43	
126.80	1787	1869	289.3	- 6.55	
134.47	1772	1854	288.2	- 6.48	
138.20	1765	1847	286.8	- 6.51	
140.75	1761	1843	287.4	- 6.54	
142.75	1757	1839	283.1	- 6.62	
154.89	1734	1816	283.8	- 6.39	
168.30	1709	1791	279.7	- 6.43	
177.50	1682	1764	276.7	- 6.31	
187.70	1662	1744	276.8	- 6.48	← ANNUAL LAYER 322

FRIEDLI AND COWORKERS, BERN, SWITZERLAND

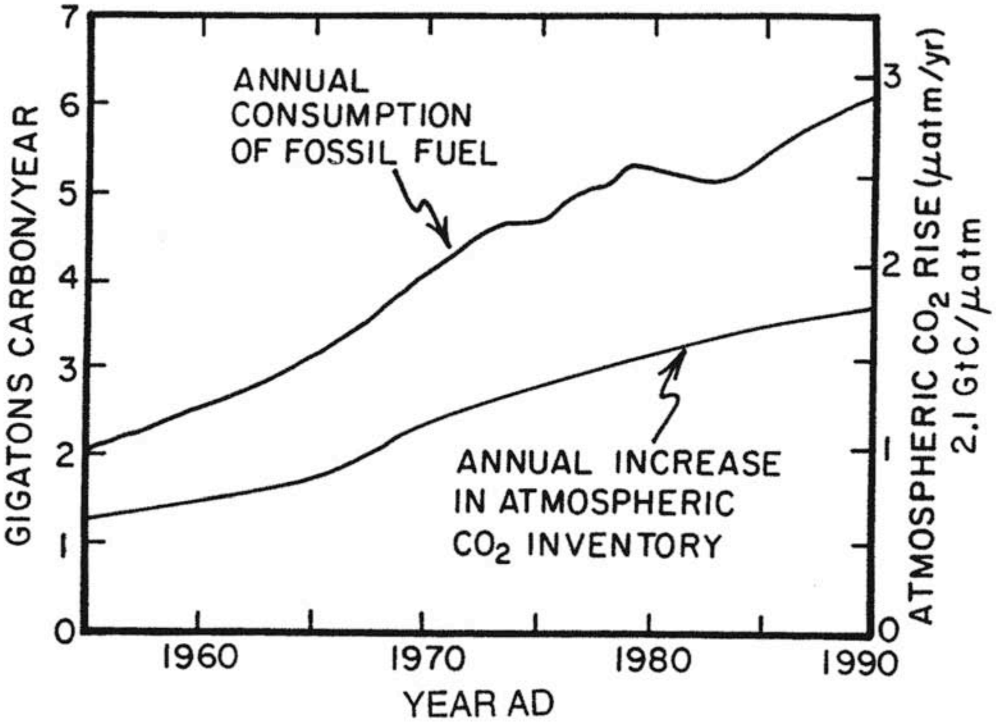
TIME HISTORY OF FOSSIL FUEL CONSUMPTION



FOSSIL FUEL EMISSIONS (GtC/yr)

	1950	1960	1970	1980	1990
COAL	1.1	1.4	1.6	2.5	2.5
OIL	0.4	0.9	1.8	1.9	2.4
GAS	0.1	0.2	0.5	0.7	1.0
$CaCO_3$	0.0	0.0	0.1	0.1	0.2
TOTAL	1.6	2.5	4.0	5.2	6.1

COMPARISON WITH THE RATE OF ACCUMULATION OF CO_2 IN THE ATMOSPHERE



OVER THE TIME PERIOD DURING WHICH THE ATMOSPHERE HAS BEEN ACCURATELY MONITORED, ITS CO_2 CONTENT HAS BEEN RISING AT A RATE ONLY ABOUT 60% THE RATE EXPECTED IF ALL THE FOSSIL FUEL CO_2 RELEASED REMAINED AIRBORNE.

storage of the missing carbon. Before exploring this question, let us review the evidence upon which carbon budgets are based.

The Knowns

Only two of the terms in the carbon budget are directly measured to a reasonably high degree of accuracy. One is the amount of CO_2 generated during each of the last 100 or so years through the burning of fossil fuels and the manufacture of cement. The number of tons of coal mined, the number of barrels of oil pumped, the number of cubic meters of natural gas recovered, and the number of tons of limestone thermally decomposed have been laboriously compiled from records kept by individual nations. The other is the CO_2 content of the atmosphere. In 1957, Charles David Keeling commenced continuous highly accurate measurement of the CO_2 content of air atop the extinct volcano Mauna Loa on the island of Hawaii. Keeling's measurement series has continued unbroken and is now supplemented by measurements at many other locations on our planet. Scientists at Bern, Switzerland and Grenoble, France discovered a means of extending this record back in time. Their trick was to extract gas stored in the bubbles contained in ice recovered from borings atop the Greenland and Antarctic ice caps. They demonstrated that this mode of cold storage nicely preserves the CO_2 content of the trapped air.

These two sets of data constitute our givens. Taken together, they tell us with clarity that, over the time spanned by the instrumental record, CO_2 has built up in the atmosphere at a bit more than one half the rate it was being generated by fossil fuel burning. The remaining three budgetary terms (described in the sections which follow: ocean uptake, deforestation, and greening) must be estimated by less direct means.

The Mirror Image Approach

The CO_2 produced by the burning of fossil fuels must be matched by an equivalent consumption of atmospheric oxygen. For coal, about thirteen molecules of O_2 disappears for each ten atoms of carbon combusted.

$$C_{10}H_6 + 13O_2 \rightarrow 10CO_2 + 3H_2O$$

For petroleum, the ratio is close to 3 O_2 molecules for each 2 carbon atoms.

$$2CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

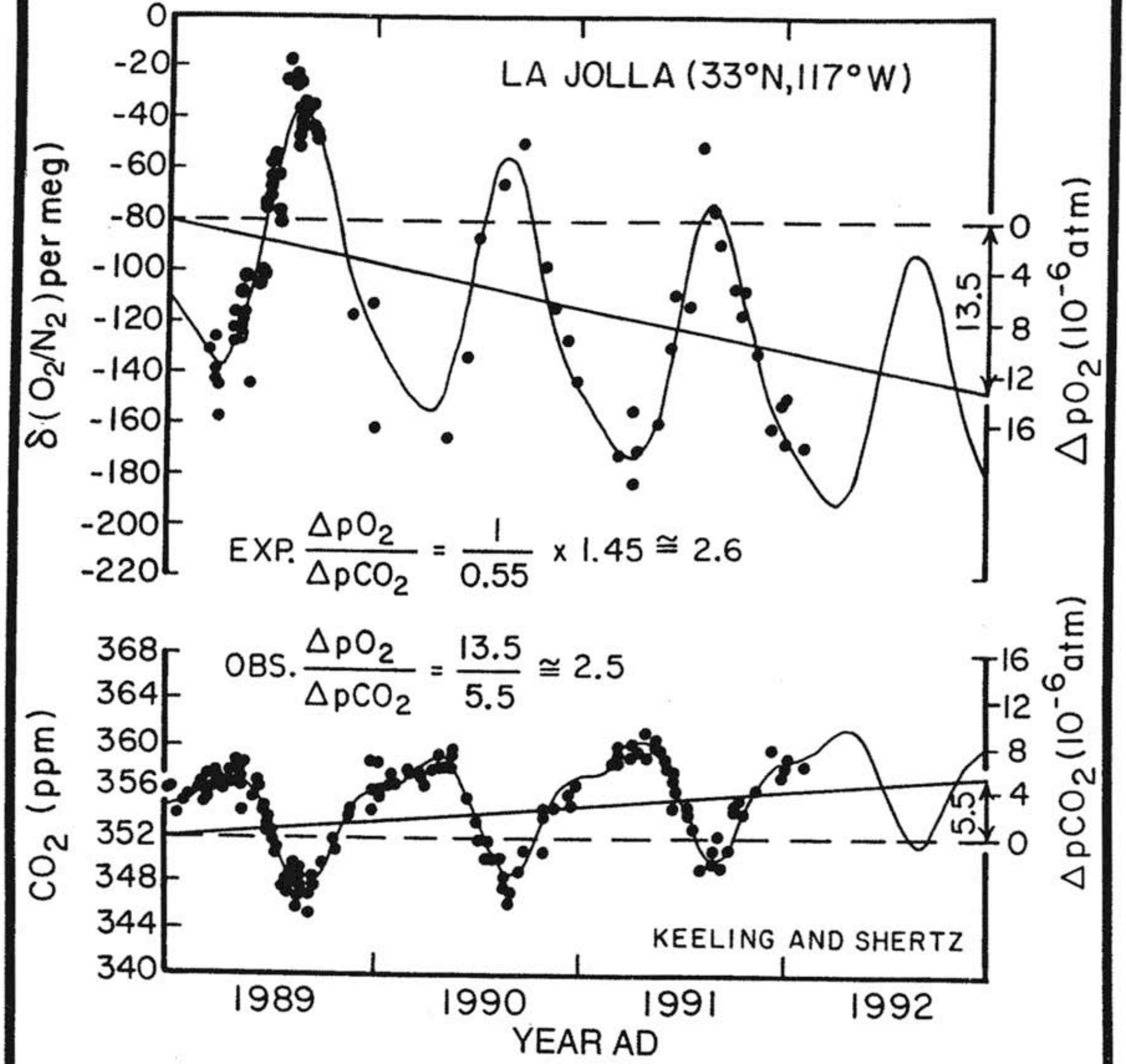
For natural gas, the ratio is 2 to 1.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The current global mix of these three fuels requires the consumption of 15 molecules of O_2 for each 10 molecules of CO_2 produced. The mirror image strategy is a simple one. The measured rate of O_2 decline is compared with that expected from the amount of fossil fuels consumed. One might ask what advantage this information would have over that obtained from comparing the observed rate of rise in atmospheric CO_2 content with the expected rate. There is a very important difference. While the ocean is capable of absorbing five sixths of all the CO_2 we have produced (and thereby constitutes a very important term in the carbon budget), no comparable term exists in the O_2 budget. The reason is that 95 percent of the earth's O_2 resides in the atmosphere and only 5 percent in the ocean. The tiny amount of O_2 which will flow from the ocean back to the atmosphere to compensate for the loss through fossil fuel burning is unimportant in the O_2 budget. Thus O_2 budgeting is far simpler than CO_2 budgeting. Dead simple in fact. The difference between the observed rate of O_2 disappearance and that expected from fossil fuel burning provides a measure of the rate of change in the overall global biomass. For each molecule of CO_2 released to the atmosphere through deforestation, about one molecule of O_2 disappears. For each unit atom of carbon stored in wood or humus as the result of global greening, about one molecule of O_2 will be released to the atmosphere. Thus if more O_2 is disappearing than required for fossil fuel combustion, then the biosphere as a whole must be shrinking. Or if less O_2 is disappearing than required for fossil fuel burning, then the biosphere must be expanding.

But two difficulties remain. As already discussed, the biospheric carbon inventory is being influenced in opposing ways by man. Farmers and foresters are

COMPARISON BETWEEN ATMOSPHERIC CO_2 AND O_2 RECORDS

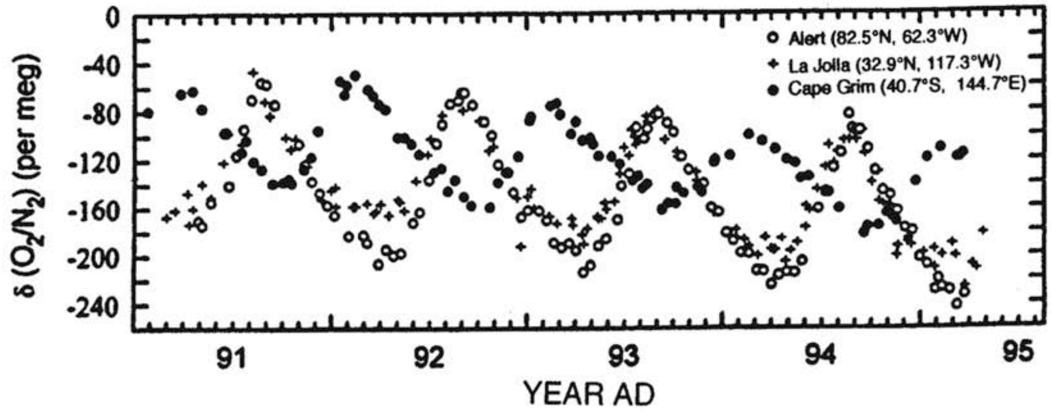


reducing its size. Greening by excess CO_2 and fixed nitrogen is increasing its size. So, for example, were measurements to reveal that O_2 is declining exactly in accord with expectation from fossil fuel burning, it would mean that losses driven by forestry and agriculture were, by chance, just balanced by gains driven by greening. In order to reach our goal of establishing how much greening is occurring, it is necessary to quantify reduction in wood and humus stocks.

The second obstacle is one of measurement. In 1997, the atmosphere contained 364 ppm CO_2. Two years from now, it will contain 367 ppm. This increase can be documented precisely with modern instrumentation. By contrast, the atmosphere contains about 209,000 ppm of O_2. The expected drop during the same two-year period from fossil fuel burning alone is about 5 ppm. This represents a change of only 0.0025%; a daunting challenge to even the most clever experimentalist.

The second challenge was not met until 1989 when Ralph Keeling succeeded in developing a method capable of determining changes in the O_2 content in air to an accuracy of 0.8 ppm. Then, working together with his colleague Shertz, he succeeded in demonstrating that over the three-year period from 1989 to 1992, the O_2 content of air in La Jolla, California dropped at a rate consistent with that expected from global fossil fuel burning. However, at that point the uncertainty in this result was big enough to permit the possibility that the biosphere was either shrinking or expanding at a rate up to 2 gigatons a year. As this range covers virtually all possible scenarios, this early measurement series didn't help much. But as the years clicked by, Keeling's O_2 measurements began to pay off. In fact, he has been able to document an amazing occurrence. Between 1989 when his measurement series began and 1995, the O_2 content of the atmosphere dropped considerably less than would be expected. Taken together with the rise in CO_2 over this period, this shortfall in the magnitude of the O_2 decline indicates that during this period the split of fossil fuel CO_2 flow was 35% to atmosphere, 35% to the ocean, and 30% to the biosphere. This came as a big surprise indicating that

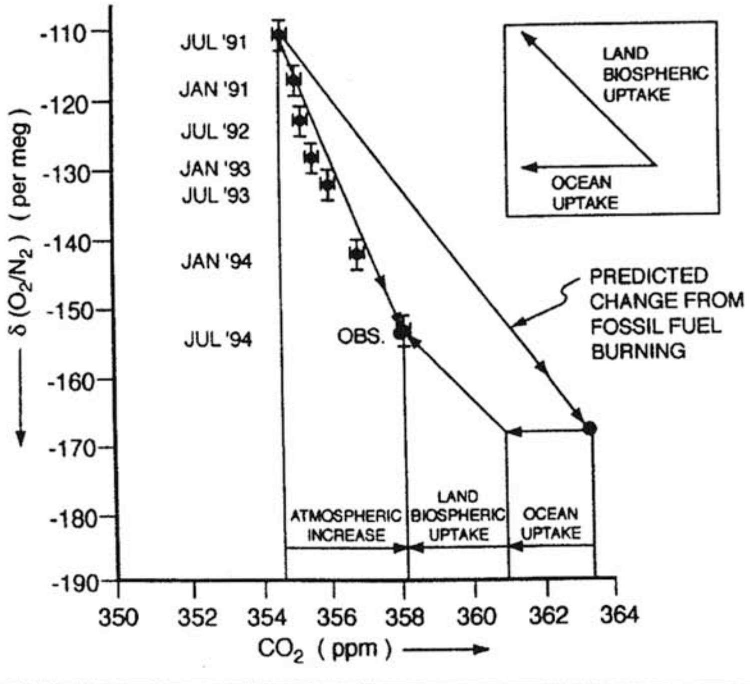
O_2 - CO_2 SYSTEMATICS



$$\delta \frac{O_2}{N_2} = \left(\frac{O_2/N_{2\,SAMP}}{O_2/N_{2\,STD}} - 1\right) \times 10^6$$

4.8 per meg = 1 μatm O_2

PO_2 = 209,500 μatm



the biosphere was taking up an average of about two gigatons of carbon per year during this time interval. If, for example, forest cutting was releasing one gigaton of carbon per year, this would require a greening of roughly three gigatons a year! We will return to this finding later in this section, but before going on, it must be stated that this rate of greening need not be entirely or even largely anthropogenic. Rather, it might reflect unusually favorable growth conditions across the globe. Even though averaged over many years, respiration must match growth; a pulse in global photosynthesis over a several year period could temporarily outstrip respiration. It is likely that such a pulse occurred in the early 1990s. If so, then respiration will soon gain the upper hand and eliminate this short term excess storage. This finding emphasizes the need for a record of sufficient duration so that the influence of changes in global photosynthesis induced by short term climate changes can be averaged out.

Shortly after Keeling developed his index of refraction technique for precise O_2/N_2 ratio measurement, Sowers and Bender came up with a nearly as precise a means to accomplish this task using conventional mass spectrometry. Impatient with the prospect of the long wait for a definitive result, they developed a hindcasting method. It involves getting air samples from deep in the 70 or so meter thick layer of firn which caps the Antarctic and Greenland ice caps. Firn is partially lithified snow which has open pores which provide access to the overlying atmosphere. But diffusion of gases through this matrix is so slow that the gas deep in the firn is replaced only once per decade or so. The first measurements by Sowers and Bender showed that indeed air from deep in the firn had a higher O_2/N_2 ratio than that in the atmosphere. It also had lower methane and carbon dioxide contents. As the evolution of the methane and carbon dioxide contents of the atmosphere over the last decade or so are well documented, these measurements served to fix the average age for any given sample of firn air. Based on this age and the O_2/N_2 ratio, Sowers and Bender hoped to obtain a rate of O_2 decline for decades past. But again the uncertainty in these preliminary measurements is too great to provide a definitive answer. The reason is that despite the 5 times greater length of the Sowers-Bender record, the measurement uncertainty is considerably larger. While firn provides a superb storage environment in that it is very cold, very dry, free of bacteria, and immune to contamination from underlying earth gas, it is not perfect. The long residence time of gas in the firn allows preferential settling of heavy molecules relative to light ones. As O_2 (mass 32) is heavier than N_2 (mass 28), this settling alters the ratio of interest. Sowers and Bender were, however, armed with a means to correct for this gravitational settling effect. They measured the ratio of $^{15}N^{14}N$ (mass 29) to $^{14}N^{14}N$ (mass 28) in the same samples and used the enrichment of the heavy nitrogen molecule as a basis to correct for the gravitational enrichment of O_2 relative to N_2.

As the record in firn extends back only 10 to 20 years, in order to be successful the Sowers and Bender approach will have to be extended beyond the base of the firn into the underlying ice. In attempting this extension, they have encountered a serious problem. As the bubbles of trapped gas closed off, air diffuses in and out of the tiny residual orifices creating a small separation between O_2 and N_2. In an attempt to develop a means to correct for this separation, Jeff Severinghaus and Michael Bender are currently measuring the Ar to N_2 ratios as well as the O_2 to N_2 ratios in firn and ice. So the question is whether the hares (Bender and coworkers) springing rapidly back time can put aside potential biases created by ice storage and beat out the tortoises (Keeling and coworkers) who are forced to plod along one year at a time. Clearly, however, both results are of extreme importance. One will give information about the state of the biosphere during the coming decades, and the other about its state during past decades.

Ocean Uptake

Another way to approach carbon budgeting is to estimate without the use of O_2 data the uptake of CO_2 by the ocean. Once this term has been defined, then change in the Earth's biomass can be calculated by subtracting the CO_2 increases in the ocean and atmosphere reservoirs from the total amount of CO_2 produced by man's activities. The first point to be made in this regard is that ocean uptake cannot, at present, be estimated from the results of repeated $\sum CO_2$ inventories. Unlike the atmosphere for which a combination of measurements on air bubbles stored in ice (prior to 1958) and direct sampling (after 1958) provide a complete record of the inventory's evolution, we have no equivalent for the ocean. The first detailed and accurate global survey of the dissolved inorganic carbon content of ocean water ($\sum CO_2$) was made during the 1970s as part of the GEOSECS (Geochemical Ocean Sections Study) expeditions. But even these measurements were not of sufficient accuracy to provide an adequate base for future surveys. The problem is that even for waters which have taken up their full component of excess CO_2, the increase in $\sum CO_2$ since the 1970s has only been about one percent. The accuracy of the GEOSECS measurements is no better than 0.5%. Of course, the situation is even less favorable for sub-surface waters which have achieved only a fraction of their uptake capacity. Because of this, the direct inventory approach is at present hopeless.

During the 1990's, a far more detailed and accurate (to ±0.1%) survey was made under the banner of the global WOCE (World Ocean Circulation Experiment) program. If a similar survey is conducted 15 to 25 years hence, it will then be possible for the first time to directly measure the integrated CO_2 uptake by the ocean. But of course this result will apply only to the time between the two surveys.

In the interim, the amount of excess CO_2 which has entered the ocean must be obtained by less direct means. One approach involves ocean models designed to take into account not only the thermodynamic capacity of sea water for the uptake of excess CO_2 but also the two kinetic barriers to its uptake, namely, the resistance posed by transport across the air-sea interface and the resistance posed by vertical mixing within the sea. These models are initialized so as to be at steady state with the pre-industrial atmosphere ($pCO_2 = 280\ \mu$atm). Then the model's atmospheric CO_2 content is time stepped to follow the observations. After each step, CO_2 is exchanged between the

THERMODYNAMIC CAPACITY FOR CO_2 UPTAKE

IDEALIZED SEA WATER (NO BORATE)

CHARGE BALANCE

$$[Na^+]+[K^+]+2[Mg^{++}]+2[Ca^{++}]=[Cl^-]+2[SO_4^=]+[HCO_3^-]+2[CO_3^=]$$

OR

$$[Na^+]+[K^+]+2[Mg^{++}]+2[Ca^{++}]-[Cl^-]-2[SO_4^=]=[HCO_3^-]+2[CO_3^=]$$

OR

$$[\text{ALKALINITY}]=[HCO_3^-]+2[CO_3^=]$$

MASS BALANCE FOR DISSOLVED INORGANIC CARBON

$$[\Sigma CO_2]=[CO_2]+[HCO_3^-]+[CO_3^=]$$

CHEMICAL EQUILIBRIUM

$$CO_2+CO_3^=+H_2O \Longleftrightarrow 2HCO_3^-$$

$$K_c' = \frac{[HCO_3^-]^2}{[CO_2][CO_3^=]} \quad , \quad \alpha = \frac{[CO_2]}{pCO_2} = 0.342\ \frac{\mu mol/kg}{\mu atm}$$

EXAMPLE T = 18°C S = 35‰ $K_c' = 1445$ ALK = 2100

$pCO_2 = 280\mu atm$	$pCO_2 = 360\mu atm$	Δ
$[CO_2]$ = 9.6	$[CO_2]$ = 12.3	+2.6 μmol/kg
$[HCO_3^-]$ = 1700	$[HCO_3^-]$ = 1769	+69 μmol/kg
$[CO_3^=]$ = 200	$[CO_3^=]$ = 166	-34 μmol/kg
$[ALK]$ = 2100	$[ALK]$ = 2100	0 μmol/kg
$[\Sigma CO_2]$ = 1910	$[\Sigma CO_2]$ = 1948	+38 μmol/kg

$$\text{REVELLE FACTOR} = \frac{\Delta pCO_2/pCO_2}{\Delta\Sigma CO_2/\Sigma CO_2} = \frac{80/280}{38/1910} = 14.4$$

ACTUAL SEA WATER (INCLUDING BORATE)

CHARGE BALANCE

$$[\text{ALKALINITY}] = [HCO_2^-] + 2[CO_3^=] + [H_4BO_4^-]$$

MASS BALANCE BORON

$$[\Sigma B] = [H_3BO_3^0] + [H_4BO_4^-] = 410.6\frac{S}{35}\,\mu\text{mol/kg}$$

CHEMICAL EQUILIBRIUM

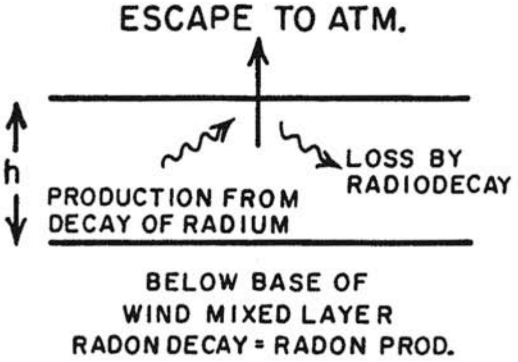
$$K_B' = \frac{[H_4BO_4^-][HCO_3^-]}{[H_3BO_3^0][CO_3^=]}$$

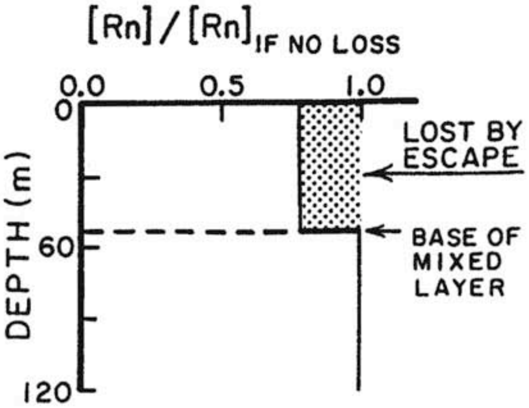
EXAMPLE $T = 18°C$ $S = 35‰$ $K_C' = 1482$ $K_B' = 2.75$
$ALK = 2216$ $SiO_2 = 0$ $NO_3 = 0$ $PO_4 = 0$

$pCO_2 = 280\,\mu atm$	$pCO_2 = 360\,\mu atm$	Δ
$[CO_2]$ = 9.6	$[CO_2]$ = 12.3	+2.6 µmol/kg
$[HCO_3^-]$ = 1702.5	$[HCO_3^-]$ = 1779.5	+77.0 µmol/kg
$[CO_3^=]$ = 203.7	$[CO_3^=]$ = 173.1	-30.6 µmol/kg
$[\Sigma CO_2]$ = 1915.8	$[\Sigma CO_2]$ = 1964.9	+49.1 µmol/kg
$[H_3BO_3^0]$ = 308.9	$[H_3BO_3^0]$ = 323.9	+15.0 µmol/kg
$[H_4BO_4^-]$ = 101.7	$[H_4BO_4^-]$ = 86.7	-15.0 µmol/kg
$[\Sigma B]$ = 410.6	$[\Sigma B]$ = 410.6	0.0 µmol/kg
$[OH^-]$ = 4.4	$[OH^-]$ = 3.6	-0.8 µmol/kg
$[ALK]$ = 2216.0	$[ALK]$ = 2216.0	0.0 µmol/kg

$$\text{REVELLE FACTOR} = \frac{\Delta pCO_2/pCO_2}{\Delta\Sigma CO_2/\Sigma CO_2} = \frac{80/280}{49.1/1915.8} = 11.1$$

AIR -SEA CO_2 EXCHANGE BASED ON RADON





$$\frac{[Rn]_{\text{MIXED LAYER}}}{[Rn]_{\text{NO LOSS}}} = \frac{\text{PROBABILITY OF RADIODECAY}}{\text{PROB. OF RADIODECAY} + \text{PROB. OF ESCAPE}}$$

PROBABILITY OF DECAY ($t_{1/2}^{\text{RADON}} = 3.85$ days = 92.4 hours)

$$\lambda_{Rn} = \frac{1}{\tau_{Rn}} = \frac{.693}{t_{1/2}} = 7.5 \times 10^{-3}\,\text{hr}^{-1} \text{ or } \tau_{Rn} = 133 \text{ hours}$$

PROBABILITY OF ESCAPE

$$\lambda_{\text{ESCAPE}} = \frac{\text{PISTON VELOCITY}^{*}}{\text{MIXED LAYER THICKNESS}} = \frac{v}{h} \text{ or } \tau_{\text{ESCAPE}} = \frac{h}{v}$$

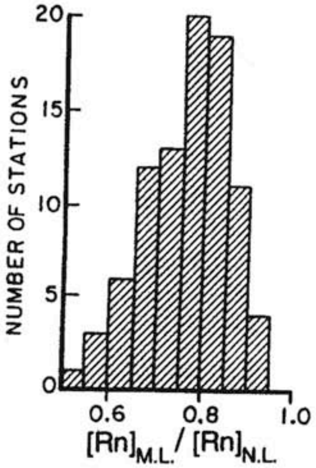
ASSUMES

1) STEADY STATE (*i.e.* [Rn] IN MIXED LAYER REMAINS CONSTANT WITH TIME)
2) NO EXCHANGE OF WATER ACROSS BASE OF MIXED LAYER (*i.e.* NO REPLACEMENT OF ESCAPING RADON FROM BELOW)

$$\frac{[Rn]_{\text{MIXED LAYER}}}{[Rn]_{\text{NO LOSS}}} = \frac{\lambda_{Rn}}{\lambda_{Rn} + v/h}$$

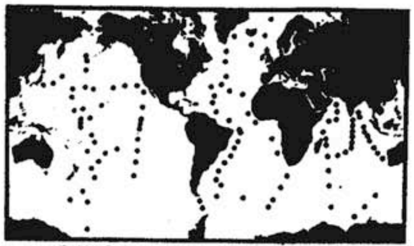
$$v = \lambda_{Rn} h \left(\frac{1 - [Rn]_{\text{M.L.}}/[Rn]_{\text{N.L.}}}{[Rn]_{\text{M.L.}}/[Rn]_{\text{N.L.}}} \right)$$

THE AVERAGE OF MEASUREMENTS AT 90 STATIONS SHOW



$h_{MEAN} = 54$ meters

$$\frac{[Rn]_{MIXED\ LAYER}}{[Rn]_{NO\ LOSS}} = 0.77$$



GEOSECS STATIONS

YIELDS A PISTON VELOCITY* OF

$$v = 7.5 \times 10^{-3} \times 54 \times \frac{1-0.77}{0.77}$$

$$= 0.12\ \frac{\text{meters}}{\text{hr}} = 2.9\ \frac{\text{meters}}{\text{day}}$$

APPLYING THIS RESULT TO CO_2 WE GET

$$I_{CO_2} = \frac{[CO_2]}{p_{CO_2}}\ v \left(\frac{D_{CO_2}}{D_{Rn}}\right)^{1/2} \leftarrow \text{RATIO OF MOLECULAR DIFFUSIVITIES} \leftarrow (1.36)^{1/2}$$

$$\left.\frac{[CO_2]}{p_{CO_2}}\right)_{\text{AT MEAN SURFACE WATER TEMPERATURE}} \cong 5.0 \times 10^{-5}\ \frac{\text{mol/m}^3}{\mu\text{atm}}$$

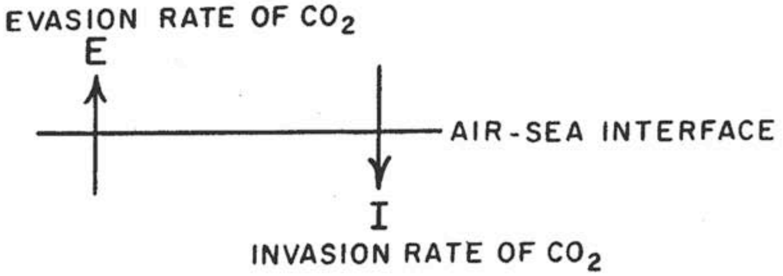
$$v = 2.9\ \frac{\text{meters}}{\text{day}} = 2.9 \times 365\ \frac{\text{meters}}{\text{year}}$$

$$I_{CO_2} = 5.0 \times 10^{-5} \times 2.9 \times 365 \times (1.36)^{1/2}$$

$$= 0.062\ \text{mol/m}^2\ \text{yr}\ \mu\text{atm}$$

* THE VELOCITY OF IMAGINARY PISTONS, ONE MOVING UPWARD PUSHING BEFORE IT GAS AT THE MIXED LAYER CONCENTRATION AND ONE MOVING DOWNWARD PUSHING BEFORE IT GAS AT THE ATMOSPHERIC EQUILIBRIUM CONCENTRATION.

AIR-SEA CO_2 EXCHANGE BASED ON NATURAL RADIOCARBON



ASSUMES:

1) PRIOR TO 1850, E $\cong$ I (*i.e.* THE SEA WAS NEITHER A SOURCE NOR A SINK FOR CO_2)
2) PRIOR TO 1850 THE ^{14}C DISTRIBUTION WAS IN STEADY STATE (*i.e.* RADIOACTIVE DECAY OF ^{14}C WITHIN THE SEA ABOUT BALANCED THE INPUT OF ^{14}C ATOMS ACROSS THE AIR-SEA INTERFACE)

THEN:

INVASION OF ^{14}C INTO SEA	$\cong$	EVASION OF ^{14}C FROM SEA	+	DECAY OF ^{14}C WITHIN SEA

$$\left.\frac{^{14}C}{C}\right)^{1850}_{ATM} I A_{SEA} \cong \left.\frac{^{14}C}{C}\right)^{MEAN}_{\substack{SURF\\SEA}} I A_{SEA} + \left.\frac{^{14}C}{C}\right)^{MEAN}_{SEA} \left[\Sigma CO_2\right]^{MEAN}_{SEA} V_{SEA}\, \lambda_{^{14}C}$$

OR

$$I \cong \frac{\left.\frac{^{14}C}{C}\right)^{MEAN}_{SEA} \Big/ \left.\frac{^{14}C}{C}\right)^{1850}_{ATM}}{1 - \left[\left.\frac{^{14}C}{C}\right)^{MEAN}_{\substack{SURF\\SEA}} \Big/ \left.\frac{^{14}C}{C}\right)^{1850}_{ATM}\right]} \left[\Sigma CO_2\right]^{MEAN}_{SEA} \frac{V_{SEA}}{A_{SEA}} \frac{1}{\tau_{^{14}C}}$$

$$\left.\frac{^{14}C}{C}\right)_{SEA}^{MEAN} \Big/ \left.\frac{^{14}C}{C}\right)_{ATM}^{1850} \cong 0.85$$

$$\left.\frac{^{14}C}{C}\right)_{\substack{SURF\\SEA}}^{MEAN} \Big/ \left.\frac{^{14}C}{C}\right)_{ATM}^{1850} \cong 0.95$$

$$\frac{V_{SEA}}{A_{SEA}} = \frac{13.7 \times 10^{17}\,m^3}{3.6 \times 10^{14}\,m^2} = 3800\,\text{meters}$$

$$\tau_{^{14}C} = \frac{1}{\lambda^{14}C} = \frac{t_{1/2}}{.693} = 8270\,\text{years}$$

$$\left[\Sigma CO_2\right]_{SEA}^{MEAN} = 2.2\,\text{mol/m}^3$$

$$I = \frac{0.85}{1-0.95} \times 2.2 \times \frac{3800}{8270}$$

$$= 17.2\,\text{mol/m}^2\,\text{yr}$$

$$pCO_2^{1850} = 280\,\mu\text{atm}$$

$$I = 0.061\,\text{mol/m}^2\,\text{yr}\,\mu\text{atm}$$

PROBABLE UNCERTAINTY ± 25% ENTIRELY DUE TO UNCERTAINTY IN $^{14}C/C)_{SURF\ SEA}^{MEAN}$

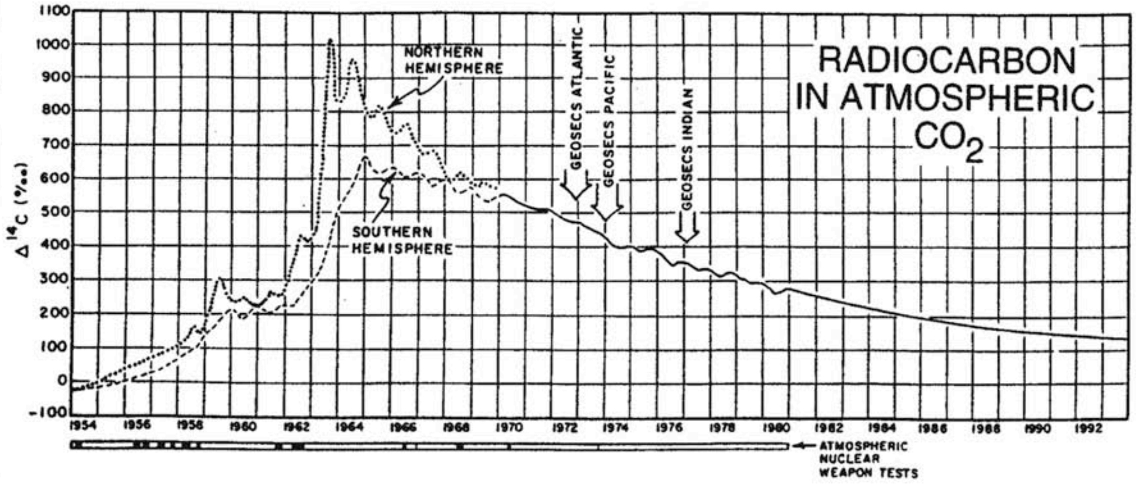
atmosphere and surface ocean and mixing occurs within the ocean. The output of the model is the evolution of the storage of excess CO_2 in the ocean.

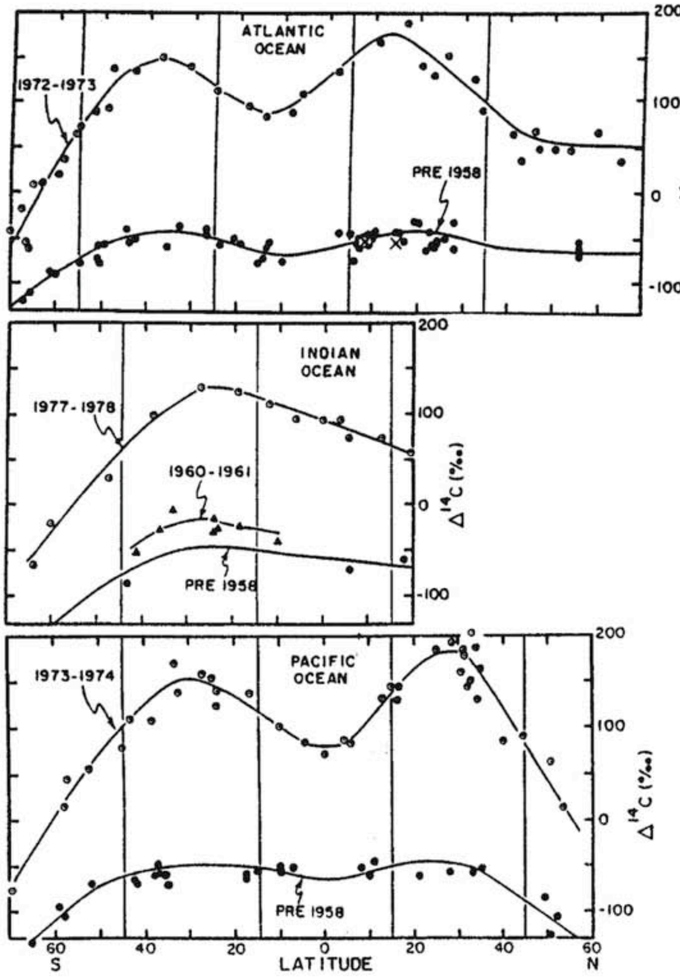
The models used for this purpose are of two types, tracer-calibrated reservoir models and atmosphere-driven dynamic models. As the reservoir models are far simpler in design, it makes best sense to discuss them first. In these models, no attempt is made to duplicate the physics associated with either air-sea gas exchange or mixing within the sea. Rather, these transports are represented by transfer coefficients. The magnitudes of these coefficients are chosen to provide the best possible match to the distribution of transient tracers whose distributions within the sea have been measured. The secret of success in this endeavor is to keep the architecture of the model as simple as possible. In this way, the number of variable parameters can be kept to a minimum. In the absence of any dynamics, such models are merely vehicles to permit the measured distributions of transients (i.e., those of bomb produced ^{14}C and ^{3}H and of industrially produced CFCs) to be used as analogues for transients whose distributions we can't document (i.e., those of anthropogenic CO_2 and greenhouse heat). In our estimation, the most successful of these models is that proposed by the Swiss scientists, Hans Oeschger and the late Uli Siegenthaler. Their model is one dimensional consisting of a well-mixed atmosphere and a two box ocean. The upper ocean box represents the wind-stirred upper ocean layer. The lower box represents the remainder of the ocean as a semi-infinite half space (it does not have to have a base because neither the calibration tracers nor the anthropogenic CO_2 reach the 3800 meter-mean depth of the real ocean). Transport through the semi-infinite half space is accomplished by a mixing process mathematically analogous to molecular diffusion. Oceanographers refer to it as "eddy diffusion". In such a model, only three parameters need to be defined: the thickness of the upper-ocean wind-mixed layer, the exchange rate of CO_2 gas between the ocean and atmosphere, and the coefficient of eddy diffusion within the main body of the ocean. The first of these is usually set at value, consistent with observation of the measured mean thickness of wind-stirred layer which everywhere caps the ocean. As discussed below, the assignment of the air-sea CO_2 exchange rate is obtained in three independent ways: i.e., radon deficiencies measured in the oceanic-mixed layer and on the distributions of natural and bomb-produced radiocarbon. These three estimates are broadly consistent. The eddy diffusivity is based on measurements of the measured penetration depth of bomb testing tritium and radiocarbon. Again, the two estimates are consistent with one another. This diffusional representation of penetration of water entering into the body of the ocean carries with it the assumption that the extent of vertical mixing varies as the square root of time. This means, for example, that mixing to 700 meters beneath the base of the mixed layer takes four times as long as mixing to 350 meters below this base. As we shall see, this assumption is consistent with the two available calibration targets. The distribution of natural radiocarbon in the ocean tells us that the entire body of the ocean (mean depth 3800 meters) is mixed on a time scale of about one millennium. The distribution of bomb radiocarbon and tritium at the time of the GEOSECS survey tells us that on the time scale of one decade, the mean penetration depth is about 380 meters (about one tenth of the ocean volume). The ratio of these two mixing depths (i.e., ~10) matches the square root of the ratio of the mixing times i.e.,

$$\frac{3800m}{380m} \cong \sqrt{\frac{1000years}{10years}}$$

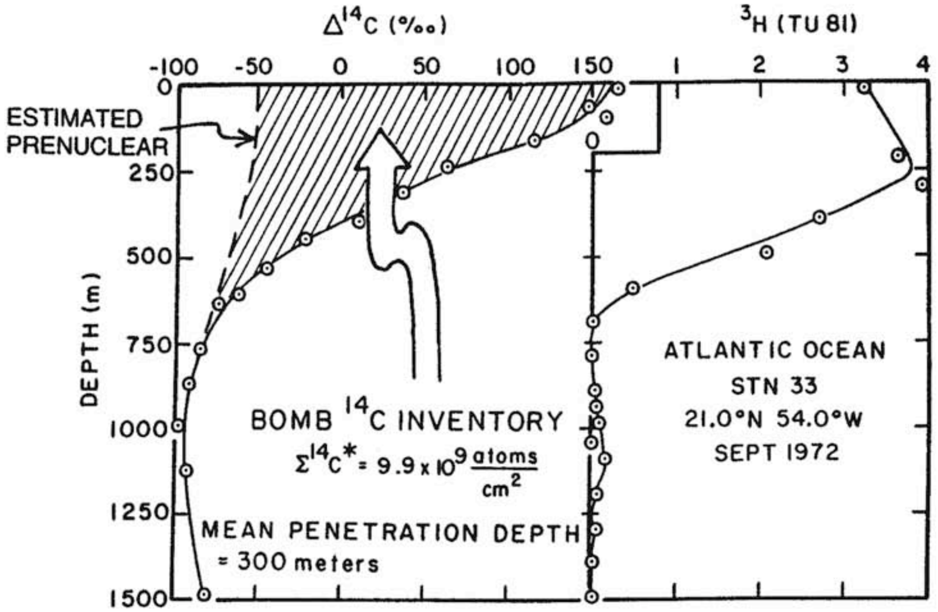
Bomb radiocarbon provides the best tracer for setting both the model's gas exchange rate and its coefficient of vertical eddy diffusion. This tracer was generated as the result of atmospheric H-bomb tests conducted during the 1950s and early 1960s. Neutrons released during these thermonuclear explosions eventually find their way, as do cosmic ray neutrons, into the nuclei of atmospheric nitrogen atoms transforming them to radiocarbon. Most of the products of these blasts were carried into the stratosphere by explosion-generated updrafts. Here the radiocarbon atoms chemically combined with

DISTRIBUTION OF BOMB TEST RADIOCARBON AT THE TIME OF GEOSECS SURVEYS

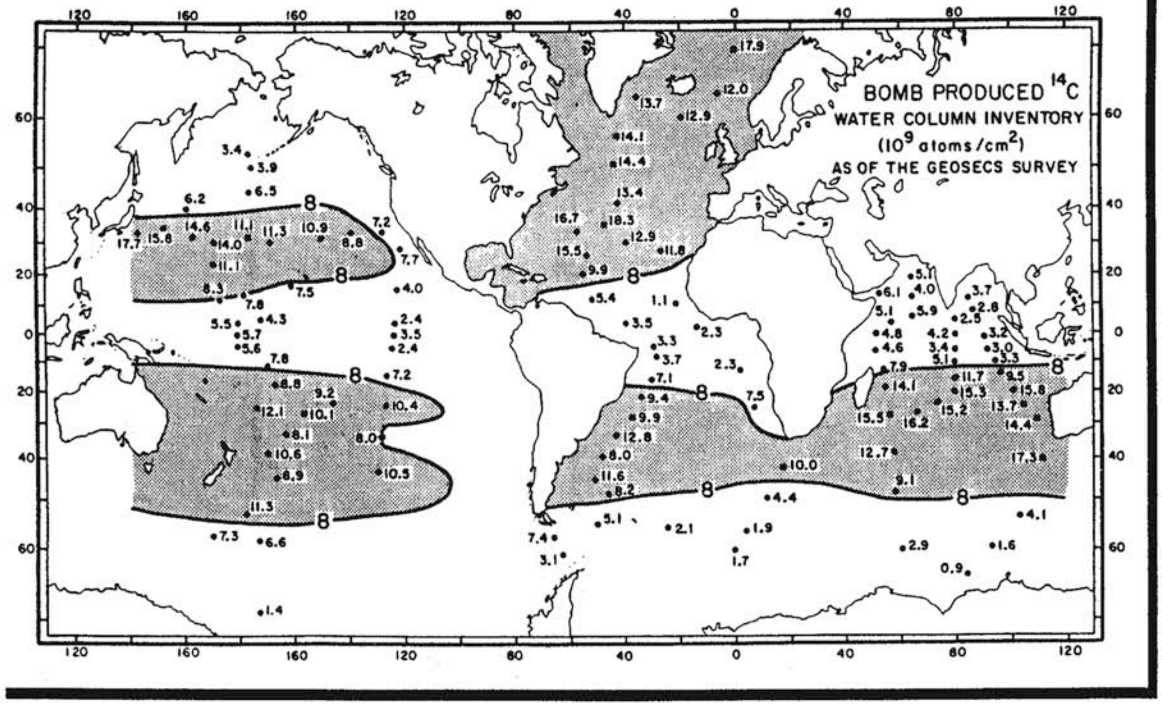




RADIOCARBON IN SURFACE OCEAN WATER ΣCO_2



MEAN PENETRATION DEPTH		
GEOSECS EXPEDITION	BOMB ^{3}H (meters)	BOMB ^{14}C (meters)
Atlantic (1972-3)	591	414
Pacific (1973-4)	336	311
Indian (1977-8)	283	309
World (1972-8)	382	344



oxygen atoms to form $^{14}CO_2$. On the time scale of a few years these tracer molecules mixed downward into the troposphere. Measurements of the ^{14}C to C ratio in CO_2 extracted from ground level air, at a number of places on the planet, thoroughly document the evolution of the resulting tropospheric transient. The $^{14}C/C$ ratio began to climb in 1954. It reached a sharp maximum in mid 1963 shortly after the treaty banning nuclear tests in the atmosphere was implemented. With the cessation of bomb testing, the $^{14}C/C$ ratio in atmospheric CO_2 began a decline which is still in progress. In the northern hemisphere where the tests were conducted, at its maximum, the $^{14}C/C$ ratio in tropospheric CO_2 reached almost twice its pre-nuclear value. In the southern hemisphere, the maximum was somewhat smaller and occurred a bit later, reflecting the roughly one-year time constant for interhemispheric mixing. After four or five years, when the distribution had become nearly uniform, all parts of the atmosphere followed the same decline. Now 35 years after the peak, the $^{14}C/C$ ratio has fallen to 11% above the pre-industrial value. The important point is that the bomb ^{14}C atoms which have left the atmosphere now reside in the ocean and in the biosphere and serve as valuable tracers.

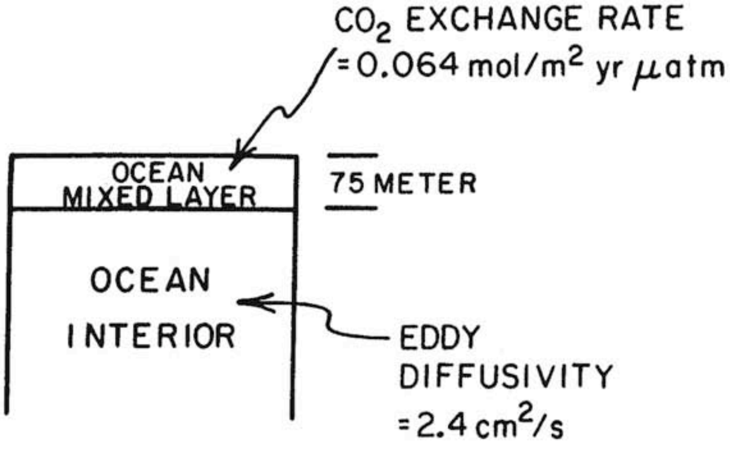
A survey of radiocarbon, encompassing the entire ocean, was conducted during the period 1972-1978 as part of the GEOSECS program. When analyzed together with results of a companion tritium survey, and with radiocarbon measurements on pre-nuclear surface water, it is possible to separate the bomb radiocarbon and the natural radiocarbon components at each station. The distribution of the bomb component is then used to fix the two parameters in the Oeschger and Siegenthaler model. This is accomplished by averaging two important properties of this distribution measured at each station: the bomb ^{14}C to C ratio in surface water and the mean penetration depth of bomb-produced radiocarbon. These two quantities are calculated for each GEOSECS station. They are then globally averaged. The result of this exercise yields an average $^{14}C/C$ ratio for surface water 16% higher at the time of the GEOSECS survey than just prior to nuclear testing and an average penetration depth of 382 meters. These two values become the targets for the calibration of the simple reservoir model. To do this, the model's atmosphere is time stepped to follow both the rise in the atmosphere's CO_2 content and the time history of its ^{14}C to C ratio. The model is run from 1954 (when the bomb ^{14}C rise commenced) to 1975, the mid time for the GEOSECS surveys. Runs are made for a range of choices of both the CO_2 invasion rate and the eddy diffusivity. One set of values best fits both targets. The results obtained in this way are 0.064 moles $CO_2/m^2.yr.\mu atm$ for the CO_2 invasion rate and 2.4 cm^2/sec for the coefficient for eddy diffusion.

Having calibrated the model's free parameters, the next step is to calculate the ocean uptake of fossil fuel CO_2. As for bomb ^{14}C, this is done by time stepping the model's atmosphere to follow the time history of atmospheric CO_2 contents obtained from measurements on ice cores and air samples. Of course, the CO_2 invasion and evasion rates and the eddy diffusivity employed are those obtained from the bomb ^{14}C calibration runs.

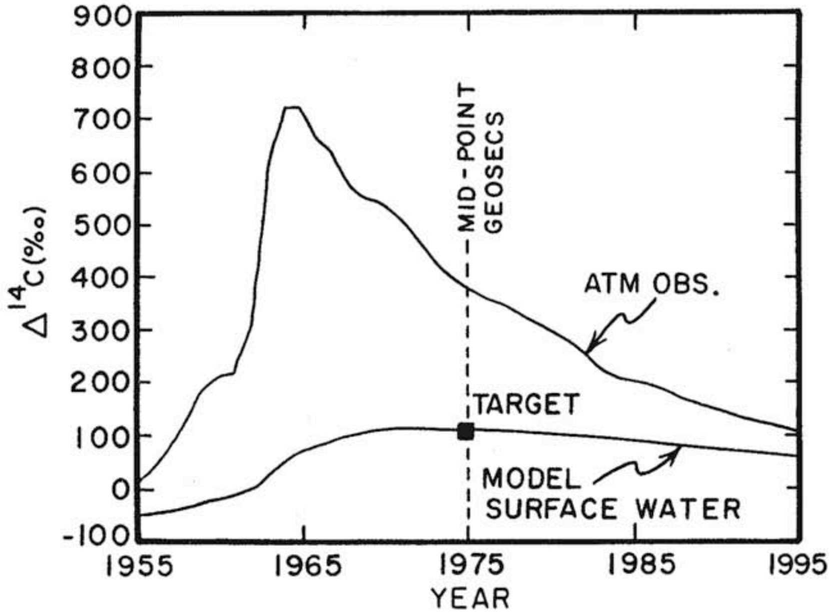
The model yields an ocean uptake of close to 2 gigatons of C per year for the 1980s. When this is combined with the observed atmospheric inventory increase, the fossil fuel input is pretty much accounted for suggesting that the inventory of terrestrial carbon remained more or less constant. In other words, gains resulting from greening more or less matched losses resulting from deforestation and agriculture.

One might ask whether this approach to ocean uptake accounts for CO_2 carried into the deep sea as part of the ocean's thermohaline circulation. The answer is that it does so only to the extent that the bomb radiocarbon carried to the deep sea has been properly accounted for. This accounting is likely quite poor because the bomb ^{14}C component in deep waters is for the most part so small that it cannot be properly identified. But a small signal distributed over a very large volume of deep-sea water could be quite important. Thus the simple box model may underestimate the amount of

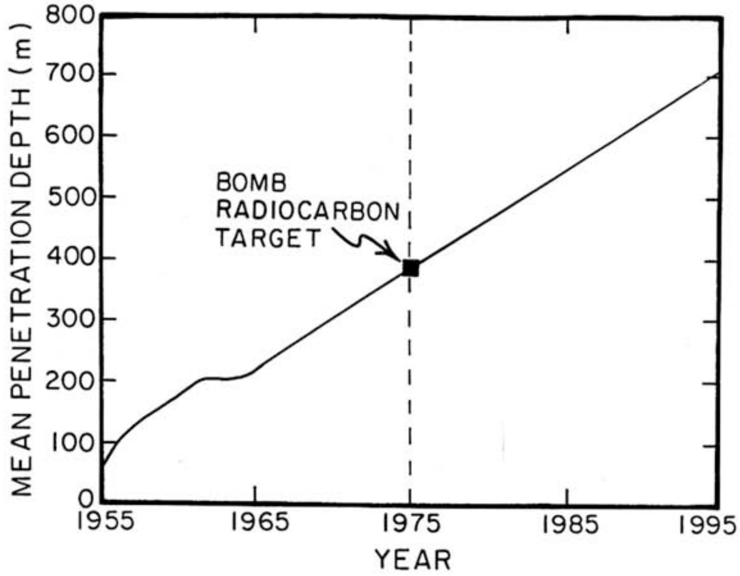
CALIBRATION OF SIMPLE OCEAN MODEL



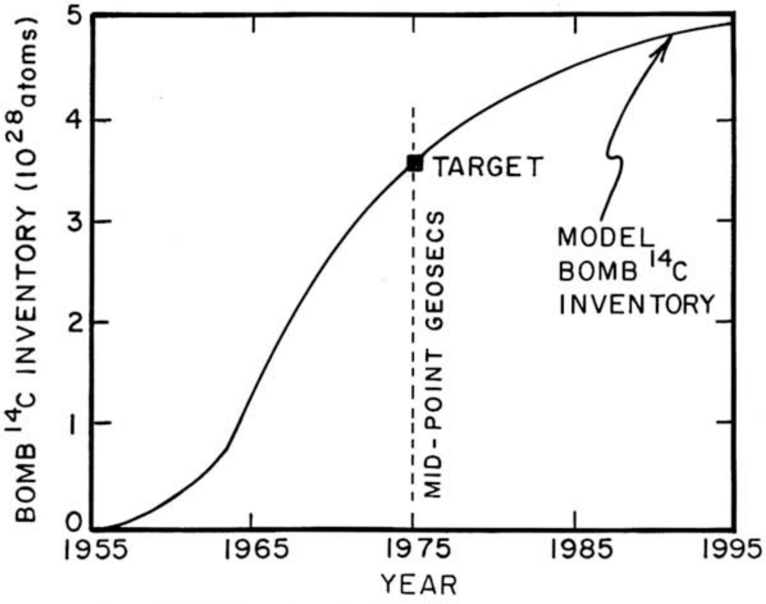
TREND IN SURFACE WATER
$\Delta\ ^{14}C$ CALCULATED USING SIMPLE MODEL



TREND IN MEAN PENETRATION DEPTH CALCULATED USING SIMPLE MODEL



TREND IN BOMB ^{14}C WATER COLUMN INVENTORY CALCULATED USING SIMPLE MODEL



CO_2 taken up by the sea. To get some idea how large the deep-sea component might be, we can make a separate estimate. The flux of water into the deep sea is thought to be about 30 Sverdrups (i.e., $30x10^6$ m^3/second). As an upper limit, we will assume this water carries with it a full component of excess ΣCO_2 (i.e., it is formed from old deep water free of anthropogenic CO_2 and it fully equilibrates with the atmosphere before descending). If so, then during the mid 1980s when the atmosphere's CO_2 content was about 345 ppm, newly formed deep water carried with it about 40 μmoles/liter of excess ΣCO_2. This yields an upper limit on the input of anthropogenic CO_2 into the deep sea of 0.5 gigatons of carbon per year. But this must be an upper limit because newly formed deep water cannot become fully charged with excess CO_2 during the brief period of winter-time deep convection.

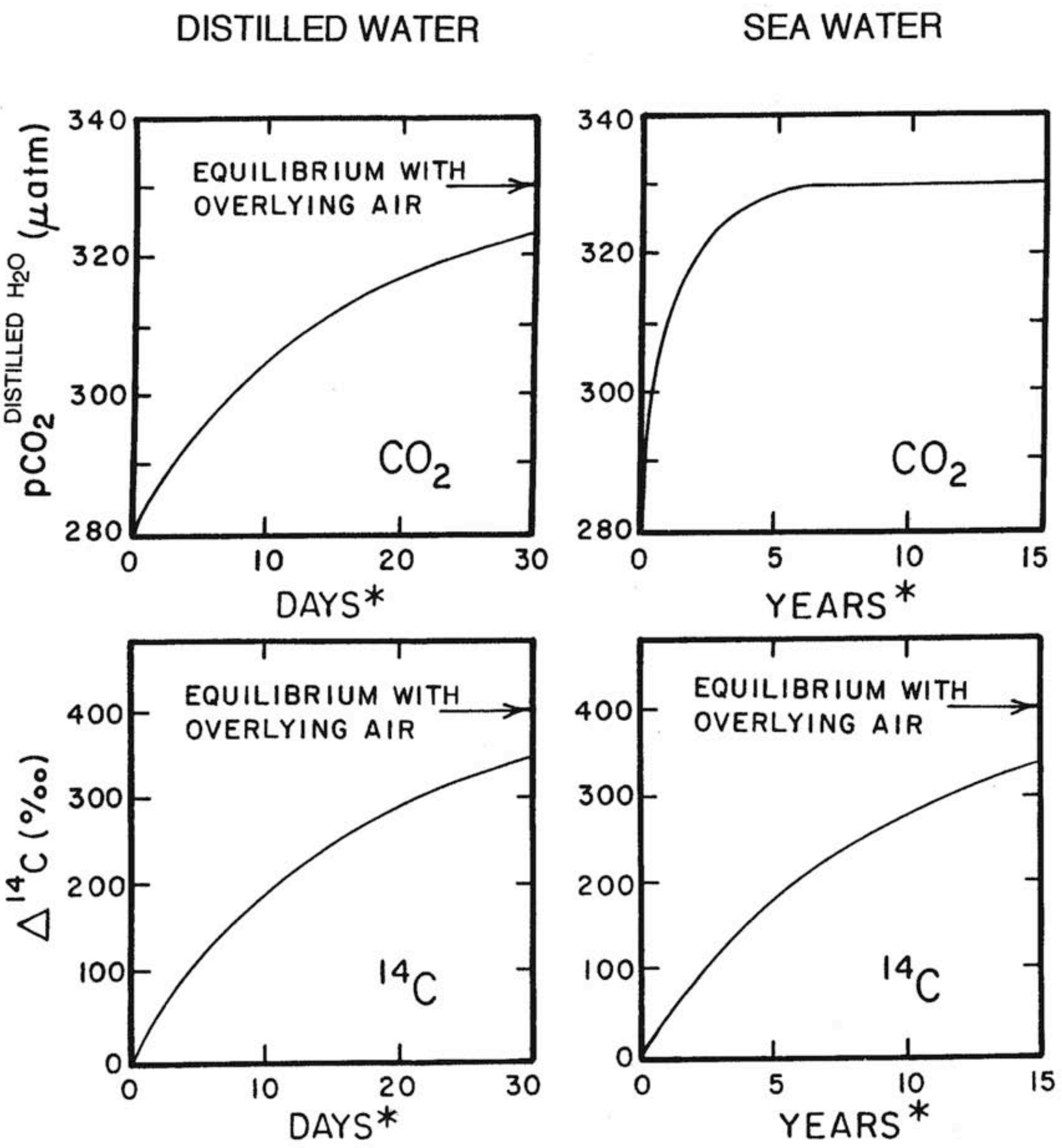
An adequate assessment of the uncertainty in the ocean uptake estimates made using tracer-calibrated one-dimensional (1-D) models is not possible. The main uncertainty comes from the basic assumption that the depth of mixing increases as the square root of time. For fossil fuel CO_2 molecules, the time available for ocean penetration is about 30 years, while for bomb radiocarbon-tagged CO_2, it is about 10 years. Hence the model drives fossil fuel CO_2 about $\sqrt{3}$ or 1.73 times deeper into the sea than bomb ^{14}C-tagged CO_2. As we have no means to directly determine the extent of ventilation of the real ocean on the time scale of 30 years, the appropriate multiplier could perhaps be as low as 1.4 or as high as 2.0. Were these limits to be adopted as a measure of the uncertainty in the ocean uptake, the answer comes out to be ±20% (0.4 gigatons of C per year during the 1980s).

There is a tracer which might be used to overcome the penetration time mismatch between bomb ^{14}C and fossil fuel CO_2. It is the reduction in atmospheric $^{13}C/^{12}C$ ratio due to the introduction of CO_2 produced by fossil fuel burning. This CO_2 has a 2% lower ^{13}C to ^{12}C ratio than that in the atmosphere. Repeated surveys of $^{13}C/^{12}C$ profiles for ocean ΣCO_2 could provide an estimate of the depth of penetration of this signal. As the anthropogenic ^{13}C anomaly is coupled directly to the production of CO_2, no time difference exists. Quay and his colleagues attempted to quantify the redistribution of the anomaly created by the release of ^{13}C deficient fossil fuel CO_2 to the atmosphere by documenting the magnitude of the decline in the $^{13}C/^{12}C$ ratio both for atmospheric CO_2 and for upper ocean $\sum CO_2$ for the period 1970 to 1990. While the uptake they obtained is consistent with that based on the tracer-calibrated 1-D ocean model, due to the large uncertainties in the measured trends, this approach did not narrow the range of uncertainty in the amount of fossil fuel CO_2 taken up by the ocean during this period.

Chemical Versus Isotope Adjustment Time

One aspect of the 1-D model results is, at least at first glance, puzzling. While, as of 1975, the increase in the CO_2 partial pressure in the model's surface mixed layer had reached 85 to 90 percent of the atmospheric increase, the $^{14}C/C$ ratio in surface water had reached only about 50% of the atmospheric increase. Why such a big difference? The obvious answer is that fossil fuel CO_2 molecules had at that time a greater mean age than bomb ^{14}C-tagged CO_2 molecules (30 years versus 12 years). Hence they had a longer time to get into the ocean. However, this is not the major reason. Rather, the slowness of the ^{14}C response has to do with a fundamental difference between the time required for equilibration of carbon isotope anomalies and the time required for the equilibration of chemical anomalies. This difference is most easily understood by considering two hypothetical 75-meter high towers. One is filled with normal sea water and the other with distilled water. The waters in both towers have the same temperature and CO_2 partial pressure (280 μatm). Also the dissolved carbon in both initially has the pre-nuclear $^{14}C/C$ ratio. The major difference is that the distilled water contains no HCO_3^- or $CO_3^=$. The lids are removed from the tower tops and fans are activated so as to generate CO_2 exchange rates of 0.064 moles/m^2.yr.μatm. The question is, "how rapidly will the CO_2 partial pressures and the $^{14}C/C$ ratios in the tower waters approach those for the overlying 1975 air ($pCO_2 = 330$ μatm and $\Delta^{14}C = 400‰$)?" For the distilled water

TWIN TOWERS EXPERIMENT



* NOTE HUGE DIFFERENCE IN TIME SCALES!

tower, both the partial pressure and isotope ratio will approach the atmospheric value with an e-folding time of 15 days. For the sea water tower, the isotope equilibration will take 200 times longer, a staggering 8.2 year e-folding time! The reason for this huge difference is that for the sea water tower, not only the isotopic composition of the 10 μmole/liter of dissolved CO_2 gas has to be exchanged but also that of the 2000 μmole/liter of HCO_3^- and $CO_3^=$ ions.

More tricky to understand is the time constant for the CO_2 partial pressure adjustment in the sea water tower. The e-folding time turns out to be close to one year, lying roughly geometrically between that for the distilled water (.04 yrs.) and that for the isotopes in the sea water ΣCO_2 (8.2 yrs.). The reason is that rise in the CO_2 partial pressure in the sea water involves mainly the adjustment of its $CO_3^=$ concentration. For surface sea water, the $CO_3^=$ concentration is about 10 times lower than the ΣCO_2 concentration and 20 times larger than the CO_2 concentration. With this tower analogy in mind, it is easy to answer our question regarding the difference between the extent of isotope (^{14}C) and chemical (CO_2) equilibration yielded by the 1-D model for the time of the GEOSECS survey. Isotopic equilibration takes ten times longer than chemical equilibration, thus the $^{14}C/C$ ratio rises toward the atmospheric value far more slowly than the CO_2 partial pressure. This factor of ten reflects the ratio of the ΣCO_2 (isotopic reservoir) to $CO_3^=$ (chemical reservoir) in surface sea water.

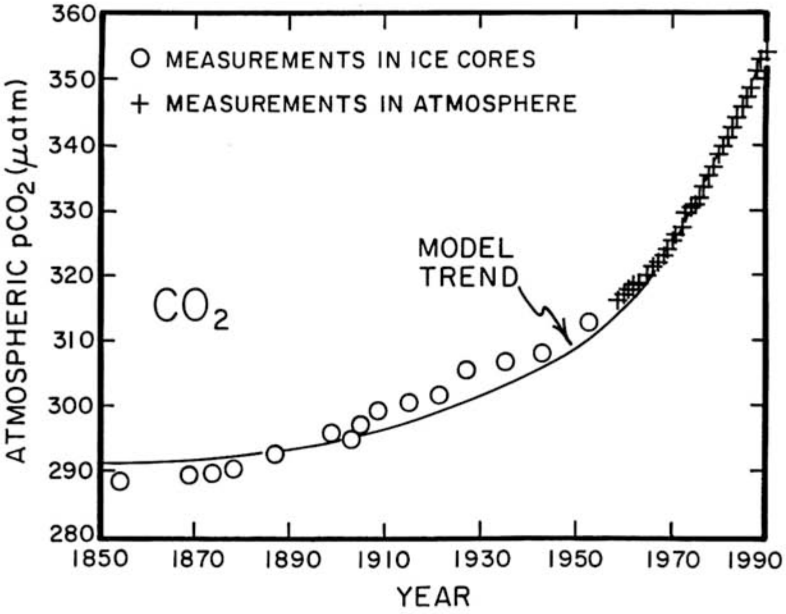
Isotopic Cross Checks

Three cross checks based on carbon isotope measurements can be used to evaluate the performance of the simple model adopted here. The first has to do with the magnitude of the change in the $^{14}C/C$ ratio for atmospheric CO_2 during the hundred-year period from 1850 to 1950 as recorded in tree rings. Because of the advent of bomb testing in the early 1950s, the $^{14}C/C$ lowering approach is viable only for the period before 1950. As the CO_2 generated by fossil fuel burning is free of radiocarbon, the $^{14}C/C$ ratio in atmospheric CO_2 should have decreased during this period. Indeed it did.

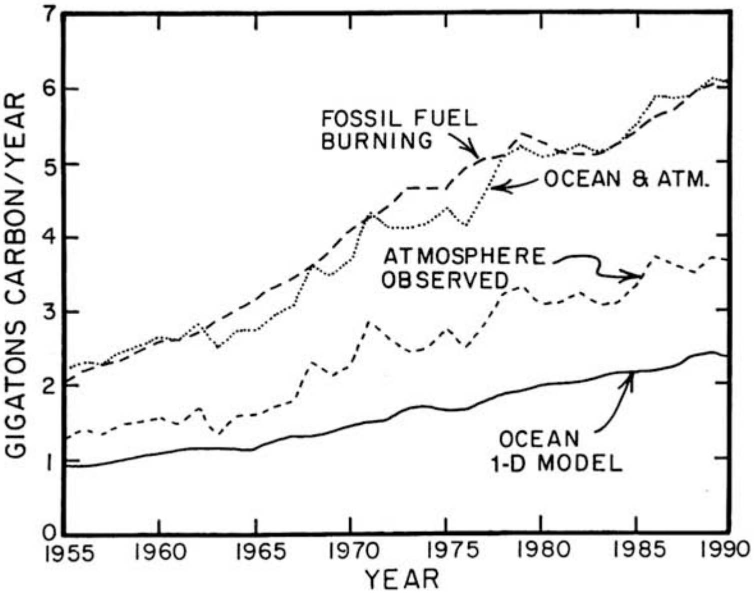
CROSSCHECKS ON THE SIMPLE 1-D MODEL

TREND IN ATMOSPHERIC CO_2 CONTENT

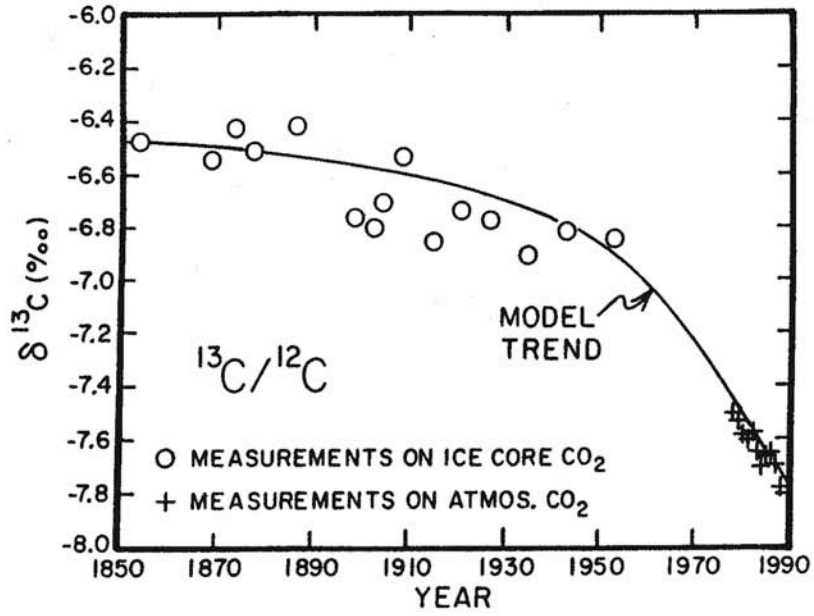
GENERATED WHEN KNOWN CO_2 EMISSIONS ARE ADDED
TO THE COMBINED 1-D OCEAN AND BIOSPHERE MODELS



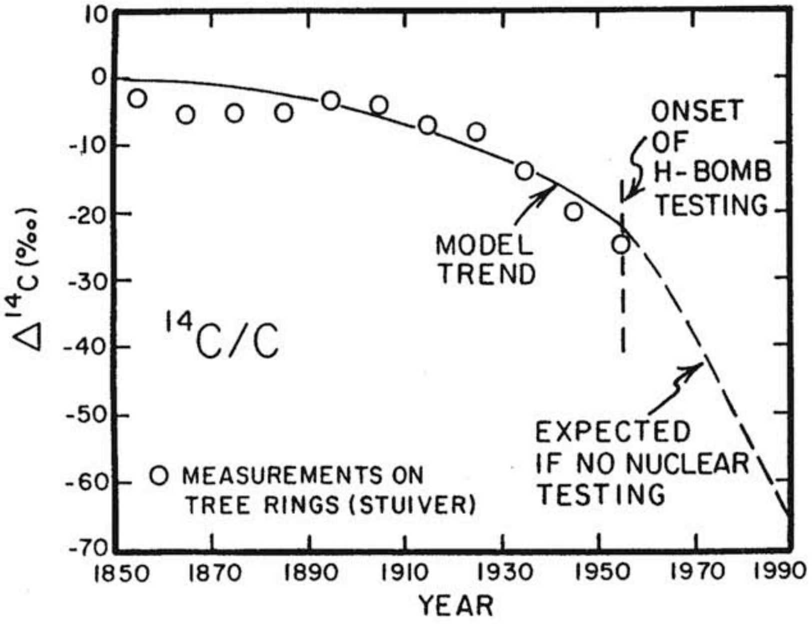
TREND IN OCEAN UPTAKE



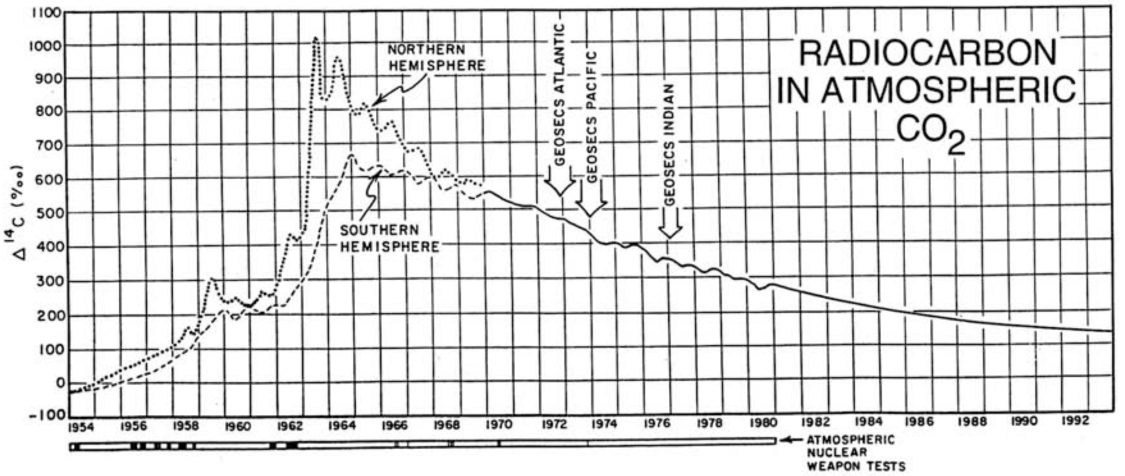
TREND IN ATMOSPHERIC $^{13}C/^{12}C$ RATIO



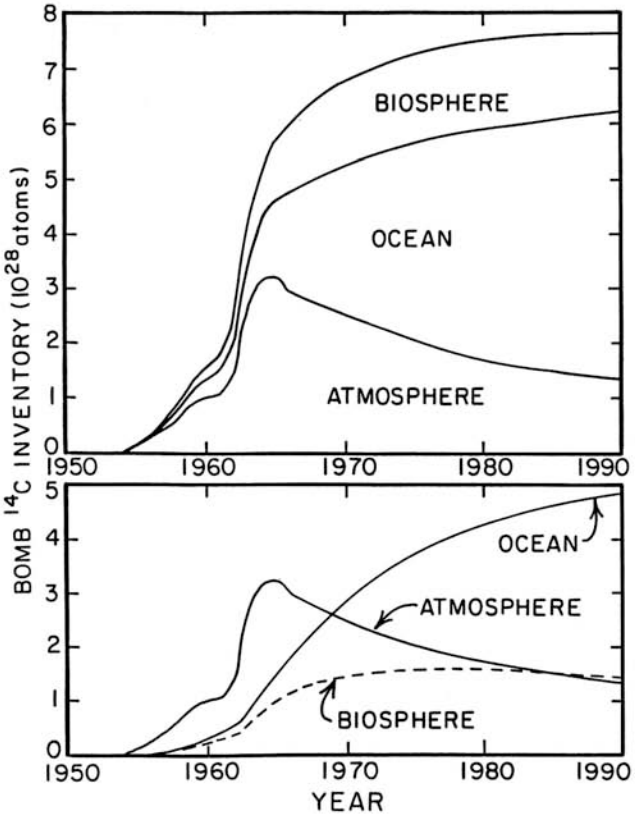
TREND IN ATMOSPHERIC $^{14}C/C$ RATIO



GLOBAL BOMB-RADIOCARBON INVENTORY*



MODEL CALCULATED BOMB ^{14}C INVENTORIES



*EXCLUDING STRATOSPHERIC EXCESS

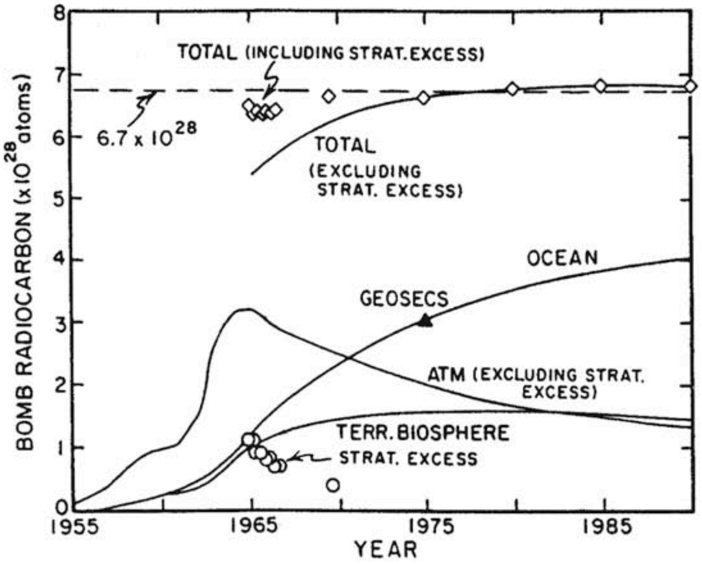
OCEAN BOMB ^{14}C INVENTORY

ESTIMATE OF OCEAN BOMB RADIOCARBON INVENTORY
AS OF JANUARY 1, 1975

	OBSERVED 10^{26} ATOMS	NORMALIZED TO JAN. 1, 1975 10^{26} ATOMS
GEOSECS ATLANTIC JULY 1972 TO MARCH 1973	104*	113
GEOSECS PACIFIC AUG. 1973 TO JUNE 1974	145	151
GEOSECS INDIAN DEC. 1977 TO APRIL 1978	73	67
TOTAL OCEAN AS OF JAN. 1975		331
CORRECTION FOR DEFICIENCY IN SHALLOW PORTIONS OF OCEAN		-26
CORRECTED TOTAL		305

*Corrected for a possible overestimate of Arctic contribution

TOTAL BOMB ^{14}C INVENTORY



The magnitude of the decrease depends not only on the amount of fossil fuel CO_2 released, but also on the extent to which this carbon was diluted by exchange of atmospheric carbon with carbon in the sea and in the terrestrial biosphere. As the amount of fossil fuel CO_2 generated is known, the magnitude of the ^{14}C to C ratio decrease tells us the extent of this dilution. Were no exchange with oceanic and biospheric carbon to have occurred, the decrease in atmospheric $^{14}C/C$ between 1850 and 1950 would have been about 12%. The observed decrease was only about 2%. The second cross check is based on the decrease in the $^{13}C/^{12}C$ ratio for atmospheric CO_2 from 1850 to present. Fossil fuel carbon has a $^{13}C/^{12}C$ ratio averaging 2% lower than that for atmospheric CO_2. Thus the release of CO_2 from fuel burning is lowering the $^{13}C/^{12}C$ ratio for atmospheric CO_2. Again the magnitude of this lowering depends not only on the amount of CO_2 released by fossil fuel burning, but also by the extent of dilution resulting from the trading of atmospheric carbon atoms with terrestrial biosphere and ocean. This approach is complicated by the fact that CO_2 released as the result of deforestation and taken up as the result of greening also has a 2% lower $^{13}C/^{12}C$ ratio than atmospheric CO_2. The third cross check involves the decrease in the atmospheric $^{14}C/C$ ratio for the time period from 1970 to present. This decline is primarily the result of mixing of the bomb ^{14}C into the oceanic and biospheric carbon reservoirs.

The strategies for harnessing each of these pieces of isotopic information are similar. The simple one-dimensional model described above is used to estimate the extent of dilution through exchange with ocean carbon. In addition, an even simpler reservoir model is used for exchange with carbon in the terrestrial biosphere. This model divides the terrestrial biosphere into three compartments and treats each as a well-mixed reservoir

	Reservoir size gigatons C	Turnover time years
Short-lived vegetation and litter	150	2

Active soil humus	500	25
Long-lived vegetation	500	60

As the biospheric contribution to the dilution is several times smaller than the oceanic contribution, the larger uncertainties associated with the terrestrial model do not seriously hamper the approach.

The cross checks are conducted as follows. The model is initiated at steady state with the atmospheric CO_2 content at 292 ppm and the $^{13}C/^{12}C$ and $^{14}C/C$ ratios at their observed pre-industrial values. Fossil fuel CO_2 is then added to the model's atmosphere in accord with the known production history. This CO_2 has a $^{13}C/^{12}C$ ratio of -25‰ and carries no radiocarbon. Uptake of excess CO_2 by the model ocean occurs during each time step as does isotopic exchange with the biosphere and ocean. Then the decline in ^{14}C and in ^{13}C obtained from the model can be compared with the observed atmospheric trends.

The bomb radiocarbon calculation is done in a different way. The ^{14}C to C ratio for atmospheric CO_2 is constrained to follow the observed values. After each time step the inventory of bomb ^{14}C atoms in the atmosphere, ocean and biosphere reservoirs is computed (for each it is equal to the total number of radiocarbon atoms minus the steady state number of natural radiocarbon atoms). The post 1964 increase in the global inventory of bomb radiocarbon is the result of the downward mixing of the excess bomb ^{14}C stored in the stratosphere (based on surveys of the $^{14}C/C$ in stratospheric CO_2).

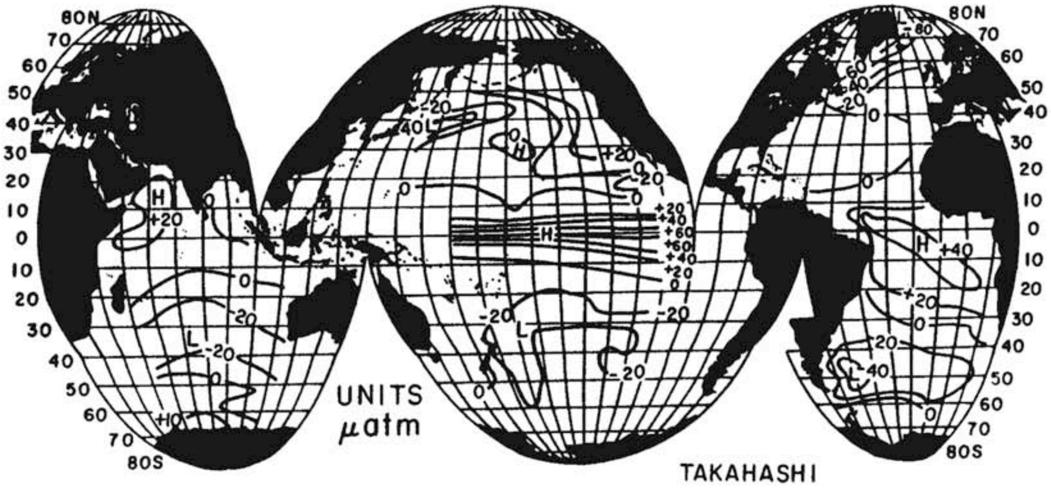
The simple tracer-calibrated model satisfactorily passes all three of these tests. It correctly reproduces the evolution of the atmosphere's ^{13}C to ^{12}C ratio and of its pre-nuclear ^{14}C to C ratio. It also is consistent with the requirement that after the test ban the total inventory of ^{14}C remained constant.

Air to Sea CO_2 Flux

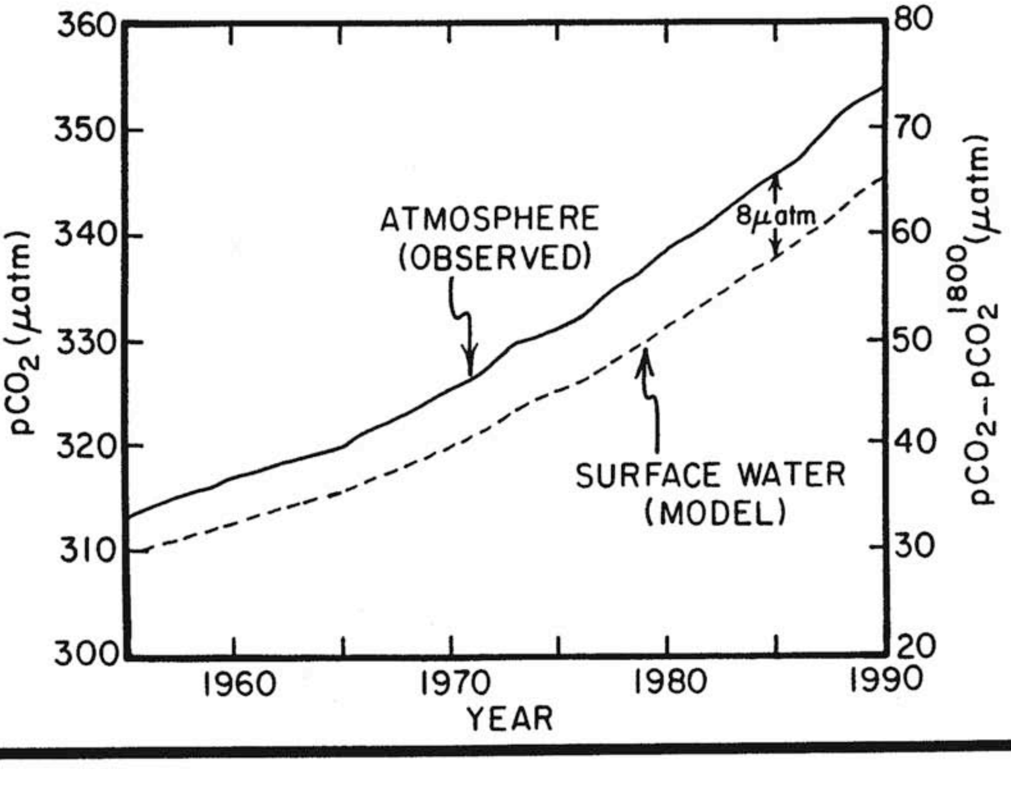
Before returning to the discussion of ocean uptake models, one other means of

AIR - SEA CO_2 DIFFERENCE

OBSERVATION: pCO_2 SURFACE SEA - pCO_2 ATMOSPHERE



PREDICTION: ONE DIMENSIONAL MODEL



determining the uptake of excess CO_2 by the ocean needs to be mentioned. The strategy is to measure the pCO_2 in surface ocean water at enough places and at enough times of year to establish the average global air-sea pCO_2 difference. Then, using the CO_2 exchange rate determined from radon, natural radiocarbon, and bomb radiocarbon distributions, the rate of transfer of CO_2 from air to sea can be calculated. To see what the magnitude of this difference might be, we can use the results for the simple 1-D ocean model. During the 1980s, about 2.2 gigatons of carbon per year entered the sea. Adopting the CO_2 invasion rate of 0.064 moles/m^2.yr.μatm, the expected air-sea CO_2 partial pressure difference would be:

$$\Delta pCO_2 = \frac{2.2x10^{15}\frac{gC}{yr}}{12\frac{gC}{moleCO_2}\,3.6x10^{14}m^2}\;\frac{1}{0.064\frac{moles}{m^2.yr.\mu atm}} \cong 8\mu atm$$

As of 1993, the CO_2 partial pressure in the atmosphere had risen by 65 μatm above its pre-industrial value. Hence the model suggests that the surface ocean had risen 65-8 or 57 μatm achieving about 88% the atmospheric increase. This situation results from the fact that the resistance to CO_2 uptake posed by the air-sea interface is small relative to that posed by mixing within the sea. This is an unfortunate circumstance for those who wish to adopt the CO_2 flux strategy, for it makes the air-sea pCO_2 difference quite small compared to the geographic and seasonal texture of sea surface CO_2 pressures. Thus it is very difficult to establish the air-sea difference with sufficient accuracy. A difference of just 3.6 μatm (i.e., 1% of the atmosphere's pCO_2) drives an ocean uptake of 1 gigaton of carbon per year! To make the situation even worse, two fairly large and as yet uncertain corrections must be introduced. The first has to do with the natural cycling of carbon from sea, to continent, to rivers, and back to sea. About 0.6 gigatons of carbon are carried by rivers to the sea as dissolved organic matter and dissolved bicarbonate. The dissolved organic matter comes from matter generated by terrestrial plants. Upon reaching the sea, it is consumed by marine bacteria returning it to CO_2 form. The bicarbonate dissolved in rivers is also generated from soil CO_2 to balance the positive charge on cations released from soils as the result of weathering. As does the dissolved organic carbon, this bicarbonate eventually reaches rivers and is carried back to the sea. Both the carbon in the dissolved organic matter and bicarbonate ions carried to the sea by rivers originated from CO_2 in the atmosphere. In order to cycle 0.6 gigatons of carbon cycled in this way requires that prior to the Industrial Revolution, the partial pressure of CO_2 in the surface sea averaged about 2 uatm higher than that in the atmosphere.

The second correction involves a temperature difference between the few tens of a micron-thick sea water 'skin' and the ambient temperature for the bulk of mixed layer water. This skin cooling is caused by heat loss during evaporation. The temperature difference created in this way is thought to average about 0.2°C. As for each 0.1°C the skin is cooled, its CO_2 partial pressure drops by a bit over one μatm. In order to balance a 0.2°C skin cooling requires that the pCO_2 of bulk mixed layer water be about 2 μatm higher than that in the overlying atmosphere.

Taken together, these two corrections suggest that, during pre-industrial time, the pCO_2 in the oceanic mixed layer water was about 4 μatm higher than that in the atmosphere. If so, then an uptake of 2 gigatons of anthropogenic carbon by the sea would require that the atmosphere average only 4 rather than 8 μatm higher in partial pressure than the ocean mixed layer. Extensive measurements are now available from most regions of the ocean. Taro Takahashi has summarized these results and concludes that on the average the surface ocean mixed layer water has a CO_2 partial pressure 4±4 μatm lower than that for the atmosphere. While consistent with expectation from the simple tracer-calibrated reservoir model, the error in this estimate remains far too large to be of use in constraining the carbon budget. For this approach to be definitive, CO_2 partial pressure measurement coverage (both geographically and seasonally) will have to be greatly expanded, river recycling and skin temperature biases will have to be accurately established, and the wind velocity dependence of in CO_2 invasion rates will have to be

EXPECTED AIR - SEA Δp_{CO_2} FOR 1980s

2 gigatons

$$\begin{array}{c}\text{EXCESS}\\ CO_2\ \text{FLUX}\\ \text{INTO SEA}\\ \text{(total)}\end{array} = \frac{2 \times 10^{15}\ \text{gC/yr}}{12\ \text{gC/mol}} = 1.66 \times 10^{14}\ \text{mol/yr}$$

$$\begin{array}{c}\text{EXCESS}\\ CO_2\ \text{FLUX}\\ \text{INTO SEA}\\ \text{(per unit area)}\end{array} = \frac{1.66 \times 10^{14}\ \text{mol/yr}}{3.5 \times 10^{14}\ \text{m}^2} = 0.48\ \text{mol/m}^2\text{yr}$$

$$\text{EXPECTED}\ \Delta pCO_2^{\text{AIR-SEA}} = \frac{0.48\ \text{mol/m}^2\text{yr}}{0.06\ \text{mol/ m}^2\text{ppm yr}} = 8\ \text{ppm}$$

BASED ON ^{222}Rn, NAT. ^{14}C AND BOMB ^{14}C

$$\begin{array}{lccccc} & \underline{\text{1800 AD}} & & \underline{\text{1985 AD}} & & \\ \text{SURF. } H_2O\ pCO_2 & 280 & \longrightarrow & 342 & = & 62 \\ \text{ATM } pCO_2 & 280 & \longrightarrow & 350 & = & 70 \end{array} \quad \frac{62}{70} = 0.89$$

AFTER CORRECTIONS FOR SKIN TEMP. AND RIVER CYCLE

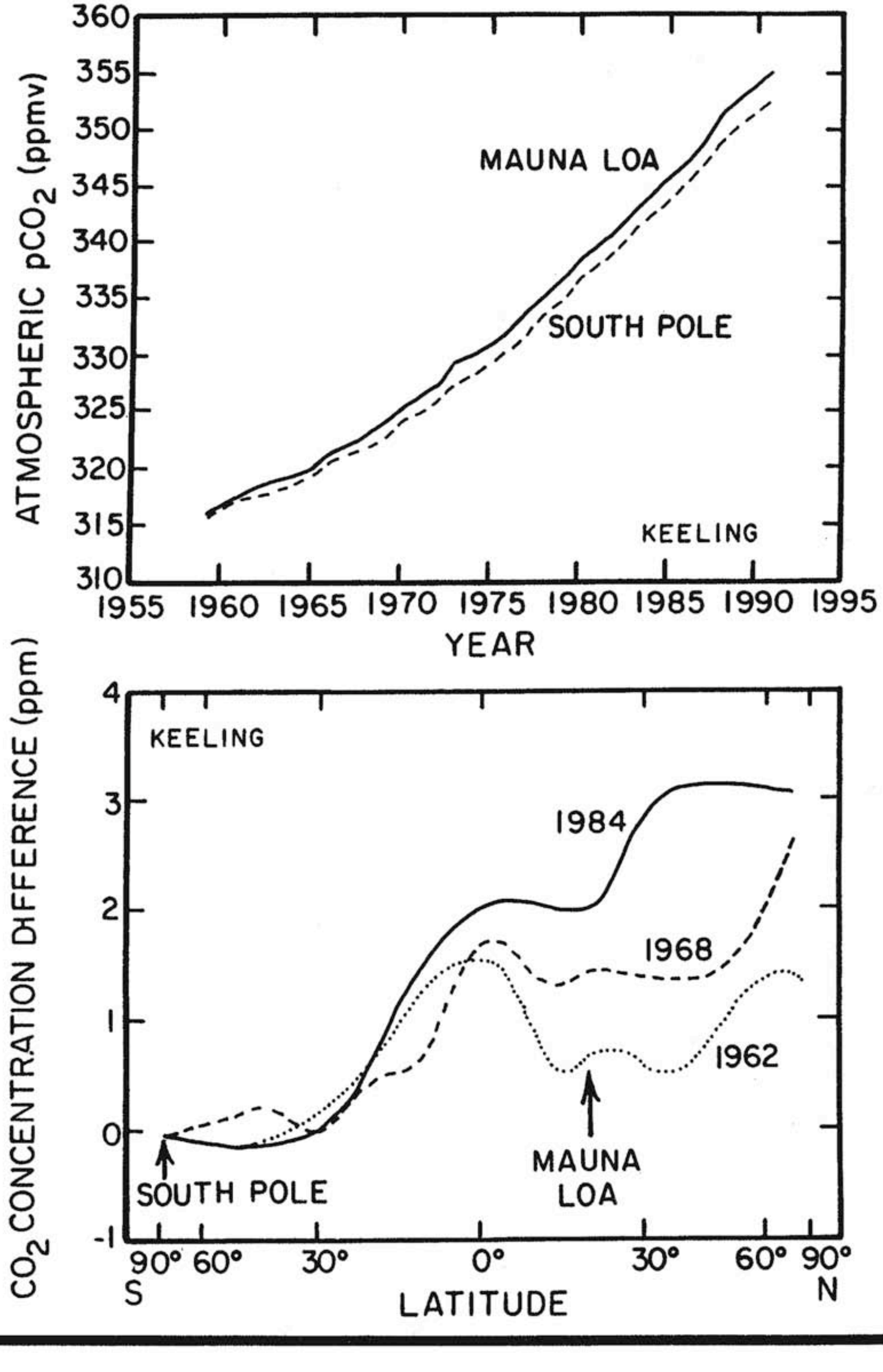
$$\begin{array}{lccccc} & \underline{\text{1800 AD}} & & \underline{\text{1985 AD}} & & \\ \text{SURF. } H_2O\ pCO_2 & 284 & \longrightarrow & 346 & = & 62 \\ \text{ATM } pCO_2 & 280 & \longrightarrow & 350 & = & 70 \end{array} \quad \frac{62}{70} = 0.89$$

IN 1985 EXPECTED $\Delta pCO_2^{\text{AIR-SEA}} = 350 - 346 = 4$ ppm taken into account. Our assessment is that this approach will never become competitive with the others available to us.

Interhemispheric CO_2 Gradient

One piece of evidence appears to be at odds with the conclusion that the amount of carbon stored in the terrestrial biosphere has remained nearly constant over the last several decades. It is based on the interhemispheric difference in the CO_2 content of the atmosphere. As expected, measurements show that northern hemisphere air has a higher mean annual CO_2 content than southern hemisphere air. We say "as expected", because 95 percent of the fossil fuel CO_2 emissions occur in the north temperate latitude belt. The problem is that atmospheric models designed to simulate meridional mixing predict a gradient nearly twice as great as is observed. Fossil fuel CO_2 is introduced into these models in accord with the actual geographic pattern of emissions. The models are programmed to dispense 2 gigatons of C per year to the oceans (uniformly across its surface). The imbalance between fossil fuel production and atmosphere-ocean inventory increase is assumed to enter the terrestrial biosphere (uniformly across the continents). As continents lie mainly in the tropical and northern temperate zones, this uptake, like fossil fuel CO_2 production, is skewed strongly to the northern hemisphere. Models programmed in this way generate an annually averaged 5 μatm difference in CO_2 partial pressure between north temperate and south temperate latitudes for the 1980s. The observed difference is only about 3 μatm. With a 5 ppm interhemispheric gradient, enough CO_2 flows to the southern hemisphere to match both the 1.6 GtC/yr rise in its atmospheric inventory and the 1.2 GtC/yr entering that 60% of the ocean surface lying in the southern hemisphere. With an interhemispheric gradient of only 3 ppm, the models would move only 3/5ths of this amount or 1.7 gigatons of carbon from the northern to the southern hemisphere. As this amount is only slightly greater than that accumulating in the southern hemisphere atmosphere, almost none is left over for uptake by the southern hemisphere ocean. Based on this information in 1989, Tans, Fung and Takahashi stunned

EVOLUTION OF INTERHEMISPHERIC CO_2 CONCENTRATION DIFFERENCE



the world's carbon budgeters by bluntly stating that the yearly ocean uptake of CO_2 had been greatly overestimated. Rather than being on the order of 2 gigatons carbon per year, it was more likely no more than one quarter this amount. If so, then greening must be even larger than we had thought, outpacing forest cutting at a 2 to 1 clip! Further, if the Tans et al. scenario is correct, the ocean is relegated to a minor role in fossil fuel CO_2 budgeting. The terrestrial biosphere becomes dominant.

In addition to the arguments presented above, two rebuttals have been put forth to counter the Tans et al. argument. One has to do with the reliability of the atmospheric transport estimates. The other has to do with the implicit assumption underlying the Tans et al. argument, namely, prior to the Industrial Revolution, no interhemispheric atmospheric CO_2 gradient existed. Let us first examine the transport rebuttal. Perhaps the atmospheric models are not capable of estimating the interhemispheric transport to better than a factor of two. If so, the Tans et al. argument crumbles. But atmospheric modelers have an ace up their sleeves in this regard. Like oceanographers, they have tracer distributions to lean on for verification. Two such tracers, ^{85}Kr and CFCs, are available. Like fossil fuel $CO_{2,}$ both tracers are generated primarily in the northern hemisphere; ^{85}Kr by nuclear reactors and CFCs by industry, and hence should be found at higher concentrations in the northern hemisphere air. ^{85}Kr is radioactive with a half life of 11 years. Thus even though its concentration in the atmosphere was not rapidly changing during the 1980s, the decay of ^{85}Kr in the southern hemisphere had to be balanced by transport across the equator. For CFCs, the atmospheric burden is steadily rising. The rise in the southern hemisphere atmosphere must be supplied by cross-equatorial transport. Models are checked to see whether they reproduce the observed meridional gradients of ^{85}Kr and/or CFCs. If the match is not satisfactory, the formulation of the mixing dynamics is tweaked until the mismatch has been eliminated. It turns out that models adjusted to meet the ^{85}Kr constraint meet the CFC constraint as well (or vice versa). Because the models which have been used to calculate the transport of CO_2 from one hemisphere to the other have passed the ^{85}Kr-CFC test, modelers are confident that the CO_2 transports they generate is sufficiently accurate that the Tans et al. argument must be taken seriously.

Even so, an escape hatch is still available. The latitudinal gradients for ^{85}Kr and for CFCs undergo only minor changes with season. By contrast, that for CO_2 undergoes large changes. During the October through April period, when respiration greatly exceeds photosynthesis in the northern hemisphere, the CO_2 content of the north temperate atmosphere rises, creating a much enhanced north to south gradient. During the May through September period when photosynthesis dominates, the CO_2 content of the air at these northern latitudes is drawn down well below that for the southern hemisphere. So the difference between the CO_2 content of air of north and south temperate zones actually changes sign during the course of a year! While the ^{85}Kr-CFC test proves that over the course of an entire year the magnitude of cross equatorial air exchange obtained in the models is correct, it does not verify that the seasonality of this exchange is correct. If, for example, the model exchanges too little air during the Fall period, when the CO_2 gradient is lower than its mean annual value, and too much air during the Spring period, when the CO_2 gradient is higher than average, the result would be an underestimation of the amount of CO_2 transported from the northern to the southern hemisphere. However, those who do this modeling are adamant that the seasonality of transport is not flawed. But as we are not conversant with their arguments, we cannot defend them. Sorry!

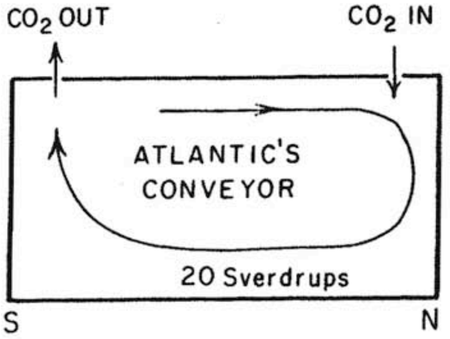
The other rebuttal shows more promise. It is based on an observation made by C. D. Keeling and M. Heimann. They examined the evolution of the difference between the annually averaged CO_2 content measured at Mauna Loa, Hawaii and that measured at the South Pole. As expected, this difference has increased with increasing fossil fuel CO_2 production. At the beginning of the records (1958), the difference was very small. As time progressed, it became larger and larger. What occurred to Keeling and Heimann was that if the trends for these two stations were extrapolated back in time, they would have intersected about 1950. Prior to 1950, the air over Antarctica would have had a higher CO_2 content than that over Hawaii! If so, then prior to the Industrial Revolution, southern hemisphere air must have had a higher CO_2 content than northern hemisphere air. In other words, at that time CO_2 must have been moving through the atmosphere from south to north. Then, as fossil fuel CO_2 generation in the northern hemisphere grew, this natural northward flow of CO_2 was compensated to an ever increasing extent by a southward flow of fossil fuel CO_2 until, about 1950, the two flows became equal, eliminating the gradient.

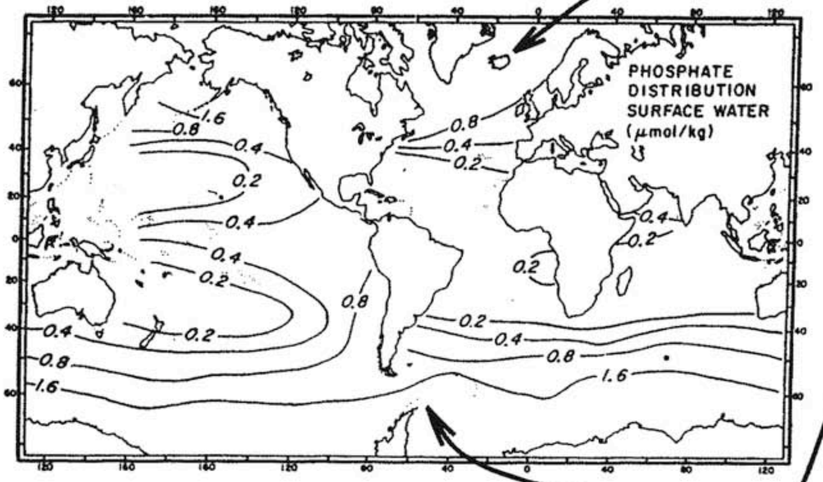
Of course, Keeling and Heimann realized that if, during pre-industrial time, CO_2 was moving from south to north through the atmosphere, then an equal amount must have somehow moved in the opposite direction. Otherwise, the CO_2 content of the northern hemisphere atmosphere would have been going up and that in the southern hemisphere going down. In fact, the ice core record tells us that neither was changing. The only possible routes for such a return flow lie in the ocean.

The most likely ocean route is via the lower limb of what is referred to as the Great Ocean Conveyor. This current system transports 20 million cubic meters per second of water northward in the upper Atlantic. In the vicinity of southern Greenland and Iceland, this water is cooled and sinks to the abyss forming a southward flowing deep water mass, referred to by oceanographers as North Atlantic Deep Water (NADW). Could it be that before sinking, this water picks up CO_2 from the northern Atlantic atmosphere? This CO_2 would then be carried the length of the Atlantic to the Antarctic, returned to the surface and dumped back into the atmosphere. In order to carry 1 gigaton of carbon per year from the northern to the southern hemisphere, NADW would have to contain 130 μmoles/liter (6%) excess $\sum CO_2$.

A means exists to assess the magnitude of this excess. It involves a comparison of the amount of $\sum CO_2$ actually present in various waters in the ocean with the amount

INTERHEMISPHERIC CO_2 TRANSPORT BY THE GREAT OCEAN CONVEYOR





PO$_4$ DIFFERENCE

$1.6 - 0.8$

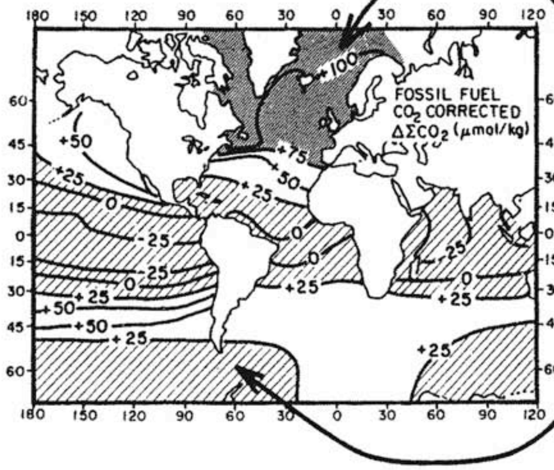
$= 0.8 \frac{\mu mol\ PO_4}{liter}$

RESPIRATION CO_2 DIFFERENCE

$\frac{C}{P}$ IN MARINE ORG.

$0.8 \frac{\mu mol\ PO_4}{liter} \times 125$

$= 100 \frac{\mu mol\ \Sigma CO_2}{liter}$



$\Delta\Sigma CO_2$

$= \Sigma CO_{2_{OBS.}}$

$- \Sigma CO_{2_{EXP.}}$

IF NO CO_2 TRANSPORT THROUGH ATMOSPHERE

$\Delta\Sigma CO_2$ DIFFERENCE

$100 - 20 = 80 \frac{\mu mol}{liter}$

N TO S CO_2 TRANSPORT

$20\ \text{Sverdrups} \times 80 \frac{\mu mol}{liter}$

$= 0.6 \frac{Gt\ C}{yr}$

they would contain were no transport of CO_2 through the atmosphere from one region of the ocean surface to another to occur. These hypothetical $\sum CO_2$ amounts are based on three measured properties of the water: salinity, phosphate content, and alkalinity (corrected for the nitrate contribution). Salinity is important because the removal of fresh water by evaporation enriches all the ions in sea water (and hence also $\sum CO_2$) and, of course, the addition of fresh water by precipitation dilutes them. The phosphate content is important because it provides a measure of the changes in $\sum CO_2$ related to biological cycles. Each mole of phosphorus removed from sea water by photosynthesis is accompanied by about 125 moles of $\sum CO_2$. Or putting it the other way around, waters rich in dissolved phosphate will have a correspondingly high respiration CO_2 content. The alkalinity is important because it provides a measure of the amount of $\sum CO_2$ lost to the formation of $CaCO_3$ shells or gained from their dissolution. On the time scale of ocean mixing, only two chemical mechanisms exist to change the alkalinity of sea water, namely, gains or losses of Ca^{++} to $CaCO_3$ and of NO_3^- to organic tissue. The change in the sum of the alkalinity and nitrate contents of the water provides a measure of the change due to calcium alone. Were no transport of CO_2 from one oceanic region to another through the atmosphere to have occurred, then $\sum CO_2$ contents calculated from the measured salt, phosphate, alkalinity, and nitrate contents of the water would be identical to the observed values (of course, a necessary part of the calculation is to reference all the calculated salinities, $\sum CO_2$s, and alkalinities to one of the measured values).

What is found when this is done is that the differences ($\sum CO_{2\ \text{measured}} - \sum CO_{2\ \text{calculated}}$) for surface waters are not all zero. Rather, they cover range of about 130 μmole/liter. The highest values are found in the northern Atlantic and the lowest in the tropical ocean. The fact that they are not all equal to zero requires that CO_2 be given up to the atmosphere from some parts of the surface ocean and extracted from the atmosphere in others. Of importance here, is that values for the northern Atlantic surface waters are considerably higher than those for the Antarctic surface waters. This is consistent with the hypothesis that the conveyor's lower limb is charged with excess $\sum CO_2$ drawn in from the atmosphere over the northern Atlantic. Part of this excess is dumped back into the atmosphere over the Antarctic Ocean. The difference in excess CO_2 content for surface waters in the northern Atlantic and those in the Antarctic is about 80 μmole/liter or enough to transport about 0.6 gigatons via the lower limb of the Atlantic's conveyor belt from the northern to the southern hemisphere. This is about 60% of the amount needed to void the Tans et al. argument. Of course this assumes that all 20 Sverdrups of NADW make it to the Southern Hemisphere and that all this water upwells in the Southern Hemisphere.

But what is responsible for the great excess of $\sum CO_2$ in surface waters in northern Atlantic waters relative to those in the Antarctic? The answer has to do with the fact that the northern water has a much lower phosphorus content than the southern water. Winter surface waters in the northern Atlantic have about 0.8 μmoles/liter PO_4 while those in the Antarctic average about 1.6 μmoles/liter. The difference of 0.8 μmoles/liter corresponds to about 100 μmoles/liter of respiration CO_2. This difference endows Antarctic surface waters with a higher CO_2 partial pressure than those in northern Atlantic, creating a tendency for CO_2 to escape from Antarctic waters and invade northern Atlantic waters. If buckets containing these waters were placed side by side in a sealed air space, then the excess respiration CO_2 would escape from the Antarctic bucket and invade the northern Atlantic bucket. This transfer would continue until the difference in CO_2 partial pressure was eliminated. At this point the water in the Antarctic bucket would have lost 50 μmoles/liter of CO_2 and that in the northern Atlantic bucket would have gained 50 μmoles/liter of CO_2. This would create a 100 μmole/liter difference in the $\Delta\sum CO_2$ values for these waters. Of course, in the real world, the transfer does not go to completion. Surface waters do not remain in contact with the atmosphere long enough to either give up or absorb their full component of CO_2. It is for this reason that an 80

A LOWER LIMIT ON OCEAN UPTAKE OF FOSSIL FUEL CO_2

ATMOSPHERIC CAPACITY

$$\underset{\underset{\dfrac{1000\,\frac{\text{g AIR}}{\text{cm}^2}}{29.5\,\frac{\text{g AIR}}{\text{mol AIR}}} \times 10^4\,\frac{\text{cm}^2}{\text{m}^2}}{\uparrow}}{3.4 \times 10^5\,\frac{\text{mol AIR}}{\text{m}^2}} \times \underset{\underset{\text{atm } CO_2 \text{ DURING 1980 s}}{\nwarrow}}{3.5 \times 10^{-4}\,\frac{\text{mol } CO_2}{\text{mol AIR}}} \times \underset{\underset{\text{AREA OF EARTH}}{\nearrow}}{5.1 \times 10^{14}\,\text{m}^2}$$

$$= 60.7 \times 10^{15}\,\text{mol}$$

OCEAN CAPACITY

$$\frac{\overset{\left[\Sigma CO_2\right] \text{ SURF. } H_2O}{2\,\frac{\text{mol}}{\text{m}^3}}}{\underset{\underset{\text{BUFFER FACTOR}}{\nearrow}}{9}} \times \underset{\underset{\text{MEAN DEPTH OCEAN}}{\uparrow}}{3.8 \times 10^3\,\text{m}} \times \underset{\underset{\text{AREA OCEAN}}{\uparrow}}{3.6 \times 10^{14}\,\text{m}^2}$$

$$= 304 \times 10^{15}\,\text{mol}$$

$$\frac{\text{OCEAN CAPACITY}}{\text{ATMOS. CAPACITY}} > \frac{\overset{\text{MINIMUM FRACTION OF OCEAN AVAILABLE FOR UPTAKE}}{0.1} \times 304 \times 10^{15}}{60.7 \times 10^{15}} \cong \frac{1}{2}$$

I.E. FOR AN ATMOSPHERIC INCREASE OF 3.0 GtC/yr, THE OCEAN UPTAKE MUST BE AT LEAST 1.5 GtC/yr.

μmole/liter difference in $\Delta\Sigma CO_2$ is observed rather than the full 100 μmole/liter difference. The residual excess of respiration CO_2 in Antarctic surface waters provides the driving force for the expulsion of CO_2 to the atmosphere and the residual deficiency in respiration CO_2 in the northern Atlantic the driving force for the uptake of CO_2.

Thus the answer to the apparent mismatch between the magnitude of the net cross-equatorial transport of CO_2 and the accumulation of anthropogenic in the southern hemisphere atmosphere and ocean lies in some combination of inadequacies in the atmospheric models and ocean transport of CO_2 via the conveyor. The reason is that we see no way that fossil fuel CO_2 uptake by the ocean can have been any less than about 1.5 GtC/yr. during the 1980s. Our confidence stems from the depth to which bomb testing ^{14}C and ^{3}H had been mixed into the sea as of the time of the GEOSECS program (i.e., circa 1975). These results show that on a decade time scale nearly 10% of the ocean is exposed to the atmosphere. As fossil fuel CO_2 molecules have had three decades to penetrate the sea, regardless of the mixing model adopted, they must have equilibrated with substantially more than 10% of the ocean volume. The distribution coefficient of CO_2 between the atmosphere and one tenth the ocean reservoir would be about 2 to 1. During the 1980s the amount of CO_2 accumulating in the atmosphere averaged about 3 gigatons. Hence at least 1.5 gigatons per year must have entered the sea. This is the absolute minimum!

Ocean Uptake Revisited

Despite its tracer underpinnings and the cross checks provided by the atmospheric O_2 decline and reductions in the atmospheric $^{13}C/^{12}C$ and $^{14}C/C$ ratios, the simple reservoir model approach can yield answers no better than ±15% (i.e., ±0.3 gigatons of uptake for the 1980s). The very simplicity of these models denies the possibility of greater accuracy. To do better will require the development of models which simulate the physics of the ocean's mixing. Models for this purpose are now in use in several laboratories around the world. Particularly advanced are those at the NOAA Geophysical

Fluid Dynamics Laboratory in Princeton and at the Max Planck Institute for Meteorology in Hamburg. While it is beyond the scope of this book to describe, in detail, the architecture of these models, a brief accounting is necessary in order to provide an appreciation for their strengths and limitations. The model ocean is divided into egg crate-like boxes with edges several degrees on a side. Ten to twenty such boxes are stacked above each grid square. The thicknesses of these boxes increases logarithmically with depth in the model ocean. The model crudely replicates both the geography and bathymetry of the real ocean. Water flow between adjacent boxes is driven by wind stresses applied to the sea surface and by density differences prescribed across the model's surface. In models designed to estimate the uptake of CO_2 by the ocean over the last century, the winds, temperatures and salinities are held at the observed climatic means. In their more advanced form, these models include seasonality in these forcing factors. Natural radiocarbon is carried as a passive tracer in these runs. The model ocean is then run for several thousand model years to insure that its circulation has reached steady state. The temperatures, salinities, circulation patterns and radiocarbon distributions for the model ocean's interior are then compared with those for the real ocean. Attempts are then made to remove anomalies between model output and observation by modifying the model's wind field, its surface density field, its passage geographies, and its horizontal and vertical eddy diffusivities. As the impacts of such adjustments are globally complex, they are not equivalent to the tuning carried out for the simple reservoir models where the adjustment of each variable parameter has a predictable impact. Rather, changes are made and the new steady state fields are observed. Often improvements in one aspect are accompanied by deteriorations in others.

While the achievement of a match with the observed density and radiocarbon fields provides evidence that the model's large scale thermohaline circulation is more or less correct, this agreement does not guarantee that the ventilation rate of its thermocline and polar water column is correct. As these are the regions where anthropogenic CO_2 is currently being stored, it is important to verify the correctness of this smaller scale ventilation. Clearly, the distribution of the transient tracers produced by bomb testing (^{3}H and ^{14}C), by reactors (^{85}Kr) and by industry (CFCs) are ideal for this purpose. Unlike the distribution of natural radiocarbon which is sensitive mainly to mixing processes on the century time scale, the distributions of transient tracers are dictated by mixing processes which occur on the time scale of decades. The challenge faced by modelers during the next decade will be to adjust the architecture of their models so as to achieve a satisfactory match to the observed distributions of these tracers.

For the near term, the most powerful constraints are offered by the joint use of bomb ^{14}C and ^{3}H data. We say joint use because taken alone each tracer has a major drawback. For radiocarbon, the drawback is that a separation must be made between the natural component and the bomb component. This drawback does not apply to tritium, for the bomb component overwhelms the natural component. The drawback for tritium stems from the rather large uncertainties related to the geographic pattern and timing of its input to the sea. Unlike radiocarbon which was spread fairly uniformly through the troposphere and entered the sea as the result of CO_2 exchange, tritium was quickly carried to the planetary surface in precipitation and water vapor. Consequently, its input was subject to large and not well understood geographic gradients. Fortunately, by combining information from the limited number of pre-nuclear radiocarbon data points for surface ocean water and the limit of penetration as established from tritium, it has been possible to make a reasonably reliable separation between the contributions of natural and bomb-testing radiocarbon for most parts of the ocean of interest. This endeavor has been greatly improved by the realization that in the ocean's thermocline a very strong correlation exists between the distributions of dissolved silica and natural radiocarbon.

Down the road a few years, powerful constraints will come from man-made CFCs. No natural background exists. They are quite well mixed through the atmosphere. Their solubilities are well known and their concentration in surface water should be very close to equilibrium with the overlying atmosphere. We say "down the road" because CFCs are late comers on the tracer scene. The GEOSECS program was conducted prior to the advent of the technology used for CFC measurements in sea water. Measurements were begun in about 1980. As a result of this late start until the recent WOCE surveys, we lack a global survey. So the full power of the freon constraint awaits the assimilation of the data gathered by this program.

It is interesting to note that ocean circulation models (OCMs) yield CO_2 uptake estimates very similar to those obtained employing the simple tracer-calibrated reservoir models. While both approaches adopt the same thermodynamic capacities and CO_2 exchange rates, the all important rates of physical mixing are handled in totally different ways. The parameters in the simple reservoir models are constrained by transient tracer data. To date, the OCMs have been tuned only to fit the large scale distribution of natural radiocarbon. Hence the match between estimates of ocean uptake of anthropogenic CO_2 obtained by these two quite different classes of models adds confidence to claims that we have a firm handle on this aspect of the carbon budget. It also demonstrates that the reservoir modelers lucked out in their assumption that penetration to greater depths proceeds in accord with the square root of time. By chance, the real ocean came close to following this simple relationship.

Global Greening

Every approach to establishing a carbon budget leads to the conclusion that as the result of human activity the Earth is being greened. On the average over the past 40 years greening must have more or less matched biomass losses attributable to forest cutting. An exception is that during the early 1990s, R. Keeling's O_2 measurements make it clear that greening has exceeded these losses; the terrestrial biosphere appears to have been packing away carbon.

If during the 1980s greening balanced forest cutting, then presumably we could estimate its magnitude from forest statistics. The oft-quoted satellite-based figure of about 1.6 gigatons of carbon per year for the current losses resulting from forest cutting is subject to a large uncertainty. For example, two components of the forest cutting estimates have recently been revised downward. An analysis of satellite observations suggests a reduction in estimates of the acreage cut in the tropics by as much as 30%. New surveys of the mean standing biomass in the tropical forest being cut are also significantly lower than those previously adopted value. Another correction which must be made is that in many northern area forests previously cut are now regrowing. Together, these corrections may bring the net annual decrease in forest stocks resulting from the combination of deforestation and reforestation down to a gigaton or less. Assuming that during the 1980s the humus content of agricultural lands had stabilized, the required rate of greening would then be 0.9 ± 0.3 gigatons of carbon per year.

Is it feasible that carbon is being packed away in the terrestrial biosphere at this pace as the result of increases in the availability of CO_2 and fixed nitrogen? Let us first examine the amount of growth enhancement to be expected from the availability to all plants of excess atmospheric CO_2. As of 1997, the CO_2 content of the atmosphere (365 ppm) was 1.3 times higher than prior to the Industrial Revolution (280 ppm). This extra CO_2 must foster more rapid photosynthesis and hence more rapid production of wood and humus. In turn, an increase carbon storage should result. But by how much?

As is the case for the ocean, estimates based on repeated inventories are not feasible. It is difficult enough to get adequate data to quantify the highly visible impacts of forest cutting across the globe, let alone the data required to document forest fattening and soil humus enrichment. Rather, as for the ocean, we must attempt to model these changes. These models require on three pieces of information. The first is the acceleration of growth rates observed in chamber experiments in which plants are grown under conditions differing only in CO_2 partial pressure. In particular comparisons are made between growth at normal CO_2 and growth at doubled CO_2. The second concerns the size of the reservoirs being greened. Other things being equal, the bigger the reservoir, the more carbon it will pack away. The third is the response time for carbon storage in these reservoirs. By response time, we mean the ratio of the amount of carbon stored in the particular reservoir to that added to the reservoir each year as the result of new growth. These times range from a year or two for leaves and twigs, litter on the ground, and fine rootlets in soils to millennia for the most resistant components of soil humus.

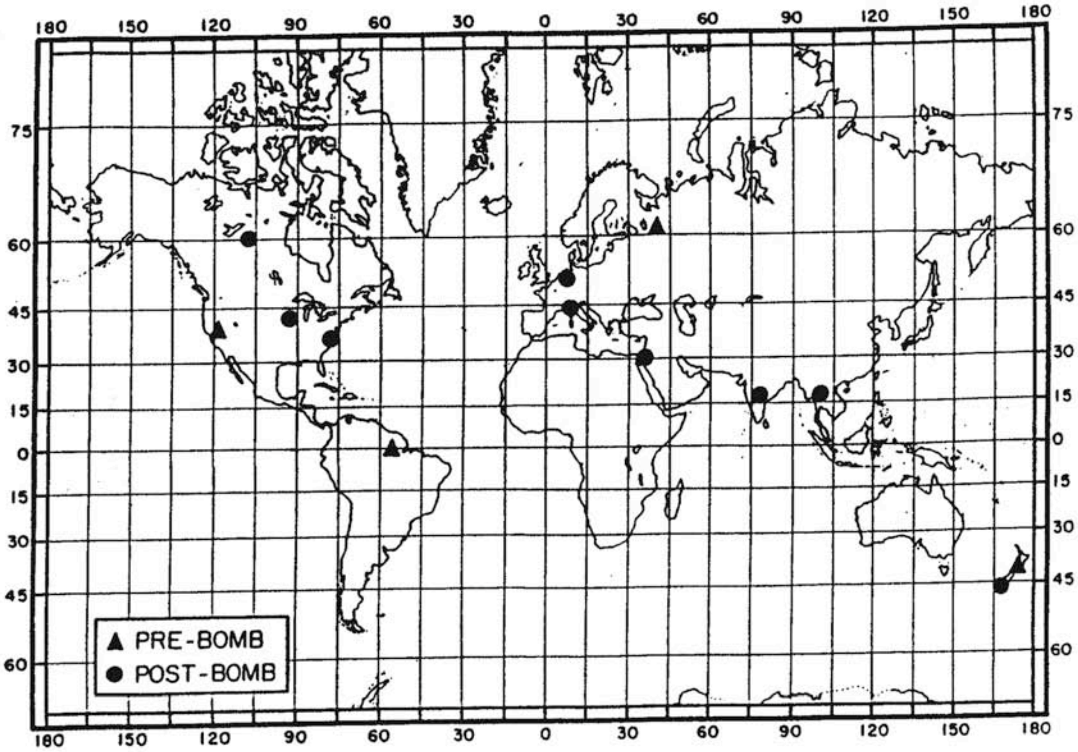
Let us go back over these one at a time. Nearly 1000 growth chamber experiments have been conducted. Most often, the growth rate at ambient CO_2 is compared with that at twice ambient CO_2 . While a great variety of species have been used, these tests are by necessity confined to plants or parts of plants small enough to be conveniently housed in chambers. Also the plants are generally well lighted, generously fertilized and adequately watered. Further, for trees the duration of the experiments is only a small fraction of their lifetime. Because of this, a general criticism is leveled at the results of these experiments. As growth conditions are optimal, the response in chambers is likely to exceed that expected for wild environments where not only CO_2 is in limited supply. But as the chamber results are all we have to go by, they are, by necessity, the basis for the greening calculations. One can only add the caveat that the response of plants in the wild may well be smaller than that in the chambers. Hence estimates made in this way are generally considered upper limits. The median growth enhancement observed for plants grown in chambers with CO_2 contents 100% above ambient is 33%. The assumption is then made that this ratio also applies to the smaller CO_2 enhancements experienced by plants in the wild. For example, plants grown in a chamber whose CO_2 content is 365 ppm would be expected to grow at a rate about 10%

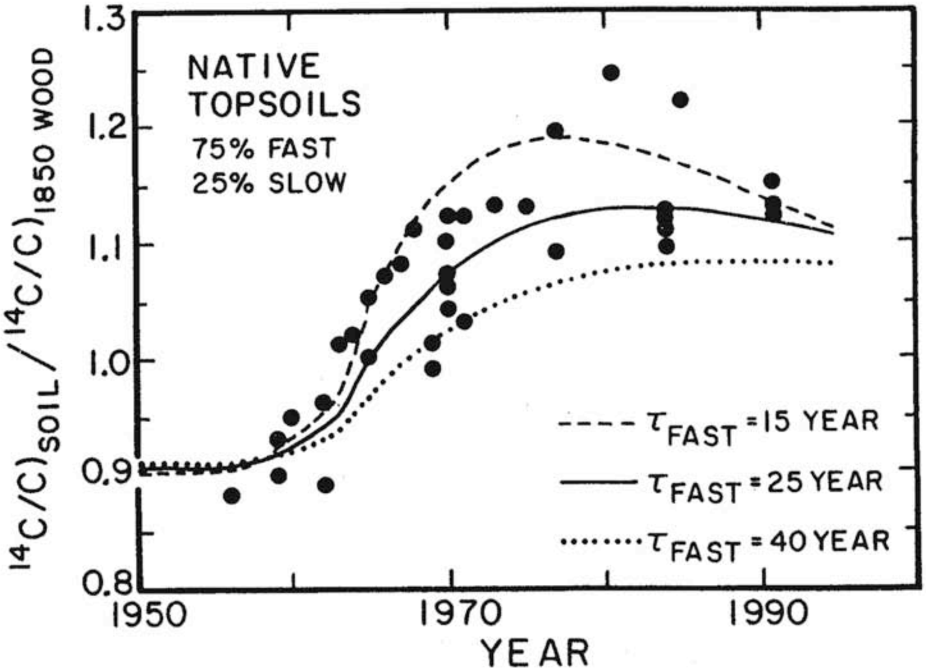
faster than plants in an identical chamber with a CO_2 content of 280 ppm (i.e., the CO_2 content is 30% higher, so growth rate is 10% higher).

Now the extent of biomass increase in a given reservoir as of 1997 will depend not only on the degree to which the rate of photosynthesis has increased, but also on the turnover time for carbon in the reservoir of interest. The carbon inventory of soil litter reservoir would be expected to pretty much keep pace with the increasing rate of photosynthesis. For today's CO_2 content of 365 ppm, the litter production should be 10% higher than that in the year 1800. Hence the amount of litter should also be about 10% larger. By contrast, no increase in the amount of the millennial time-scale component of soil humics would be expected. For reservoirs with turnover times in the range of a decade to several centuries, the inventory increase will lag the photosynthesis increase. Hence the increase will be smaller than 10%.

To understand this, let us consider a simple model. Think of a hypothetical reservoir of organic matter analogous to a soil. Each year new material is added to the reservoir, tending to increase its size. Each year organic matter within the reservoir is consumed by bacteria, tending to decrease its size. We will assume that prior to the 19th century, the reservoir was at steady state (i.e., input was matched by loss). We also assume that the mean time of survival for each unit of organic matter added to the reservoir is 25 years. If so, then the inventory of organic carbon in the reservoir at that time would have been 25 times the annual input rate. The importance of this turnover time to the inventory response is easily understood if one considers what would happen if the production rate of organics in a reservoir previously at steady state were suddenly to increase by 10% and thereafter remain at this level. Initially, the input rate of new litter would be 10% higher than the rate of bacterial consumption of the material in the reservoir, so the organic content of our hypothetical soil would begin to rise. The rise would continue until the amount of organic matter in the reservoir had become 10% greater than that initially present. Since the bacterial population would grow in

RADIOCARBON MEASUREMENTS ON NATIVE TOPSOILS



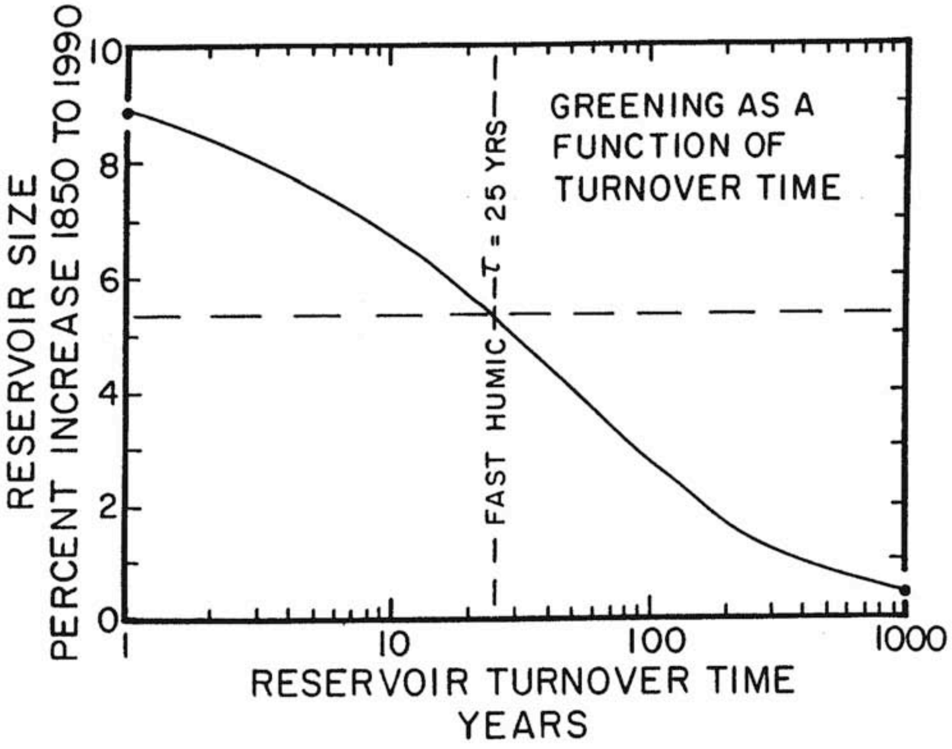


FAST TURNOVER INVENTORY IN 1850

~ 500 GIGATONS CARBON

INCREASE IN INVENTORY FROM 1850 TO 1990

.054 × 500 = 27 GIGATONS CARBON



proportion to the food supply, at this point, bacterial destruction would once again balance the input of new litter. The buildup of the inventory toward this new steady state value would proceed as follows. After 25 ln2 or 17.3 years, it would be 5% greater; after 2x25 ln2 or 34.6 years, it would be 7.5% greater, after 3x25 ln2 or 51.9 years, it would be 8.75% greater, and so forth.

Assigning residence times to components of the soil humus reservoir proves particularly difficult, for its complex of chemical compounds must have a very wide range of survival times. Unlike trees which build annual rings, soils have no equivalent built in clock. Our best source of information comes from radiocarbon measurements made on bulk humus (i.e., on soil samples from which rootlets and litter have been removed). Measurements based on soils sampled prior to the onset of nuclear testing (i.e., prior to the rise in atmospheric radiocarbon) yield an average radiocarbon age of roughly a millennium. By contrast, soils collected subsequent to the bomb-testing-induced peak in atmospheric radiocarbon yield ^{14}C to C ratios 10 to 20 percent higher than those for the pre-nuclear atmosphere. These results confirm the expectation that a wide spectrum of turnover times exists for the organic compounds in soils. While not permitting this spectrum to be defined, the radiocarbon measurements allow the organics in soils to be divided into two categories, those with lifetimes so long that little change in amount (or in $^{14}C/C$) would be expected during the period of CO_2 greening, and those with lifetimes short enough to respond to greening (and to the bomb ^{14}C transient). An estimate of the turnover time for the long residence time component is obtained from radiocarbon measurements on humus from the subsoil. It is assumed that these organics are dominated by the long-lived component. The age obtained on such samples averages 3500 years. Knowing this age and also the bulk age for top soil, it is possible to divide the soil organics into two types and to say what fraction of the carbon falls in each. The result is that with regard to greening about 25% of the carbon is inert and about 75%

‘active’. The turnover time of the active reservoir carbon is obtained through modeling of its response to the bomb radiocarbon transient. What is found is that the best fit to the data for native soils is obtained using a turnover time of 25 years for the ‘active’ reservoir.

This exercise is much akin to that for the one dimensional ocean model. A globally averaged top soil is divided into a part which is greened and a part which responds too slowly to be greened. This corresponds to a division of the ocean into a part which is accessible to fossil fuel CO_2 and one which is isolated from contact with the atmosphere. Measurements of bomb radiocarbon permit the transient response of the active reservoir to be constrained. It must be emphasized, however, that the reliability of soil model does not match that of the ocean model. It is based on far shakier assumptions and is documented by a far, far smaller data set.

Nevertheless, the soil model provides at least a rough estimate of the extent to which natural soils are being greened. Assuming that 500 gigatons of carbon reside in the active reservoir of soils, 3.3% faster growth for each 10% higher atmospheric CO_2 content, and a 25-year turnover time for carbon in this pool, the rate of accumulation of extra carbon in the Earth's soils would be about 0.6 gigaton of carbon per year. Because of the major uncertainties involved in this calculation, this result can be taken only as an indication that the CO_2 induced greening of the soil reservoir could make a significant contribution to explaining the whereabouts of the missing carbon.

Greening of the wood reservoir can be treated in a similar fashion. This carbon reservoir has a similar size as the active soil reservoir (i.e., 500 gigatons of C), but because of its longer turnover time, the rate at which forests are packing away excess carbon should be somewhat smaller, more like 0.3 gigatons of carbon per year for the 1980s.

The response time of the short lived leaf, litter, rootlet reservoir is so short that its size should closely follow the atmospheric CO_2 rise. During the 1980s, the CO_2 content of the atmosphere was rising at the rate of 1.5 ppm per year. Using the 0.33 greening factor, this means that the rate of production of such material was rising at the rate of 0.14%/year. As the size of this reservoir is about 150 gigatons of carbon, the rate of increase is estimated to be 0.2 gigatons per year.

Taken together, the greening of these three reservoirs adds up to about one gigaton per year. This is about the amount required to balance the carbon budget. One might conclude from this that the results obtained in chamber experiments are providing reasonable estimates of what goes on in the real world.

But the situation is very likely much more complicated for there is another potential greening agent. Most ecosystems, whether they be terrestrial or aquatic, respond to additions of fixed nitrogen. Repeated forest surveys in six European countries show that a substantial increase (~25%) in standing stock of wood occurred between 1970 and 1990. Prior to industrialization, growth in all European forests was nitrogen limited. Currently, because of the fallout of anthropogenic NO_3 and NH_3, the fixed nitrogen is super abundant. Hence the most likely explanation for the fattening of these forests is driven by fixed nitrogen fertilization rather than by excess atmospheric CO_2. While not well established, the amount of fixed nitrogen fallout attributable to anthropogenic sources is about 0.05 gigatons of nitrogen/yr. As the C/N ratio in soils is about 12 and that in aquatic plants about 7, it is tempting to assume that for every mole of fixed nitrogen reaching the planet's surface, about 10 moles of carbon are sequestered. If so, then about 0.5 gigatons of carbon are being stored each year as the result of the fallout of ammonia and nitric acid.

There may however be a flaw in the assumption that fixed nitrogen is used only once and then stored until respiration or decay makes it available for recycling. Rather, it may become part of the photosynthetic factory instead of the product. If so, the number of carbon atoms stored per fixed nitrogen released to the environment may exceed the 10 to 1 ratio assumed above.

Support for the conclusion that nitrogen is an important player in greening comes from the measurements of the interhemispheric gradient in ^{13}C to ^{12}C ratios in atmospheric CO_2. In order to make a self consistent picture for ^{13}C, CO_2 and O_2, it is necessary to call on the temperate forests of the northern hemisphere as a major site for greening. As most agricultural-, industrial- and automotive-derived fixed N is released in the north temperate zone and since its lifetime in the atmosphere is too short to permit long distance transport, nitrogen fertilization occurs mainly in this zone

Projections to the Future

If international agreements in limiting CO_2 emissions such as that concluded in 1997 in Kyoto are to be implemented, then it will be necessary to have models which permit us to predict the evolution of the CO_2 content of the atmosphere for any given fuel use scenario. Essential to this enterprise are dynamic ocean models. Not only must these models be able to correctly reproduce the temperature and salinity distributions in the sea and the evolution of the transient tracer distributions, but these models will have to undertake the more difficult task of predicting the response of the ocean's operation to the expected warming and freshening of high latitude surface ocean waters. The consequent slowdown in ventilation of the thermocline and deep sea will tend to reduce the rate of uptake by the ocean of fossil fuel CO_2. But countering this to some extent will be the more efficient utilization of the NO_3 and PO_4 in high latitude surface waters.

Putting aside the possible slowdown in ocean circulation, two factors will alter the split of excess CO_2 between the ocean and the atmosphere. First, the $CO_3^=$ and HBO_3^- ion contents of surface waters will gradually become depleted. Already the $CO_3^=$ content is about 25 percent lower than during pre-industrial times. This diminishment will be reflected by a reduction in the proportion of the CO_2 taken up by the sea. Second, as the growth rate of atmospheric CO_2 content slows the mean age of fossil fuel CO_2 molecules will increase. This lengthening will be reflected by an increase in the proportion of the CO_2 taken up by the sea. Will these factors more or less cancel one another? On the short term the answer is likely 'yes'. The reduction in capacity will be just about balanced by the increase in 'swimming' time. To see why this is the case, let's say that by the year 2025 the CO_2 content has risen to 415 ppm (i.e., by 100 x [415-360]/360 or 15 percent). If during the same time period, the mean lifetime of fossil fuel CO_2 molecules rises from let's say 30 to 40 years. Then, the fraction of the ocean available for CO_2 uptake will rise by a factor of $\sqrt{40 / 30}$ or 1.15. Hence, in this case, the two changes would indeed cancel one another.

Another possibility would be to increase the uptake of CO_2 by the ocean through the addition of fertilizer. The sinking to the ocean interior of the excess organic debris created in this way would lower the CO_2 content of surface water. This deficiency would be compensated by the invasion of CO_2 from the atmosphere. As plant productivity in the temperate regions of the ocean is limited by the availability of fixed nitrogen, one possibility would be to purposefully add ammonia or nitrate. But such an approach would in a sense be self defeating for more CO_2 could be emitted to the atmosphere by the facilities in which the nitrogen was fixed than would be removed from the atmosphere as a result of its application to temperate ocean surface waters.

More promising is the addition of iron to those areas of the surface ocean in which sizable quantities of unused NO_3 and PO_4 are present (mainly the Southern Ocean). The late John Martin pioneered this concept by clearly demonstrating that the sparsity of iron limited plant productivity in these regions. His critics were silenced when an open ocean experiment conducted in the eastern equatorial Pacific produced a dramatic drawdown of nitrate and of CO_2 partial pressure. Further, the required amounts of iron are relatively small - only one mole of iron for each 1000 moles of PO_4 and 16,000 moles of NO_3 utilized by plants. Hence for each mole of iron, the CO_2 removed could range as high as 125,000 moles. Expressed in terms of Redfield ratios:

Fe:P:N:C

1:1000:16,000:125,000

But iron fertilization is not the panacea for the rise of atmospheric CO_2 content. Model calculations reveal that even if all those regions of the ocean containing unutilized NO_3 and PO_4 were continually dosed with iron for the next 150 years and if this fertilization allowed full utilization of the upwelled NO_3 and PO_4, the rise in the CO_2 content of the atmosphere would only be reduced by 10 percent. If, for example, in the absence of fertilization the CO_2 content of the atmosphere were to reach 750 ppm in the year 2150, then fully successful iron fertilization between now and then would hold this rise to 680 ppm. But keep in mind that if at that time the iron fertilization program were to be abandoned, then the CO_2 removed in this way would be returned to the atmosphere.

CO_2 Management

As the CO_2 content of the atmosphere rises and the planet warms, more and more attention is likely to be focused on stemming this rise. The option of purposeful removal of CO_2 from the air can be ruled out. To do so by scrubbing air would require far, far more energy per CO_2 molecule removed than was gained by producing the CO_2 molecule in the first place! While plants could surely do the job, the cost of harvesting and conversion to a form which could be permanently stored (i.e., carbon block) would be prohibitive.

A more reasonable approach would be to capture the CO_2 created by fossil fuel burning at the source. This CO_2 could be liquefied under pressure and buried either on the ocean floor or in deep wells on the continental interiors. Of course, the capture, liquefaction and storage of CO_2 would require energy. Estimates are that were this to be done, energy derived from fossil fuels would double in cost.

Summary

This section's puzzle regarding the fate of fossil fuel CO_2 boils down to an assessment of the carbon storage in the terrestrial biosphere. What is the balance between the positive terms in its budget (greening by CO_2 and fixed nitrogen and regrowth of previously cut forests) and the negative terms (forest cutting and agriculturally-induced losses of soil humus)? As we have seen averaged over the last several decades, the estimates obtained using tracer-calibrated box models and using ocean general circulation models yield answers which suggest that the sum of excess CO_2 stored in the atmosphere and in the ocean comes close to matching the amount of CO_2 generated by the burning of fossil fuels. This result suggests that during the 1980s global greening was responsible for an increase in the standing biomass of forest and soil carbon of about one gigaton per year. This requires that the excess CO_2 in the atmosphere and excess fixed nitrogen in soils has caused plants to grow about 10% faster. Thus, by chance, cutting around the "edges" of the terrestrial biosphere was matched by a fattening in its "middle". But there is no guarantee that this balance will hold in the future. It is easy to imagine scenarios where greening will wane to the extent that the terrestrial biosphere becomes a net source, thereby aggravating the buildup of CO_2 in the atmosphere.

Commentary on Keeling's World Plates

pg. 2

The consensus view of the annual perturbations experienced by various Earth surface carbon reservoirs during the 1980s. The fossil-fuel source is estimated from records of coal, oil and natural gas production kept by each nation. The deforestation contribution is estimated using satellite photography and ground-based standing biomass measurements. The magnitude of ocean uptake is based on modeling. Greening (i.e., the increase in terrestrial biomass resulting from CO_2 and fixed N-induced growth enhancement) is determined by difference.

pg. 4

In the upper panel is shown the atmospheric CO_2 record for Marina Loa Hawaii from 1958 to 1993. In addition to the temporal trend driven by fossil fuel burning, there are internal changes resulting from small mismatches between respiration and photosynthesis (see for example, the dramatic flattening in the early 1990s). The seasonal cycle is driven by the strong late spring and early summer drawdown of CO_2 by plant growth in the extensive northern hemisphere temperate regions. In the lower panel is shown the atmospheric methane record.

pgs. 6-7

Sufficiently accurate direct measurements of the CO_2 content of the atmosphere are available only for the period 1958 to present. Fortunately, this record can be extended back in time using air trapped in polar ice. One problem in this regard is establishing the exact age of the trapped air. Measurements on material from a shallow core from Antarctica show that the close off of pores in the firn begins at a depth of 60 meters and is complete by about 80 meters. The age of the siple ice at the depth of the midpoint of this close off interval is 95 years (as determined by counting annual layers). Based on CFC measurements, the replacement of the air at the base of the firn via diffusion down through the web of pores is estimated to be about 13 years. Hence the air in bubbles is 82 years less than that of the ice in which the bubbles are encased. Of course, as the bubble close off is not instantaneous but is spread over a period of time and as the diffusive ventilation of the firn mixes air of different ages, the air trapped at any given depth is a mixture spanning a decade or so.

As can be seen on page 7, the ice-core-derived reconstruction of atmospheric CO_2 content and of an $^{13}C^{12}C$ tie in nicely with atmospheric measurements.

pgs. 8-9

Breakdown of the magnitude of individual CO_2 sources as a function of time. While the dramatic use of petroleum use leveled off in the early 1970's, coal and natural gas took up the slack. Since 1957 when CO_2 monitoring began, the rate of increase of the atmosphere's CO_2 content has averaged about 60 percent the rate of CO_2 emissions from fossil fuel burning.

p. 12

Comparison of the La Jolla, California record for O_2 decline with that for the CO_2 rise. When the seasonal cycle is removed, O_2 shows a 13.5 μatm decline over this period and CO_2 a 5.5 μatm rise. Two reasons exist for this difference. First, 145 moles of O_2 are required to produce 100 moles of CO_2 (the extra oxygens are required to convert the H in the fuel to H_2O). Second, part of the CO_2 goes into the ocean.

pg. 14

In the upper panel is shown the relationship between atmospheric O_2 trend for a four-year period. In the lower panel is a comparison between the predicted and observed cumulative trends for O_2 and CO_2. The predicted trend is that expected if the atmosphere were a closed system. In order to account for the difference between the observed and predicted trends, it is necessary to invoke not only CO_2 uptake by the ocean but also a significant increase in the amount of carbon stored in the terrestrial biosphere.

pgs. 18-19

Sea water takes up significant amounts of fossil fuel CO_2 mainly because it is a basic solution. CO_2 from the atmosphere mates with carbonate ion in the sea to form two bicarbonate ions. As shown on the left, were sea water free of borate, the reaction carbonate ion would enhance the uptake by more than a factor of 13 (i.e., 34/2.6) over that resulting from the solution of CO_2 gas alone. When the reaction with borate is included, the enhancement of uptake reaches almost a factor of 19 (i.e., 49.1/2.6). Also note that by adding fossil fuel CO_2 to the sea, we are gradually eroding its capacity for further uptake. Both the $CO_3^=$ and $H_4BO_4^-$ are being consumed. The Revelle factor is the percentage increase in the partial pressure of CO_2 in the atmosphere required to raise the $\sum CO_2$ content of surface sea water by one percent.

pgs. 20-21

Radon measurements in the ocean-mixed layer provide an estimate of the rate at which gases pass back and forth across the air-sea interface. By measuring the ratio of radon concentration in the water to that which would be present were no radon to escape to the atmosphere (i.e., that amount of ^{222}Rn were its decay rate to just match its production by the decay of its parent ^{226}Ra). Measurements at a large number of stations from throughout the world ocean reveal that on the average about three quarters of the equilibrium amount of radon atoms are present in surface water. The remaining one quarter escape to the atmosphere. This means that the probability of escape is about one third the probability of radio decay. As the mean life of a radon atom with regard to radio-decay is about 5.6 days, the mean lifetime with regard to escape must be about 17 days. The mean thickness of the wind stirred upper ocean at these stations averaged 54 meters. The gases in one seventeenth of this (a layer three meters thick) are replaced each day. However, one correction must be made when this radon-based result is to be applied to other gases such as CO_2. The rate escape of a gas is related to its molecular diffusivity in water: the higher its diffusity, the greater its escape probability.

pgs. 22-23

The distribution of natural radiocarbon permits an estimate of the rate at which CO_2 moves back and forth across the air-sea interface to be made. Assuming that prior to nuclear testing the distribution of ^{14}C was close to steady state, the net number of ^{14}C atoms passing from the atmosphere into the sea must have balanced the number of ^{14}C atoms undergoing radio-decay within the sea. The net number of ^{14}C atoms entering the sea is proportional to the gas exchange rate and to the difference between the $^{14}C/C$ ratio in atmospheric CO_2 and that in surface mixed $\sum CO_2$. The number of ^{14}C atoms undergoing radio-decay within the sea is proportional to the amount of $\sum CO_2$ in the sea and its mean $^{14}C/C$ ratio. The CO_2 exchange rate obtained in this way is consistent with that based on radon measurements.

pgs. 26-27

Measurements on CO_2 extracted from the atmosphere at different times and places document the evolution of the nuclear-testing induced transient in the atmospheric $^{14}C/C$ ratio. Because the ^{14}C produced during tests was injected largely into the stratosphere of the northern hemisphere during and just after the period of large scale nuclear testing, CO_2 in the atmosphere of the northern hemisphere had a higher $^{14}C/C$ ratio than that in the southern hemisphere. However, soon after the ban on atmospheric testing had been implemented, the $^{14}C/C$ ratio in the two hemispheres even out.

Through gas exchange, this excess ^{14}C entered the surface ocean. At the time of the global ocean survey carried out during the 1970s, the $^{14}C/C$ ratio in surface water $\sum CO_2$ had risen by about 160‰ over its pre-nuclear value. The vertical distribution of this excess ^{14}C (and also of tritium released as the result of bomb tests) provides a measure of the depth to which pollutants added to the ocean surface are mixed into its interior on a timescale of about one decade. The so called mean penetration depth is calculated by creating a rectangle on the concentration depth plot whose horizontal side equals the surface excess of ^{14}C (or ^{3}H) and whose vertical side is such that the area in the rectangle is equal in area to that of the observed excess (crosshatched in diagram).

At the mid-point of the GEOSECS survey (1975), these isotopes had penetrated to a mean depth of 360 ± 30 meters (i.e., into nearly 10% of the ocean's volume). Based on these measurements, the number of radiocarbon atoms beneath each square centimeter of sea surface can be computed (using $\sum CO_2$ measurements as well as $^{14}C/C$ measurements). The geographic pattern of these inventories is strongly influenced by the sea’s major circulation systems. The inventories are lower than average in zones of upwelling (i.e., the tropical ocean, the circum Antarctic Ocean and the northern-most Pacific Ocean). In these regions, it is as if the ^{14}C were being added to a fountain in which the waters rise to the surface and then move laterally. The northern Atlantic breaks the global symmetry of this pattern for it is the birthplace of much of the world's deep water (in other words, a zone of downwelling instead of a zone of upwelling).

pgs. 30-31

A simple one-dimensional model yields a remarkably good simulation of the uptake of fossil fuel CO_2 by the sea. It consists of a well-mixed surface layer taken to be 75 meters thick in accord with temperature profiles measured throughout the world ocean. This wind-stirred layer is underlain by the density-stratified main body of the ocean. Vertical mixing in the sea’s interior is assumed to proceed in accord with the square root of time (i.e., by eddy diffusion). The CO_2 exchange rate between air and sea and the vertical mixing rate in the stratified part of the ocean are selected so as to give the best possible fit to the horizontally-averaged distribution of excess nuclear-testing ^{14}C as surveyed during the GEOSECS program. Vertical mixing is modeled in this way because the time required to mix the entire ocean (i.e., 1000 years as determined from the distribution of natural radiocarbon) is 100 times longer than the time required for tracers to spread through the upper 10% of the sea. The CO_2 exchange rate and vertical mixing rate are constrained to match the GEOSECS observations (i.e., the increase in $^{14}C/C$ ratio in average surface water and the mean penetration depth of bomb-testing ^{14}C and ^{3}H). Of course, if the model yields a match to the surface excess and to the mean penetration depth, it will also yield the observed total ocean inventory of bomb-testing radiocarbon.

pg. 34

While the time required to exchange the gases in the oceanic mixed layer with overlying air is measured in weeks, the time required for the oceanic mixed layer to reach equilibrium with either a change in the CO_2 content or $^{14}C/C$ ratio in the overlying atmosphere is far longer. This difference can be best understood by comparing the response of two 75 meter high columns of water to a stepwise change in the CO_2 content and $^{14}C/C$ ratio in the overlying air. One column contains distilled water (which is free of HCO_3^- and $CO_3^=$). The other is sea water. As the distilled water contains only CO_2 gas, its response to the stepwise change is rapid with no difference in timing between the CO_2 content and the isotopic ratio. By contrast, because of dissolved HCO_3^- and $CO_3^=$, the sea water responds much more slowly. As its ΣCO_2 content exceeds its CO_2 content by a factor of 200 ($\Sigma CO_2 \cong 2000$ μmol/kg and $CO_2 \cong 10$ μmol/kg) its response time for isotopic change is 200 times longer than that for the distilled water. The response time for the ΣCO_2 content of the sea water lies roughly geometrically between the response time for the distilled water column and the isotopic response time for the sea water. In simplest terms, the reason is that uptake of CO_2 is dictated by the $CO_3^=$ content of the surface sea water (~200 μmol/kg) which lies roughly geometrically between that for ΣCO_2 (~2000 μmol/kg) and that for CO_2 (~10 μmol/kg).

pgs. 36-37

The simple 1-D ocean model can be put to three additional tests. First, if CO_2 is fed into the atmosphere in accord with the fossil fuel emissions, does the model generate a rise in atmospheric CO_2 in accord with observation (assuming that the terrestrial biosphere has remained nearly null). In order to pass this test, the model must be initiated with an atmospheric CO_2 content of 292 μatm rather than the value of 280 μatm obtained from ice core measurements. The second test is to match the decline in $^{13}C/^{12}C$ ratio resulting from the addition to the model's atmospheres of ^{13}C deficient fossil fuel CO_2. As can be seen, the model passes this test handily. The third test is to match the decline of $^{14}C/C$ ratios resulting from the addition to the model's atmosphere of ^{14}C-free CO_2 from fossil fuel burning. Again, the match between model and observation is quite good. It must be noted however, that the observed trend in atmospheric $^{14}C/C$ ratio contains a small natural component (due to fluctuations in the strength of the solar wind and its associated magnetic field). As this contribution cannot be accurately assessed, it is possible that by chance this natural contribution masks a deficiency in the model. It should also be noted that were there no mixing between the carbon atoms in the atmosphere and those dissolved in the sea, both the ^{13}C and ^{14}C changes would be five or so times larger than the observed changes. Hence, these are quite stringent tests of the ocean model.

pgs. 38-39

The model can be put to a fourth test. Does it produce a match to the observed post-test-ban decline in the $^{14}C/C$ ratio of the atmosphere. This crosscheck is performed in a less direct manner. The atmosphere's $^{14}C/C$ and CO_2 contents are programmed to follow their observed time trends. The model's ocean and terrestrial biosphere exchange carbon isotopes with this atmosphere. The excess radiocarbon inventories are calculated for each reservoir and then totaled. What is found is that after 1967 (i.e., the time when the entire atmosphere (including the stratosphere) had become well mixed with respect to bomb ^{14}C, the total inventory of radiocarbon remained nearly constant. This constancy is not found for the period prior to 1967 because up until this point the stratosphere retained a significant excess $^{14}C/C$ over that for the troposphere.

pg. 42

A map for the 1980s showing the difference between the CO_2 partial pressure in atmosphere and that in surface ocean constructed using measurements from along dozens of ship tracks. Although this distribution has a fair amount of texture (for example, a pronounced excess in the eastern equatorial Pacific and a pronounced deficiency in the northern Atlantic), when averaged over the entire ocean, the difference is very small (~4 μatm). But the uncertainty on this measured average (±4 μatm) and in the corrections required to compensate for the skin temperature bias (~2μatm) and for the preanthropogenic excess balancing the river flux of carbon to the sea by rivers (~2μatm), render untenable the use of this approach to make a meaningful independent estimate of the flux of fossil fuel CO_2 into the sea. All that can be said is that once corrected the observed difference is consistent with that of 8 μatm predicted by models for the same time period.

pg. 45

If, as we believe, an average 2 gigatons of fossil fuel carbon was entering the ocean during the 1980s, then based on the global mean gas exchange rate obtained from the distributions of mature ^{14}C and radon (and confirmed by the GEOSECS survey of the distribution of bomb-produced ^{14}C), an average air-sea CO_2 partial pressure difference of 8 micro-atmospheres would be required. However, as prior to the Industrial Revolution the sea surface must have had a p_{CO2} of about 2 micro-atmospheres higher than the atmosphere to balance the net transport to the sea by rivers of bicarbonate and dissolved organic matter, the actual difference is reduced to 6 micro-atmospheres. Further, as evaporation lowers the skin temperature of the ocean, a further correction is required lowering the expected difference to only 4 micro-atmospheres.

pg. 47

Comparison of the annually averaged atmospheric CO_2 record from atop the extinct volcano, Mauna Loa, on the island of Hawaii with that from atop the Antarctic ice cap. As can be seen, when in 1958 these records began, the two stations recorded nearly the same mean annual CO_2 content and since then, the difference has steadily grown. In one sense, this is consistent with the rising production of CO_2 from fossil fuel burning

(~2.3 GtC in 1958 to ~5.5 GtC in 1985). But one would expect the difference in 1958 to have been 2.3/5.5 that in 1985. The records suggest that in 1958 the difference was close to zero. This led to the speculation that prior to 1955, the difference might have been reversed (in other words, the southern hemisphere had a higher partial pressure of CO_2 than did the northern hemisphere). If so, then one would have to postulate that a natural interhemispheric cycle exists which carries CO_2 from the northern to the southern hemisphere through the ocean and then back through the atmosphere.

pg. 51

The most obvious route for the interhemispheric ocean transport of CO_2 is the Atlantic's conveyor-like thermohaline circulation. Cold water manufactured in the northern Atlantic sinks and flows southward around the tip of Africa into the circum Antarctic deep water current. Much of this water upwells in the southern hemisphere. This water carries excess CO_2. This excess is related to the low nutrient (i.e., NO_3 + PO_4) constituent content and hence respiration CO_2 content of water sinking in the northern Atlantic. In the Antarctic, the excess respiration CO_2 associated with the much higher nutrient constituent content of surface waters (compared to that for the low latitude) more or less balances the reduction of CO_2 partial pressure caused by the lower temperature. Hence little tendency exists for CO_2 to be transported to the Antarctic through the atmosphere from other parts of the surface ocean. However, in the northern Atlantic, the compensation by respiration CO_2 is not adequate and hence the cooling creates a surface water deficit in $\sum CO_2$ of about 100 μmol CO_2/kg. About 80 μmol/kg of this deficit is compensated by the uptake of atmospheric CO_2. Because of this, the conveyor exports about 0.6 Gt of carbon to other parts of the ocean. While not enough to create a south to north preanthropogenic atmospheric CO_2 gradient big enough needed to explain the seemingly too low current interhemispheric difference in atmospheric CO_2 content, transport by the conveyor might explain up to half of it. A more complete explanation of this phenomenon is provided by the authors in a paper published in *Nature* (1992, v. 356, p. 587-589).

pg. 54

An estimate of the minimum amount of fossil fuel CO_2 taken up by the sea during the 1980s can be obtained by assuming that the mean penetration depth of fossil fuel CO_2 into the sea was no greater than that of bomb produced ^{14}C (or ^{3}H) at the time of the GEOSECS survey. This estimate is a lower limit because during their mean lifetime of 30 years, fossil fuel CO_2 molecules must have penetrated deeper into the sea than the bomb isotopes which, at the time of the GEOSECS survey, had had only a bit more than a decade to "swim". As the mean penetration depth of the bomb-produced tracers was as of 1975 about 360 meters (i.e., approximately, one tenth the mean depth of the sea), this means that at least one tenth of the ocean's capacity for CO_2 uptake was accomplished. This capacity is set by the $\sum CO_2$ content of the ocean water divided by the Revelle factor (or so called buffer factor) described on pg. 15. For the surface ocean, the average value of this factor is 9 (i.e., for each 9% increase in atmospheric CO_2 pressure the equilibrium increase in ocean $\sum CO_2$ will be 1%). This yields an ocean capacity one half that of the atmospheric capacity which means that for each three moles of fossil fuel CO_2 added to the atmosphere, one will enter the sea and two will remain airborne. For the 1980s, the measured increase in atmospheric CO_2 was on the order of 3.0 GtC/year. Thus at least 1.5 GtC/year must have entered the ocean during this time period.

pgs. 62-63

Radiocarbon measurements are available for only a few dozen topsoil samples collected at various places during the course of the rapid bomb radiocarbon transient. These measurements suggest that prior to nuclear testing, the $^{14}C/C$ ratio in humus from top soils averaged about 0.9 times the $^{14}C/C$ ratio for preanthropogenic terrestrial vegetation (i.e., an apparent radiocarbon age of about 900 years) and that this ratio rose (as the result of introduction bomb-testing ^{14}C) to a broad maximum in the 1970s and

1980s, about 1.1 times the preanthropogenic ratio. In order to account for both of these observations, it is necessary to call on at least two classes of soil humus, one with a turnover time measured in millennia and one with a turnover time measured in decades. The former pool is necessary to account for the low $^{14}C/C$ ratio prior to bomb testing and the latter for the uptake of appreciable amounts of bomb ^{14}C. A fit to the data can be achieved by assuming that the top-soil humus consists of 75% material with a 25-year turnover time (hence a pre-nuclear $^{14}C/C$ ratio close to 1.0) and 25% material with a 4000-year turnover time (hence a pre-nuclear $^{14}C/C$ ratio of about 0.6). While in reality the situation must be much more complicated (i.e., a wide spectrum of turnover times must exist) based on available constraints, no way exists to improve upon the very simple two reservoir model shown here.

The two reservoir model allows an estimate of the extent of CO_2-induced "greening" of soils to be made. In this calculation, the chamber-experiment-based factor of 3.5% growth enhancement per 10% increase in air CO_2 content is applied to the entire terrestrial biosphere (i.e., during the 1980s when the atmosphere's CO_2 content was about 27% higher than prior to the Industrial Revolution, the growth rate of plants and hence the production rate of new humus was, presumably, about 9% higher than prior to the Industrial Revolution.) The extent to which any reservoir increased its size as a result of this greening would depend on its turnover time. Only reservoirs such as leaves, grass, rootlets... with very short turnover times would show the full 9% increase. By contrast, the millennium response-time fraction of soil humus would show almost no greening. The fast response-time soil reservoir would be expected to show a bit more than half the maximum response. Assuming that the global reservoir of fast responding humus contain 500 Gt of carbon, its inventory should have risen by about 27 GtC since the beginning of the Industrial Revolution (an amount equal to about 9 years accumulation of CO_2 in the atmosphere at the 1980s rate).

Keeling's World Problems

1. If your car gets 30 miles to a gallon of gasoline, how many pounds of CO_2 gas does it release to the atmosphere per mile driven? (assume that gasoline has a density of 0.8 gm/cc, and a chemical formula with twice as many hydrogen atoms as carbon atoms). If you were to drive your car 20,000 miles each year, how many tons of CO_2 would you produce annually? If all 5.5 billion people on the planet were to drive cars 10,000 miles in each year, how many gigatons of carbon would be produced? How does this compare to today's fossil fuel CO_2 production rate of ~6 gigatons per year? (1 gallon = 3.785 liters, one ton = 10^6 gm, one pound = 453 gm).

2. For the year 1993, the CO_2 content of the atmosphere averaged globally was about 358 ppm by volume. What would the CO_2 content be 100 years from now (i.e., in the year 2093) if:

   a. CO_2 production remained constant at 6.0 GtC/yr.

   b. CO_2 production rose at the rate of 1% per year.

   Assume that 55% of the CO_2 produced remains in the atmosphere.

3. What would the radon based estimate for the invasion rate of CO_2 into the sea be if the ratio of the mean measured concentration of radon in the surface mixed layer to that if no radon were lost to the atmosphere were 0.60 (instead of 0.77) and the mean thickness of ocean mixed layer were 70 meters (instead of 54 meters). Give your answer in units of moles/m^2yr μatm. What would be the invasion rate of CO_2 at 280 μatm? If this were the true CO_2 invasion rate, then what would be the pre-nuclear ratio of the $^{14}C/C$ in mean surface water ΣCO_2 to $^{14}C/C$ in the atmosphere have been?

4. Assume that as of 1990 the total amount of fossil fuels burned since the beginning of the Industrial Revolution was 230 gigatons. Assuming that all this CO_2 remained in the atmosphere (i.e., no transfer into the ocean or into the terrestrial

biosphere), calculate the expected atmospheric CO_2 content in 1990. Assuming that fossil fuel carbon has an average $\delta^{13}C$ -27‰ and that no isotopic exchange of atmospheric carbon with either oceanic or biospheric carbon occurred, by how many ‰ ratio have dropped? Assume that as of 1950, a total of 70 gigatons of carbon had been added to the atmosphere as a result of fossil fuel burning since the beginning of the Industrial Revolution. Assuming that the fossil fuels are free of radiocarbon and again no isotopic exchange of atmospheric carbon with either oceanic or biospheric carbon occurred, by how many ‰ should the atmospheres $^{14}C/C$ ratio have dropped by the year 1950? Calculate the following ratios:

a. $$\frac{\text{Actual } CO_2 \text{ rise 1850 to 1990}}{\text{Expected rise if all fossil fuel } CO_2 \text{ remained airborne}} = \_\_\_\_\_$$

b. $$\frac{\text{Actual } {}^{13}C/{}^{12}C \text{ drop 1850 to 1990}}{\text{Expected drop if no isotopic exchange with carbon in other reservoirs}} = \_\_\_\_\_$$

c. $$\frac{\text{Actual } {}^{14}C/{}^{12}C \text{ drop 1850 to 1950}}{\text{Expected drop if no isotopic exchange with carbon in other reservoirs}} = \_\_\_\_\_$$

The definitions of $\delta^{13}C$ and $\Delta^{14}C$ are as follows:

$$\delta^{13}C = 1000 \text{ x } \frac{({}^{13}C/{}^{12}C_{atm} - {}^{13}C/{}^{12}C)_{\text{mean ocean}}}{({}^{13}C/{}^{12}C)_{\text{mean ocean}}}$$

$$\Delta^{14}C = 1000 \text{ x } \frac{({}^{14}C/C_{atm} - {}^{14}C/C)_{atm}^{1850}}{{}^{14}C/C_{\ atm}^{\ 1850}}$$

Both are akin to percentage differences from the ratio measured in a reference material. But they are given in parts per thousand instead of parts per hundred. Assume that in 1850 the atmosphere contained 550 gigatons of carbon and that this CO_2 had a $\delta^{13}C$ value of -6.5‰.

5. Calculate the composition of sea water at equilibrium with an atmosphere with a CO_2 partial pressure of 560 μatm. Assume sea water to be borate free and to have

an alkalinity equal to 2100 μmol/kg and a K_c value of 1445. You can get the answer either by trial and error or as by solving a quadratic equation. For the former, guess at a $CO_3^=$ concentration. Then use the charge balance equation to calculate the corresponding HCO_3^- concentration. Then substitute both in the equilibrium constant equation (along with CO_2 = 20 μmol/kg).

Example:

guess $CO_3^=$ = 100 μmol/kg

then HCO_3^- = 2100 - 2 x 100 = 1900

and $K_c = \frac{1900 \times 1900}{20 \times 100}$ = 1805 Too high!

so choose a larger $CO_3^=$ ion concentration

and repeat until K_c = 1445.

6. Explain why it is that burning of fossil fuels causes the atmospheric O_2 content to drop 13.5 μatm for every 5.5 μatm CO_2 rises, when for plant growth or plant respiration this ratio is very close to 1.
7. Explain the difference between the atmospheric radiocarbon records for the northern and southern hemispheres. Why the annual wiggles in these curves?
8. If the surface water bomb radiocarbon excess at the time of the GEOSECS survey had averaged 80‰ (instead of 160 ‰) greater than the prenuclear $\Delta^{14}C$ value (and if the mean penetration depth were the same as shown on page 29), which of the parameters in the simple model shown at the top of page 28 would have to be changed? What would its new value be? How would the ocean inventory of bomb radiocarbon atoms have differed?
9. Plants living in the surface sea produce O_2 gas. These new molecules eventually escape to the atmosphere. If the piston velocity for O_2 is 3 meters/day and the mean thickness of the mixed layer is 54 meters, how many days does the average O_2 molecule remain in the sea before escaping to the atmosphere?

10. The simple model shown on p. 28 predicts that during the 1980s the global mean air-sea CO_2 difference should have averaged 8μatm (see pg. 40). Let's say that marine chemists had succeeded in measuring this difference at enough places and seasons to convince the world that the true difference was only 4±1 μatm. How might this difference be explained?

11. Had the measurements made during the GEOSECS survey have indicated that the mean penetration depth of bomb radiocarbon tritium were ~720 meters instead of ~360 meters, then what would be the minimum amount of fossil fuel CO_2 taken up by the ocean at a time when the atmosphere was rising 3.0 GtC/year?

12. Planet X is identical to the Earth in most respects (same ocean and continent areas, same ocean and atmosphere chemistry as that for the preindustrial earth, same size atmosphere). One important difference exists; the mean depth of its ocean is only 475 meters (compared to 3800 for the Earth). Three hundred gigatons of carbon are released as CO_2 through the burning of fossil fuels. No nuclear bombs are exploded nor nuclear reactors operated. Several hundred years later, this extra CO_2 has become thoroughly equilibrated with Planet X's ocean and terrestrial biosphere. Calculate the following quantities:

    a. The atmospheric $^{14}C/C$ reduction (assume that fossil fuels are radiocarbon free)

    b. The atmospheric $\delta^{13}C$ change (assume that it started at -6.5‰ and that the carbon isotope composition of fossil fuel carbon is -26.5‰)

    c. The atmospheric CO_2 content (assume that it started at 280μatm)

    Give your answers as follows:

    a. $\dfrac{^{14}C/C_{After}}{^{14}C/C_{Before}}$ = ______________________

    b. $\delta^{13}C_{Before} - \delta^{13}C_{After}$ = ________________________‰

c. pCO_{2After}^{atm} = ________________________ μatm

The total mass of the biosphere (wood, soils...) is 1000 gigatons. Assume for simplicity that prior to Planet X's industrial revolution, its ocean and biosphere had uniform $^{14}C/C$ ratios equal to that in the atmosphere. Assume that the ocean has a uniform ΣCO_2 concentration of 1.91 moles/meter^3. The area of Planet X is 5.1 x 10^{14}m^2, that of the ocean is 3.6 x 10^{14}m^2. Assume for simplicity that the ocean has the same $\delta^{13}C$ as fossil fuels. Assume no change in biosphere size. Assume a borate free ocean with preindustrial $[CO_2]$ = 10μmol/liter, $[HCO_3^-]$ = 1700μmol/liter and $[CO_3^=]$ = 200μmol/liter. The equilibrium constant, K_c, is 1445. Do a and b first. They are relatively easy. By contrast, c is quite difficult. If you can't get c, just write down the equations.

13. If in the year 1800 A.D., forests covered one third of the Earth's land area, and if their total tree biomass was 600 GtC, how many grams of carbon were there per square centimeter forest? How many tons of biomass per hectare (a square hectare measures 100 meters on a side)? Trees can be thought of as umbrellas which when folded up become cylinders extending 20 meters above ground and 10 meters below ground with a uniform diameter equal to that of the trunk (assume it to be 50 cm). If so, on the average, how many trees would there be per hectare? Assume the density of wood to be 0.9 gm/cm^3.

14. The UN mandates that enough trees be grown such that 30 years from now the added biomass will be 60 GtC. If these trees achieve the mass given in problem #13, how many will there be? If they are spaced as in problem #13, how many hectares will be required? What fraction of the Earth's land area will this require? Three people can be supported by the food grown on a single hectare. If existing farm land were used to grow these trees, what fraction of today's farm land would this require? (Assume the population to be 5.6 billion)

15. Assume that Biosphere 2 has an area of 2 hectares and a mean height of 10 meters. Further, assume that its soils contain 2.8 gmC/cm^2 but that the vegetation can support at steady state only 0.8 gmc/cm^2. The soils cover 80% of the area of Biosphere 2. Further, assume that all the organic matter is of the 'active' variety and has a survival (i.e. replacement) time of 20 years. Still further, assume that the standing biomass of vegetation is at steady state (i.e. it is neither increasing or decreasing) and that the concrete has been sealed so that it no longer takes up CO_2. On January 1, 1994, the pO_2 was 210,000 μatm and the pCO_2 was 2000 μatm. The ratio of CO_2 creation to O_2 consumption is one mole per mole. If no remedial action were taken, how would these values change over the course of one year (i.e., what would they be as of January 1, 1995?) If instead, the Biospherians had an apparatus which allowed them to remove CO_2 by reacting it with CaO stored in anticipation of this problem, how much $CaCO_3$ would they form in the course of the year in order to maintain the initial CO_2 content of their air? If they had a second piece of apparatus which electrolized water to form H_2 and O_2, how much water would they have to electrolize during the course of the year in order to maintain the O_2 content of the air at its initial value? A gigantic problem associated with this solution would be what to do with the H_2 gas. Assuming that it could be kept separate from the O_2 generated and transferred into a balloon mounted above the roof of Biosphere 2, what would be the ratio balloon volume to the Biosphere 2 volume at the end of one year? (Assume that both the balloon and Biosphere 2 are at one atmosphere pressure).

16. Assume that over the course of the year the average daytime photosynthetic production of organic C is three times the consumption rate of excess soil carbon by bacteria. If the biomass of Biosphere 2 is to be at steady state, this creation of new biomass must be exactly balanced by oxidation of old biomass. One difference: assume that respiration occurs at a uniform rate round the clock (i.e., no diurnal cycle) but

photosynthesis occurs only during an 8-hour period from 8 am to 4 pm (i.e., it is shut down during the other 16 hours). If on a typical morning at 8 am the CO_2 partial pressure in Biosphere 2 air is 2500 μatm, what will it be at 4 pm when photosynthesis stops? The volume occupied by one mole of air at one atmosphere pressure and 25°C is 24.6 liters.

Super Problem

In the year 2401, David Ralph Keeling, a distant descendant of the clan made famous in the 20th century by their measurements of CO_2 and O_2 in the Earth's atmosphere, is sent to assess what terrible fate befell a colony established by biospherians sent forth from Earth in the year 2081 to Kri, a planet of the neighboring star Ciolki. After three centuries of what seemed to be an extraordinarily successful venture, radio communication abruptly ceased. Twenty years have passed since this last report was transmitted. As he steps forth from his speed-of-light space ship, young Keeling is struck by a horrible stench. Hulks of dead animals and plants strew the landscape. A quick survey by rotocoptor confirms that some catastrophe must have struck down all life on the planet. Only the most primitive of bacteria appear to have survived; they slowly devour the rotted remains.

Dee-Ar, as he is known to his friends, has been assigned by the expedition leader to assess whether this disaster could be related to the heavy exploitation of Kri's vast graphite reserves. While the colony was established by 8 biospherians, its population soared to a staggering 4 billion just before the catastrophe struck.

Question #1: Assuming that the catastrophe happened exactly 300 years after the first group of 8 babies were born, if every woman on planet Kri gave birth to one set of quadruplets (2 boys and 2 girls) and if everyone lived to the age of 80, then what was the designated child-bearing age?

Dee-Ar's task is complicated by the fact that the Krians were very secretive about their affairs. Communications with Earth were restricted to the bare minimum of information agreed upon before the original biospherians were forced to leave Earth. And try as he may, Dee-Ar can locate no records what-so-ever concerning Kri's carbon cycle. The only information comes from measurements made by the expedition team. Kri was selected for colonization because it so closely resembled Earth in size and surface character. Its ocean covers almost half the planet and its atmosphere exerts a pressure of 1000 gm/cm^2 and is made of 20% O_2 and 80% N_2. The CO_2 pressure measured by the investigation team is 4000 μatm. Based on the number of graphite burning power plants Dee-Ar sees during his overflight, he is convinced that the CO_2 pressure must now be a good bit higher than it was prior to colonization. Further, the absence of any mountain glaciers puzzles him, for clear evidence of fresh morraines as much as 2 kilometers below the tops of the highest peaks is noted by the expedition's geologist, Dr. Dentons. Had the descendants of the biospherians created so large a greenhouse warming that these glaciers melted away in a span of just 300 years? A further clue comes from the tropics where temperatures now average 40°C. The remains of abandoned cities demonstrate to Dee-Ar that the tropics were once inhabited. Did a greenhouse warming drive people to higher latitudes? Fortunately, Kri's equatorial plane is alined with its orbit; otherwise, hot summers would have made even temperate latitudes unsuitable for agriculture.

Dee-Ar rues the absence of glaciers, for they would have archived both the post-colonization CO_2 rise and O_2 decline. Then an idea came to him. Maybe the $^{14}C/C$ and $^{13}C/C$ ratios in trees might provide the needed information. Dee-Ar first makes measurements on matter from plants killed by the catastrophe, on CO_2 from Kri's air and on $\sum CO_2$ from Kri's sea. He finds:

	$\delta^{13}C^*$	$\frac{^{14}C/C^{**}}{^{14}C/C_{stan.}}$
Atm CO_2	-15‰	.75
Ocean $\sum CO_2$	- 6‰	.75
Trees	-33‰	.75

*Relative to Earth PDB

**Relative to Earth 1850 (normalized to wood remove effects of stable isotope fractionation)

He repeats these measurements at various locations and depths in the ocean and finds to his surprise that they are everywhere the same. "My, such rapid air-sea CO_2 exchange and ocean mixing", he muses. As the biospherians had been banned from Earth because of their violent stand against both nuclear power and nuclear weapons, Dee-Ar feels safe to assume that no man-made ^{14}C is present on Kri.

Of course, by themselves, these measurements provide no information regarding perturbations in Kri's carbon cycle resulting from colonization. Then Dee-Ar lucks out. He finds a large tree (now leafless) fenced off and marked with a plaque, which reads "Planted in 2090 from a seedling carried to Kri from Earth. Although a tropical species devoid of rings, Dee-Ar is confident that he can construct a rough time scale based on the radial distance from the tree's center. He measures both carbon isotope ratios at frequent increments along a radial traverse. He is pleased by the results. For the inner-most three quarters of the boring, the ratios remain nearly uniform. Then, in the outer quarter, both ^{14}C and ^{13}C show an exponential drop. The values for the pre-colonization steady state are

$$\delta^{13}C = -22\%$$
$$^{14}C/C = 1.5\ ^{14}C/C\ \text{1850 earth wood}$$

To aid in the interpretation of these results, Dee-Ar makes the following measurements

ΣCO_2^{sea} = 10,000 μmol/liter

Mean depth sea = 380 meters

Area of sea = 2.5×10^{14} m^2

Volume of sea = 9.5×10^{16} m^3

He also makes a rough estimate that the terrestrial biomass (now all dead) was, prior to the catastrophe, about 500 GtC. As Kri was devoid of life before colonization, this 500

GtC must have been produced during the last 300 years. Dee-Ar further assumes that its half replacement time was 25 years.

Q-2. From this information, Dee-Ar calculates how much coal was burned. What answer does he obtain?

Dee-Ar's next step is to calculate the expected $^{13}C/^{12}C$ ratio change assuming that the only perturbation is from coal burning. He makes carbon isotope measurements on Kri's graphite and finds that it has a quite uniform ratio of -25‰. At first Dee-Ar is puzzled to see that the ^{13}C decline measured in the tree is smaller than that predicted from his coal consumption estimate. Then he realizes that the difference is the result of biosphere growth and that he can use it to check his rough estimate of Kri's standing biomass.

Q-3. What result does he obtain?

Having established the amount of excess CO_2 added to Kri's atmosphere-ocean system, Dee-Ar's next task is to attempt to reconstruct the pre-colonial CO_2 partial pressure. He equilibrates Kri's sea water with air containing 3600 and 4400 ppm CO_2 and measures the ΣCO_2 in these two sea water samples

p_{CO_2} μatm	ΣCO^2 μmol/liter
3600	9950
4000*	10,000**
4400	10,050

*Kri's atmospheric CO_2 content

**Kri's ocean ΣCO_2

He also demonstrates that the p_{CO_2} and $\sum CO_2$ of Kri's ocean is everywhere the same.

Q-4. What does Dee-Ar conclude about the pre-colonial atmospheric CO_2 content?

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Part II

MARTIN'S WORLD

CO_2'S GLACIAL HIDEOUT?

CONTENTS

MARTIN'S WORLD:

CO_2'S GLACIAL HIDEOUT?

The selection of the hero of this section has proven difficult. Under consideration were those who first measured the low CO_2 *contents of air trapped in glacial age ice, those who used carbon isotope ratios and cadmium contents in foraminifera to set constraints on scenarios designed to explain this drop, and those who demonstrated that the high latitude outcrops of the deep sea dictated the* CO_2 *content of the entire surface ocean and in turn that of the atmosphere. But in the end, we selected a dark horse, David Archer, who at the time this book was being written, put his finger on what appeared to be the mechanism responsible for the atmosphere's glacial to interglacial* CO_2 *cycle. He obtained microelectrode* O_2 *and pH data from the upper few centimeters of deep sea sediments which clearly demonstrated the importance of bacterial respiration as a driver of calcite dissolution. Encouraged by preliminary boron-isotope-based paleo pH measurements which suggested larger deep sea* $CO_3^=$ *concentrations during glacial time, Archer showed that an increase in the rain rate of organic matter could generate the required* $CO_3^=$ *ion change with little or no change in lysocline depth. But alas, now five years later, Archer's hypothesis has like its predecessors fallen on hard times. Danny Sigman, while a graduate student at Woods Hole, demonstrated that the requisite large separation between the saturation horizon and the lysocline required by this hypothesis could not be sustained. So in this second edition, we replace David Archer with the late John Martin who pioneered the concept that the availability of iron limits plant productivity in many parts of the oceans. He also pointed out that the large excess of iron carried to the sea during glacial time by the several-fold higher dust rain may have been responsible for the* CO_2 *drawdown.*

Introduction

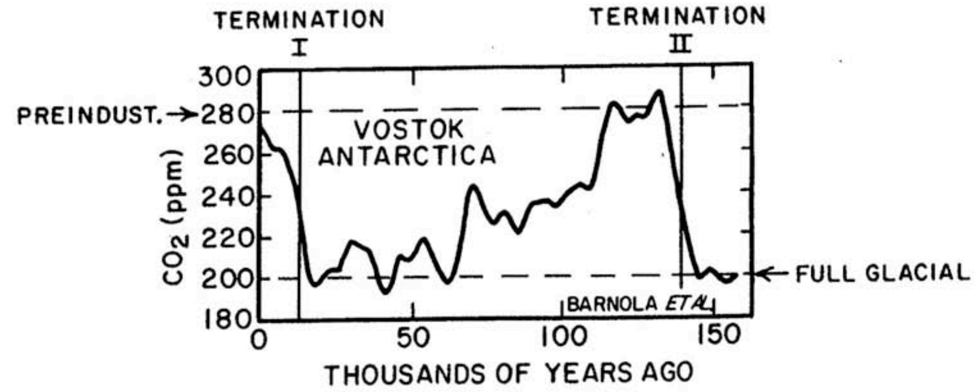
This section's puzzle concerns the cause of the glacial to interglacial difference in the atmosphere's CO_2 content. Twenty-five years ago, groups in Bern, Switzerland and in Grenoble, France independently made measurements on air trapped in polar ice which stunned the world of paleoclimatology by revealing that the atmosphere's CO_2 content was substantially lower during the last glacial period. Measurements made subsequent to this discovery confirmed these preliminary findings. During times of peak glaciation, the CO_2 content of the atmosphere averaged about 200 parts per million. By contrast, prior to the Industrial Revolution, it was 280 parts per million. Any doubts regarding the validity of these observations were put aside when the French group published their marvelous set of CO_2 measurement on air trapped in the Vostok Antarctica ice core. This record, revealed that the 80 parts per million rise in CO_2 content which occurred at the close of the last glaciation (i.e., Termination I) also characterized the close of the proceeding glaciations (i.e., Terminations II, III and IV).

Pinpointing the cause of these changes has proven to be a far more difficult task than anyone imagined. One thing is clear, because the ocean contains 60 times more carbon than the atmosphere, the search for an explanation must be focused on the factors controlling the ΣCO_2 content and alkalinity of surface ocean water. Over the last decade a number of clever scenarios have been put forward. But each in turn has bitten the dust, defeated by its failure to conform to observational constraints recorded in marine sediments.

Ice Core Measurements

Although a strong case can be made for the validity of the 80 parts per million rise in atmospheric CO_2 content between peak glacial and peak interglacial time, one unsettling aspect of the record exists. It has to do with a series of CO_2 content fluctuations associated with the millennia duration Dansgaard-Oeschger (D-O) oxygen isotope cycles which punctuate last glacial interval in the Greenland ice core record. During the cold portion of each of these cycles, the CO_2 content of the air trapped in the ice is close to the ambient glacial value of 200 parts per million. But during the warm portion of each of these cycles, CO_2 contents midway between the glacial and interglacial

THE CO_2 RECORD IN ICE CORES

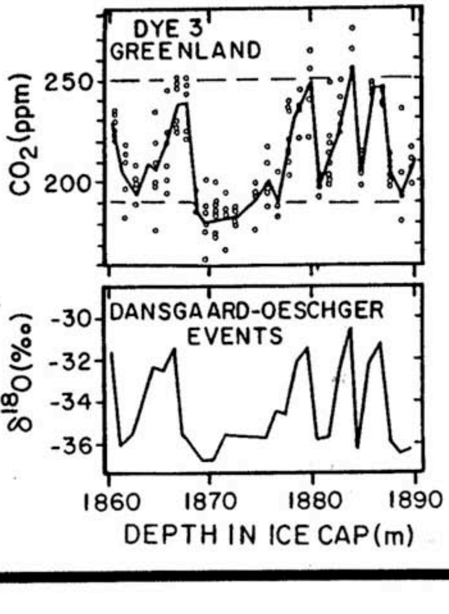


FULL GLACIAL CO_2 CONTENTS OF ICE CORE AIR

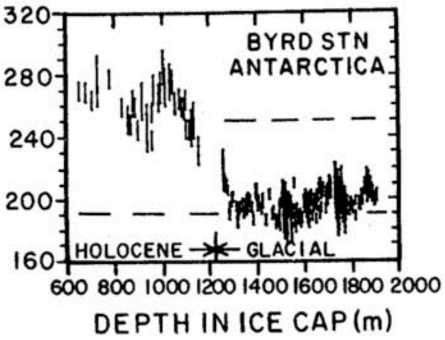
ICE CORE	CO_2 (ppm)	REFERENCE
VOSTOK ANT.	200	BARNOLA *ET AL.*, 1987
BYRD ANT.	195	NEFTEL *ET AL.*, 1988
DYE 3 GRN.	195	OESCHGER *ET AL.*, 1985

DISQUIETING RESULTS

GREENLAND
DYE 3
~30,000 TO ~40,000 YRS AGO



ANTARCTICA
BYRD STN
~6000 TO ~45,000 YRS AGO



values (i.e., at about 240 parts per million) are found. Three lines of argument strongly suggest that these high values must be spurious. First, a detailed series of measurements on the Byrd Station Antarctica ice core, covering the same time period, fail to show any values deviating significantly from the glacial ambient (i.e., 200 ppm). As the atmosphere mixes pole to pole on a time scale of about one year, no mechanism exists to support Greenland to Antarctic differences of more than about one part per million. Hence, one or the other of these records must be misleading. The second argument has to do with the high rates of change of CO_2 content at the transitions between the cold and warm phases of the D-O cycles. The 40 ppm rises occur on a time scale of decades. As these rise rates rival those experienced during the last several decades of intense fossil fuel burning, it is difficult to conceive a mechanism by which they might have been driven. Finally, the expected offset between the gas record and the ice record discussed in Keeling's World is not found. Rather, the CO_2 and ^{18}O shifts occur at the same depth. This suggests that the extra CO_2 was generated in the ice after lithification was complete.

Despite this blemish in the ice core CO_2 record, a strong case can be made in defense of the 80 ppm CO_2 content difference between glacial and interglacial time. The most powerful argument is based on the agreement of the results from ice formed under the ultra cold, low dustiness and low accumulation rate conditions which prevailed during glacial time at Vostok, Antarctica and those from ice formed under the less cold, high dustiness and high accumulation rate conditions which prevailed during glacial time in Greenland.

If the 240 parts per million values found for the warm portions of the Greenland D-O events are indeed spurious, then what mechanisms might be responsible?

Melting: The air-filled pore space in polar ice contains only about 2.5 micromoles of CO_2 per liter of ice. Distilled water close to its freezing point in contact with air contains about 25 micromoles of dissolved CO_2 per liter. Hence, were melting followed by refreezing to occur in the firn, significant amounts of excess CO_2 would be built into the ice. This excess CO_2 would initially be dissolved in the ice, but it might subsequently migrate to the air-bearing voids. While a possible explanation for the high CO_2 contents observed of the warm parts of Dansgaard-Oeschger cycles, this explanation suffers from a serious drawback. The refrozen melt water would not be expected to be homogeneously distributed. Rather, were this the correct explanation, one would expect a large sample to sample scatter in CO_2 content. Yet, the scatter for samples from the warm glacial intervals is no greater than that for those from the cold glacial intervals. Further, as Holocene ice contains no melt-induced excess CO_2, why should that from colder glacial times?

Clathrates: As ice is buried ever more deeply in the polar caps, the bubbles are squeezed to ever smaller size. At one kilometers depth, the pressure is nearly 100 times atmospheric. Below this depth, the air crystallizes into solids known as clathrates. When clathrate-containing ice from these depths is brought to the surface, the bubbles slowly reform. The annealing process responsible for their recreation takes a year or more. The question then arises as to whether the composition of the reformed gas phase has been altered. First of all, extractions accomplished by melting give results similar to those accomplished by the standard crushing method. A strong argument against the importance of this bias is that no offset in CO_2 content is seen as between ice from above and below the depth of clathrate formation. Were such an offset to occur, it would produce differences in the CO_2 verses time records obtained from ice cores differing in accumulation rate, for the ice at the depth of clathrate formation would be older for low than for high accumulation rate sites. Additional evidence against clathrate-induced biases comes from the Vostok record where an 80 ppm rise in CO_2 is found across both Termination I (above the depth of clathrate formation) and Termination II (below the depth of clathrate formation).

$CaCO_3$: The dust in polar ice consists, in part, of $CaCO_3$. The aerosols in polar ice contain H_2SO_4 and HNO_3. Interaction between the calcite and the strong acids constitutes a potential source of excess CO_2. As the dust and aerosols are located on grain boundaries, any CO_2 produced in this way would likely find its way into the air-filled voids. During glacial intervals, the concentration of calcium in the Greenland ice reaches several micromoles per liter. Most of this calcium was initially contained in $CaCO_3$. Hence, if this $CaCO_3$ were subsequently to be dissolved by interaction with aerosol acids, then several micromoles of CO_2 per liter of ice would be released to the grain boundaries. Then why doesn't this interaction bias all the CO_2 results from Greenland ice cores? The answer must be that during interglacial intervals there is too little $CaCO_3$ to contribute significant amounts of CO_2 and during peak glacial colds the $CaCO_3$ completely neutralizes the acid in the firn allowing the excess CO_2 to escape to the atmosphere before the air bubbles close. This is the preferred explanation.

In summary, clearly the last word has yet to be written with regard to the validity of paleoatmospheric CO_2 content estimates that are based on measurements made on air trapped in polar ice. But it is unlikely that future work will reveal a sizable bias in the 80 ppm CO_2 content difference between times of full glacial and full interglacial conditions. This difference is almost certainly real; therefore, some mechanism must exist which explains it.

Whole Ocean $\sum CO_2$ Inventory

The discussion of mechanisms which might be responsible for the glacial to interglacial change in the atmosphere's CO_2 content focuses on the ocean. The reason is that on the time scale of more than one oceanic mixing time (i.e., ~1000 years) the atmosphere's CO_2 content is dictated by the state of the ocean's chemistry. Even when the buffering capacity of the ocean is taken into account, its effective carbon reservoir is about six times greater than the atmosphere's. Hence, on the time scale of glacial cycles, it is the ocean which tells the atmosphere what CO_2 content it must have. While surface waters call the atmosphere's tune, their chemistry, in turn, is held in the grip of that of the much larger underlying deep sea reservoir. So we will start by considering those processes which influence the $\sum CO_2$ and alkalinity of the deep ocean. Then we will consider those processes which control the offset in $\sum CO_2$ and alkalinity between surface waters and those in the deep sea. Finally, we will be concerned with the temperature and salinity of surface water which for any given chemical composition sets their CO_2 partial pressure and therefore that of the atmosphere.

The CO_2 partial pressure of any given sample of sea water depends on its excess of alkalinity over $\sum CO_2$: the greater this excess, the higher the $CO_3^=$ ion content and the lower the CO_2 partial pressure. On the time scale of glacial to interglacial cycles (i.e., ~10^4 years), the alkalinity of sea water changes primarily as the result of deposition or dissolution of $CaCO_3$. For each mole of $CO_3^=$ fixed into or released from $CaCO_3$ the alkalinity is changed by two equivalents (one unit of carbon per two units of charge carried by the Ca^{++} ion.). This extra unit of charge is what counts for it changes in the excess of alkalinity over $\sum CO_2$. The excess of alkalinity over $\sum CO_2$ is balanced by the conversion of HCO_3^- to $CO_3^=$. As we shall see, $CaCO_3$ storage in and retrieval from deep sea sediments has very likely played a role in the glacial to interglacial CO_2 change. But it is not clear whether this role is a major or minor one.

In addition to the formation and dissolution of $CaCO_3$, the concentration of $\sum CO_2$ is changed by the creation and destruction of terrestrial organic matter. Storage of carbon in trees and humus removes CO_2 from the ocean-atmosphere reservoir. Oxidation of previously stored organic matter returns the CO_2 to the ocean-atmosphere reservoir. Taken together, tree wood and soil humus contain several times more carbon than does the atmosphere. Fortunately, a means exists to estimate how the sizes of these reservoirs changed between glacial and interglacial time. As the carbon isotope composition of terrestrial organic material ($\delta^{13}C \sim -25‰$) is quite different than that for average ocean-atmosphere carbon ($\delta^{13}C \sim 0‰$), inter-reservoir transfers lead to shifts in the carbon isotope composition of average ocean-atmosphere carbon. Measurements on benthic foraminifera from deep sea sediments suggest that the average ^{13}C content of carbon in

GLACIAL TO INTERGLACIAL CHANGE IN CARBON DISTRIBUTION

(GIGATONS OF CARBON)

	GLACIAL	INTERGLACIAL	$\Delta_{G \to I}$
OCEAN	35,740	35,100	-640
ATMOSPHERE	360	500	+140
	36,100	35,600	-500
			-1.4%
TER. BIOS. (*I.E.* WOOD & HUMUS)	1500	2000	+500

CARBON ISOTOPE BUDGET

$$35{,}600(+0.50\text{‰}) + 500(-25\text{‰}) \equiv 36{,}100(+0.15\text{‰})$$

AVERAGE $\delta^{13}C$ FOR HOLOCENE OCEAN ΣCO_2

AVERAGE $\delta^{13}C$ FOR WOOD & HUMUS

AVERAGE $\delta^{13}C$ FOR GLACIAL OCEAN ΣCO_2

INTERGLACIAL	GLACIAL
$\delta^{13}C_{O+A}$	$\delta^{13}C_{O+A}$
0.50‰	0.15‰

$$\Delta_{G \to I} = 0.35\text{‰}$$

IMPACT ON OCEAN CHEMISTRY

(T = 2°C, S = 35 ‰)

INTERGLACIAL

ALKALINITY	2270 μeq/kg
ΣCO_2	2085 μmol/kg
$CO_3^=$	129 μmol/kg
pCO_2	280 μatm

GLACIAL (BEFORE $CaCO_3$ COMPENSATION)

ALKALINITY	2270 μeq/kg
ΣCO_2	$1.014 \times \Sigma CO_{2\,INT}$ = 2115 μmol/kg
$CO_3^=$	112 μmol/kg
pCO_2	336 μatm
ΔpCO_2	+56 μatm

GLACIAL (AFTER $CaCO_3$ COMPENSATION)

ALKALINITY	2270 + 52 = 2322 μmol/kg
ΣCO_2	2115 + 26 = 2141 μmol/kg
$CO_3^=$	129 μmol/kg
pCO_2	296 μatm
ΔpCO_2	+16 μatm

the ocean-atmosphere reservoir was about 0.35‰ lower during glacial than during interglacial time. This requires a transfer of an amount of carbon equal to 1.4 percent of that in today's ocean-atmosphere reservoir. When equilibrated with the carbon dissolved in the sea, this extra CO_2 creates a 56 ppm higher glacial atmospheric CO_2 content. But after compensation through the interaction with $CaCO_3$ in marine sediments (see below), the increase is reduced to only 16 ppm. So we have an embarrassment on our hands; our task has grown rather than diminished. We now have to find a way to change the atmosphere's CO_2 content by 96 parts per million rather than 80 ppm!

Physical Properties Of Surface Water

The partial pressure of CO_2 in surface water depends not only on its chemical composition but also on its temperature and salinity. Before considering the more difficult question of what determines the chemical offset between surface and deep waters, let us consider the possible contribution to the glacial to interglacial change in the atmosphere's CO_2 content of temperature and salinity.

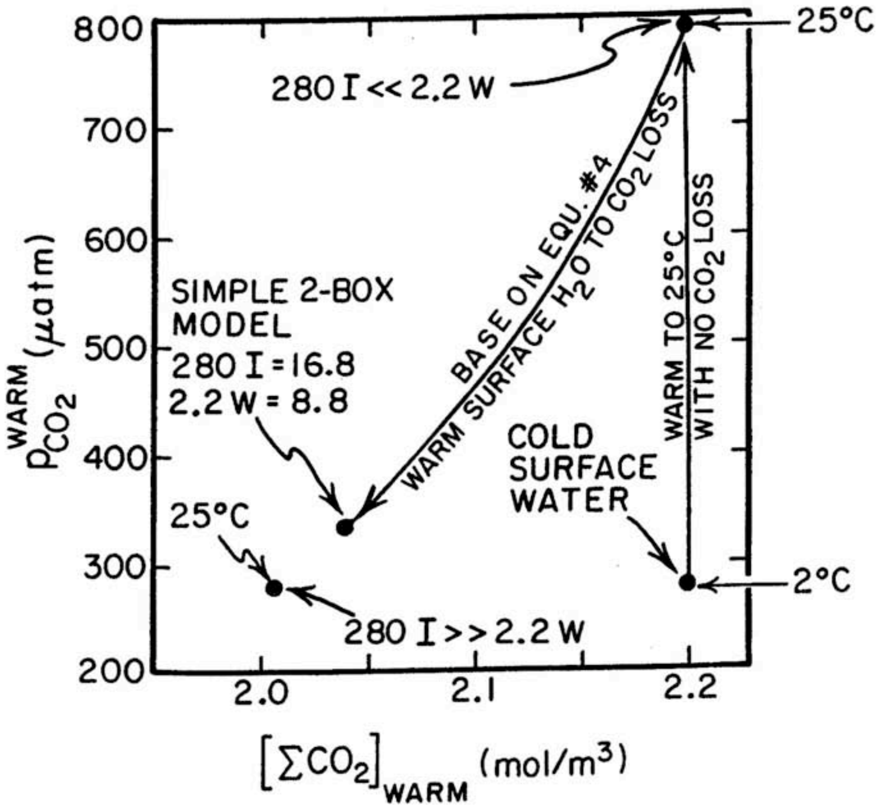
The first point to be made in this connection is that despite their relatively small combined area (~ 20% of the total) the cold portions of the surface ocean have an influence on the atmosphere's CO_2 partial pressure exceeding that for their more extensive warm counterparts. This important concept was simultaneously articulated by three groups: McElroy and Knox at Harvard, Toggweiller and Sarmiento at Princeton and Siegenthaler and Wenk at Bern. What the Harvardton Bears showed was that because the deep sea is ventilated from polar regions, the chemistry of cold surface waters is closely tied to that of the chemically dominant deep sea reservoir. Further, because CO_2 can be transported through the atmosphere from one part of the surface ocean to another, a tendency exists for the CO_2 partial pressure of warm surface waters to be drawn toward that for cold surface waters. If, for example, the CO_2 pressure in the warm surface ocean tended toward higher values than that for cold surface ocean, then CO_2 would escape to the atmosphere from the warm regions and be reabsorbed in the cold regions. The extent to which this CO_2 equalization is achieved depends on the ratio of the rate of interchange of CO_2 gas between air and sea to the rate of interchange of water between the ocean's warm and cold realms. The higher this ratio, the stronger the influence of the cold surface ocean on the CO_2 partial pressure for warm surface waters and therefore for the atmosphere as well.

A relatively simple test can be applied to any ocean model to determine its equalization index. This test can be carried out by arbitrarily changing the coefficient relating CO_2 partial pressure to CO_2 gas content of the model's warm surface waters (i.e., those lying between 40° N and 40° S). The model is then run until a new CO_2 steady state is achieved. The object of the test is to see by how much the transfer of CO_2 from warm to the cold surface ocean reduces the arbitrarily imposed excess or deficiency of CO_2 pressure in the warm ocean. If, for example, an initial CO_2 partial pressure excess of 30% for warm surface water drops to a steady state excess of 6%, then the equalization index would be 0.2. The lower the model's equalization index the less sensitive it is to conditions in the warm surface water sphere.

The simple three-box models used by the Harvardton Bears to illustrate this point, were constrained to yield the observed distribution of natural radiocarbon both between the atmosphere and surface ocean and between the warm surface and deep ocean. In order to match this ^{14}C distribution, for these very simple models the CO_2 exchange had to be rapid with respect to thermohaline circulation. As a consequence, the equilibration index was quite small. Hence these simple models suggest that glacial to interglacial changes in temperate and tropical surface water have relatively little impact on the atmosphere's CO_2 content.

Rather, the Harvardton Bears would contend that were the glacial cooling to have played a significant role in lowering the atmosphere's CO_2 content, it must have operated in the polar regions where deep waters form. In today's ocean, deep waters form in two places, in the Southern Ocean and in the northern Atlantic. No significant deep water

SIMPLE ABIOTIC MODEL FOR THE HARVARDTON BEAR EFFECT *

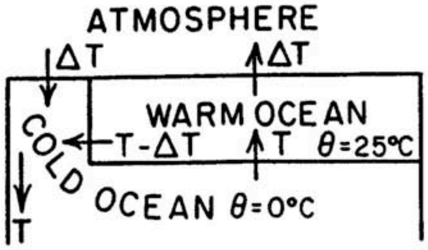


	$p_{CO_2}^{COLD}$	$p_{CO_2}^{WARM}$	$p_{CO_2}^{ATMOS.}$	
TRANSPORT DOMINATES	280	790	688	INDEX = 1.00
MODEL ($W = 4 \frac{m}{yr}$, $I = .06 \frac{mol}{m^2\, yr\, \mu atm}$)	280	335	324	INDEX = 0.11
GAS EXCHANGE DOMINATES	280	280	280	INDEX = 0.00

$$\text{HARVARDTON BEAR INDEX} = \frac{324-280}{688-280} = 0.11$$

* THE COLD RESERVOIR IS ASSUMED TO BE SO LARGE IN SIZE RELATIVE TO THE WARM RESERVOIR THAT ITS CHEMISTRY REMAINS CONSTANT: $p_{CO_2} = 280\ \mu atm$

$[\Sigma CO_2] = 2.2\ mol/m^3$



$$1)\quad T = \overset{\substack{\text{UPWELLING}\\(\text{m}^3/\text{m}^2\,\text{yr})}}{W} \times \overset{\substack{\text{CONC.}\\(\text{mol/m}^3)}}{\left[\Sigma CO_2\right]_{COLD}} \times \underset{\substack{\text{FRACTION}\\\text{WARM}}}{f}\ \overset{\substack{\text{OCEAN AREA}\\(\text{m}^2)}}{A} = 4\times 2.2\times 0.8\,A \text{ mol/yr}$$

$$2)\quad \Delta T = (\overset{\substack{\text{CO}_2\text{ PARTIAL}\\\text{PRES. }(\mu\text{atm})}}{p_{CO_2}^{ATMOS.}} - 280)\ \overset{\substack{\text{CO}_2\text{ INV. RATE}\\(\text{mol/m}^2\text{yr}\,\mu\text{atm})}}{I} \times \underset{\text{FRACTION COLD}}{(1-f)}\overset{\substack{\text{OCEAN AREA}\\(\text{m}^2)}}{A}$$

$$= (p_{CO_2}^{ATMOS.} - 280)\ 6\times 10^{-2}\times 0.2\,A$$

$$3)\quad \frac{\Delta T}{T} = \frac{(p_{CO_2}^{ATMOS.} - 280)\ 1.2\times 10^{-2}}{4\times 2.2\times 0.8} = 1 - \frac{\left[\Sigma CO_2\right]_{WARM}}{2.2}$$

SOLVING FOR $p_{CO_2}^{ATMOS.}$

$$p_{CO_2}^{ATMOS.} = 868 - 267\left[\Sigma CO_2\right]_{WARM}$$

COMBINE WITH

$$p_{CO_2}^{ATMOS.} = 0.8\ p_{CO_2}^{WARM} + 0.2\times 280$$

TO GIVE

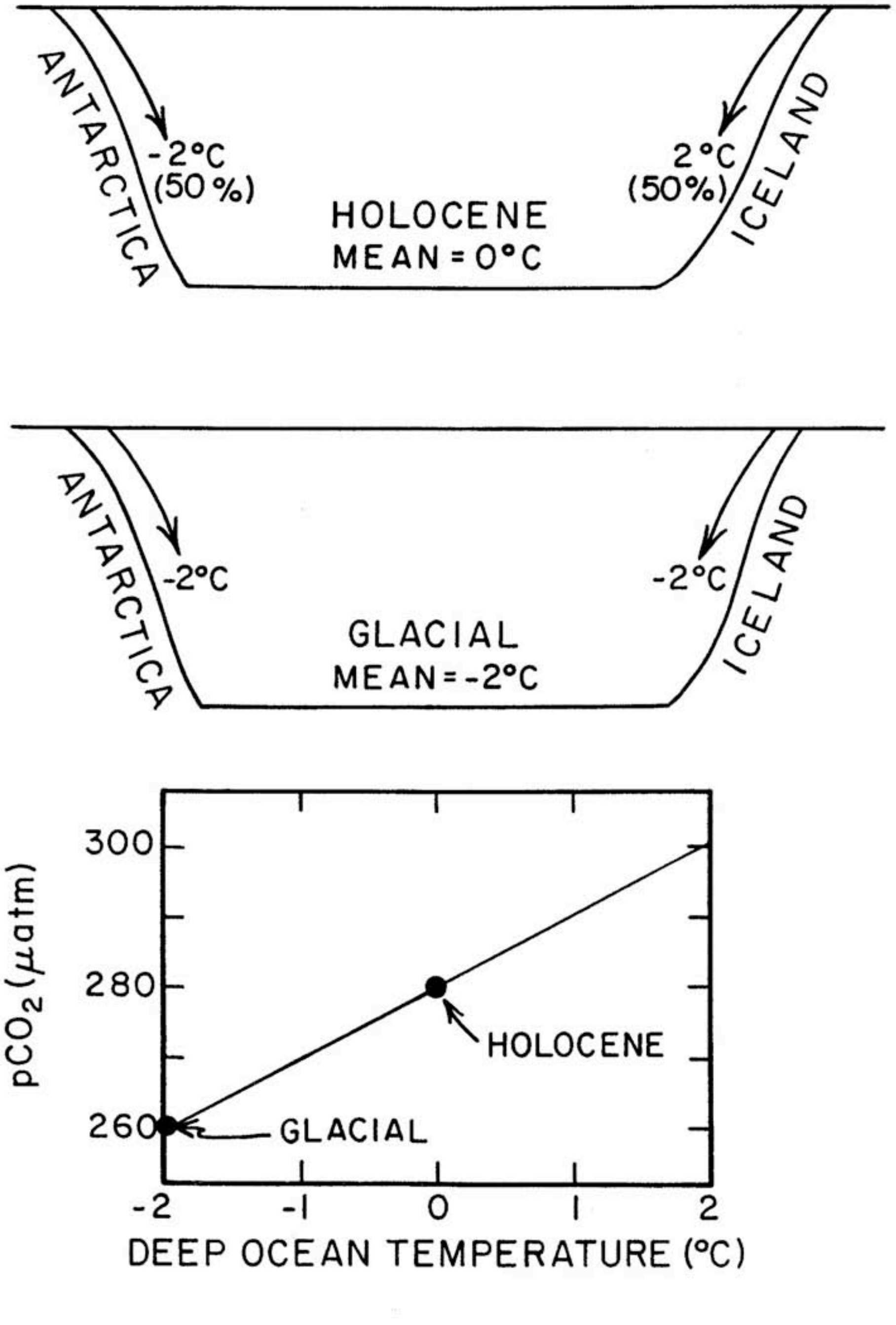
$$4)\quad p_{CO_2}^{WARM} = 1015 - 334\left[\Sigma CO_2\right]_{WARM}$$

WHICH IS THE REQUIREMENT FOR MATERIAL BALANCE OF CARBON formation occurs in the northern Pacific. A number of lines of evidence lead us to believe that the deep waters which formed during glacial time were on the average somewhat colder than those which form today. Hence, so also must have been the surface waters in the polar regions where deep waters form. However, it is difficult to believe that this cooling was greater than 2˚ C. The reason is that the temperature of deep water formed around Antarctica is currently very near the freezing point so it is as cold as it can get. Thus if a change occurred, it must have been in the northern Atlantic. As the waters currently sinking in this region of the ocean have temperatures averaging about 2°C, glacial age deep waters formed in the Atlantic could have been as much as 4°C colder than today's average. However, as in today's ocean only about half of the deep water currently forms in the northern Atlantic, it is difficult to accept that the overall deep ocean cooling was more than about 2°C. A 2°C cooling would lower the CO_2 partial pressure by only 20 micro-atmospheres. Again, small potatoes!

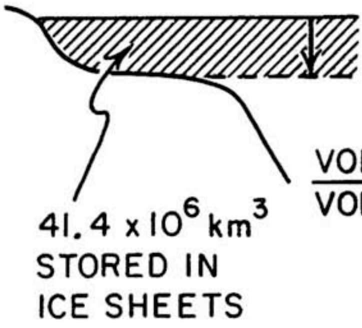
With the advent of ocean general circulation models, it was possible to check whether the equilibration index for the real ocean is indeed as low as predicted by the three box models. It turns out that these models yield similar indices.

What about salinity? We know that sea level stood about 115 meters lower than today during peak glacial time. Hence, the ocean's volume was about 3 percent smaller than today's. As the salt inventory remained the same, the ocean's salinity must have been 3% higher. Other things being equal, this would raise the atmosphere’s CO_2 partial pressure by about 10 μatm. Taken together with the temperature-induced change in CO_2 content of about 20 μatm the net change would be only 10 μatm. Hence, it can be concluded that the changes in the physical properties of surface water did not play a significant role in the glacial to interglacial CO_2 change. Together they failed to more than compensate for the 16 ppm increase driven by a reduction in the size of the terrestrial biosphere. So, after all this, we are left with close to the original 80 μatm to explain!

ROLE OF POLAR TEMPERATURES



ROLE OF SALINITY

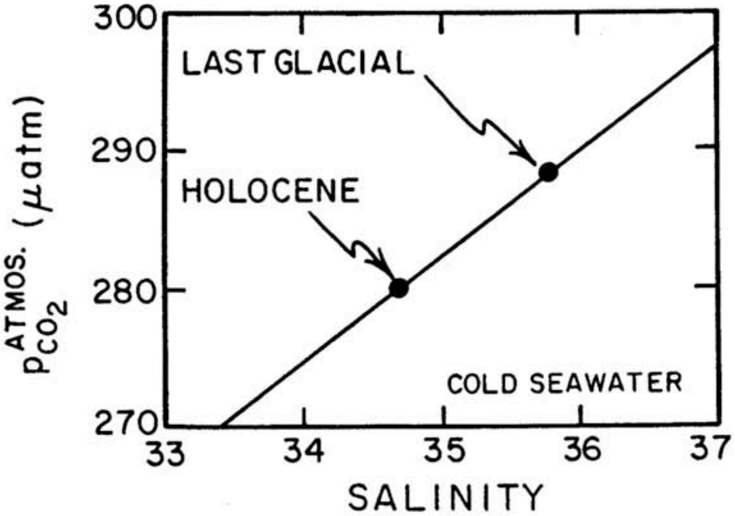


SEA LEVEL DOWN ~ 115m
AT TIME OF LAST
GLACIAL MAXIMUM

$$\frac{\text{VOLUME GLACIAL}}{\text{VOLUME HOLOCENE}} = \frac{3800-115}{3800} = 0.97$$

MEAN DEPTH
TODAY'S OCEAN

$$\text{SALINITY GLACIAL OCEAN} = \frac{34.7}{.97} = 35.8$$

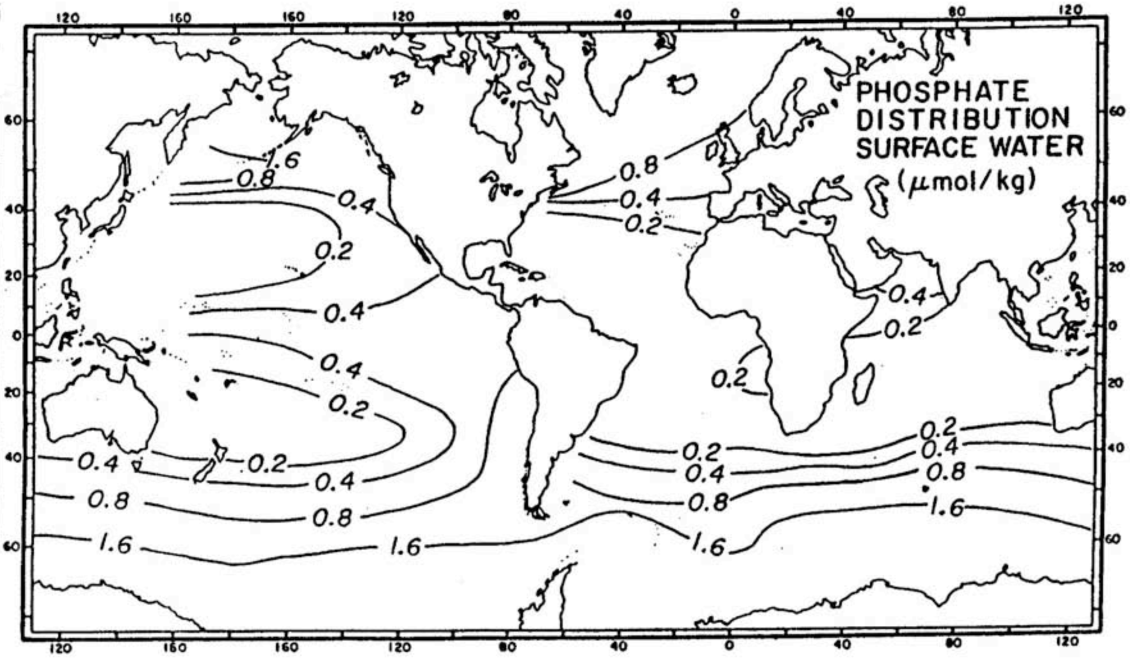


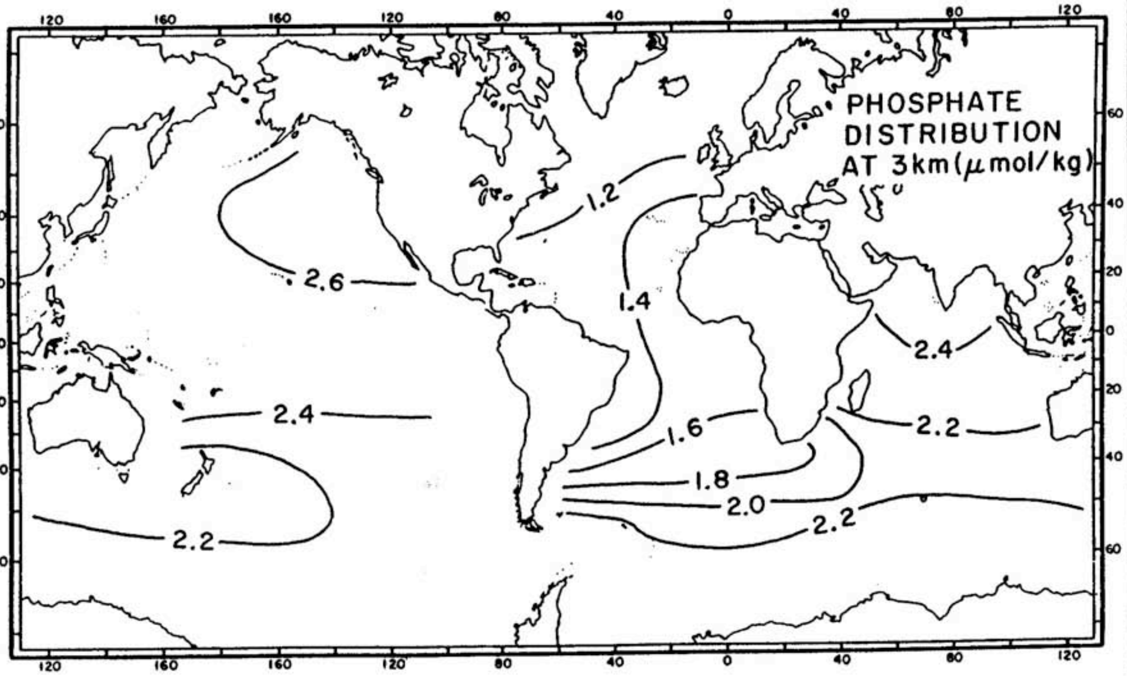
Biologic Pumping

From the very beginning of this quest, attempts to explain the low CO_2 content of the glacial atmosphere have focused on the CO_2 pumping action by marine organisms. Plants living in surface water convert CO_2 into organic matter. Some of this organic matter falls to the sea's interior where it is oxidized releasing the CO_2. Hence the action of this biologic cycle holds the CO_2 partial pressure in surface waters below that for waters of the sea's interior. In much of the ocean, this pumping action is limited by the availability of the nutrients, phosphate and nitrate. On the average microorganisms utilize about 16 nitrogen atoms and about one phosphorus atom per 125 carbon atoms. As the molar ratio of nitrate to phosphate in the sea is close to 16, currently these two nutrients appear to colimit plant productivity. However, in regions of strong upwelling such as the Southern Ocean, the eastern tropical Pacific and the northern Pacific, much of the NO_3 and PO_4 reaching the surface goes unused. To some extent, this inefficiency in usage is due to a scarcity of iron. If for some reason, the nutrients available in these regions of the ocean were to be utilized with 100% efficiency, then the atmosphere's CO_2 content would fall below its glacial level. Deep waters formed along the margins of the Antarctic continent leave the surface carrying about 1.6 micromoles per liter of PO_4 (i.e. about three quarters the average deep sea concentration). Those forming in the northern Atlantic carry about 0.8 micromoles per liter. It is this situation the Harvardton Bears had in mind when they proposed the dominance of high latitude surface waters in setting the atmosphere's CO_2 content. It is then tempting to postulate that the extent of nutrient utilization in these regions was greater during glacial time and consequently the atmosphere's CO_2 content was lower.

A large boost was given to the Harvardton Bears scenario by John Martin's discovery that in those regions of the surface ocean where the efficiency of nutrient utilization is low, the scarcity of iron may be the villain. The conclusions he drew from his early experiments carried out on the decks of ships were proven to be right on the

GLOBAL PO_4 DISTRIBUTION



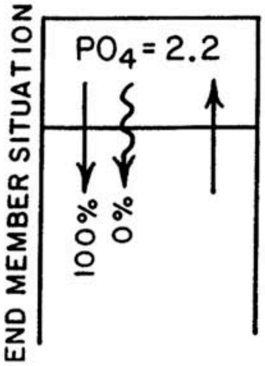


money by a large scale *in situ* fertilization experiments conducted in the eastern tropical Pacific. Much of the nitrate and phosphate present in the iron-fertilized patch were utilized, the chlorophyll content increased and, of course, the CO_2 content of the surface water was drawn down. Martin pointed out in a paper published shortly before his death that the iron made available by the very large excess dust fall of glacial time likely permitted a higher degree of utilization of nutrients in the Southern Ocean. However, because the expected ^{13}C signal in the glacial-age shells of Southern Ocean planktonic organisms was not found, his paper was not received enthusiastically by most marine geochemists. As outlined below, a new twist on Martin's idea may change this.

Unfortunately, a key prediction made by this hypothesis appears not to have been fulfilled. It has to do with the carbon isotope record for Southern Ocean surface water kept by the shells of planktonic foraminifera. During photosynthesis in cold water, the heavy isotope of carbon, ^{13}C, is discriminated against by about 25‰. Because of this, the $^{13}C/^{12}C$ ratio in surface ocean ΣCO_2 water is greater than that in deep water ΣCO_2. Hence, were the biologic pumping action at high latitudes stronger during glacial time, then the $^{13}C/^{12}C$ ratio for planktonic foraminifera shells formed in surface waters in these regions should have been more positive than now. But this is not the case. In the Southern Ocean, the $^{13}C/^{12}C$ ratio in both planktonic and benthic foraminifera was about 0.9‰ lower during peak glacial time than during peak interglacial time. These results suggest that the $^{13}C/^{12}C$ difference between surface and deep water was about the same for glacials as for interglacials. Hence the carbon isotope record appears to be telling us that the efficiency of nutrient utilization in the Southern Ocean was similar to today's.

Finally, further support for the absence of any large increase in the efficiency of nutrient utilization throughout the Southern Ocean appeared to come from nitrogen isotope measurements made on organic material from circum Antarctic sediments. During the conversion of NO_3 dissolved in the sea into NH_3 incorporated into the amino acids in plant matter, there is an 8‰ depletion of the heavy nitrogen isotope (^{15}N).

DEPENDENCE OF ANTARCTIC SURFACE WATER, CO_2 PARTIAL PRESSURE AND CARBON ISOTOPE RATIO ON THE EFFICIENCY OF NUTRIENT UTILIZATION

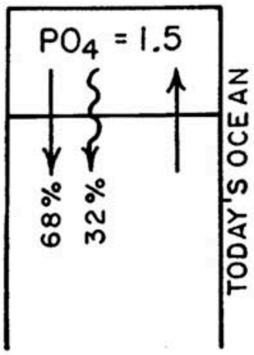


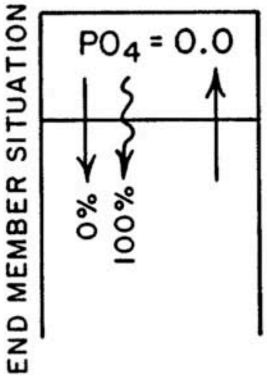
UTILIZATION EFFICIENCY=0%

	SURF.	DEEP	
PO_4	2.2	2.2	µmol/L
NO_3	35	35	µmol/L
ΣCO_2	2200	2200	µmol/L
pCO_2	514	514	µatm
$\delta^{13}C$	0.0	0.0	%

UTILIZATION EFFICIENCY=32%

	SURF.	DEEP	
PO_4	1.5	2.2	µmol/L
NO_3	24	35	µmol/L
ΣCO_2	2113	2200	µmol/L
pCO_2	280	514	µatm
$\delta^{13}C$	1.2	0.0	%





UTILIZATION EFFICIENCY=100%

	SURF.	DEEP	
PO_4	0.0	2.2	µmol/L
NO_3	0	35	µmol/L
ΣCO_2	1925	2200	µmol/L
pCO_2	103	514	µatm
$\delta^{13}C$	3.8	0.0	%

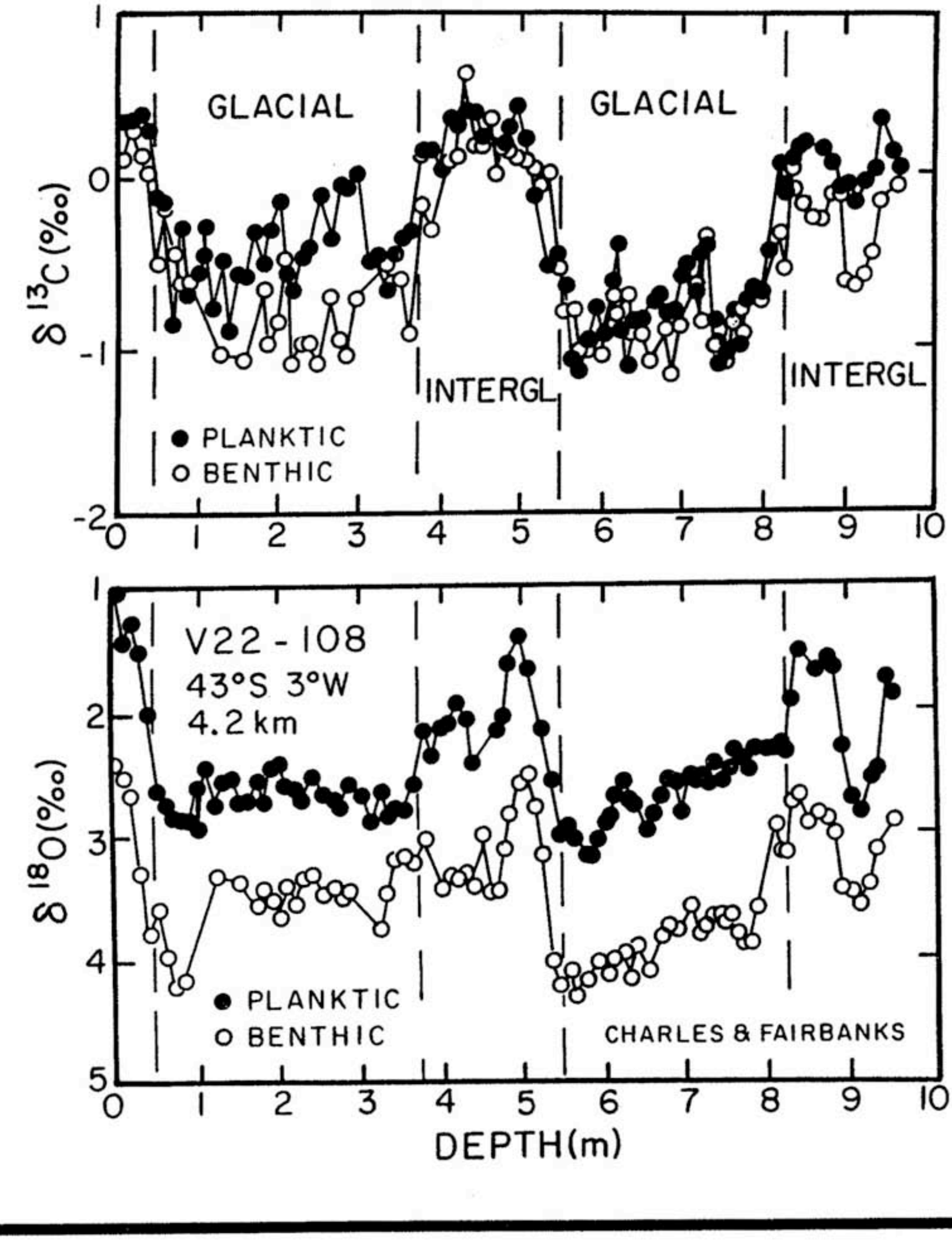
REDFIELD RATIOS : $PO_4 : NO_3 : \Sigma CO_2$ = 1 : 16 : 125

$\delta^{13}C_{\text{ORGANIC MATTER}} = -30\%$

ANTARCTIC SEDIMENT

CARBON ISOTOPES RECORDS FOR SURFACE AND DEEP WATERS OVER THE LAST TWO GLACIAL CYCLES

(AS DEFINED BY OXYGEN ISOTOPE CHANGES)

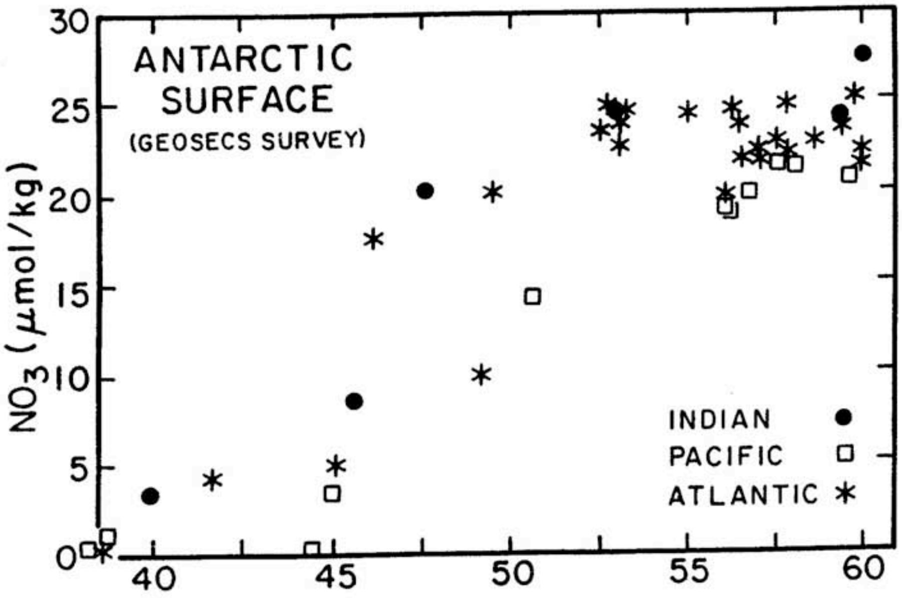


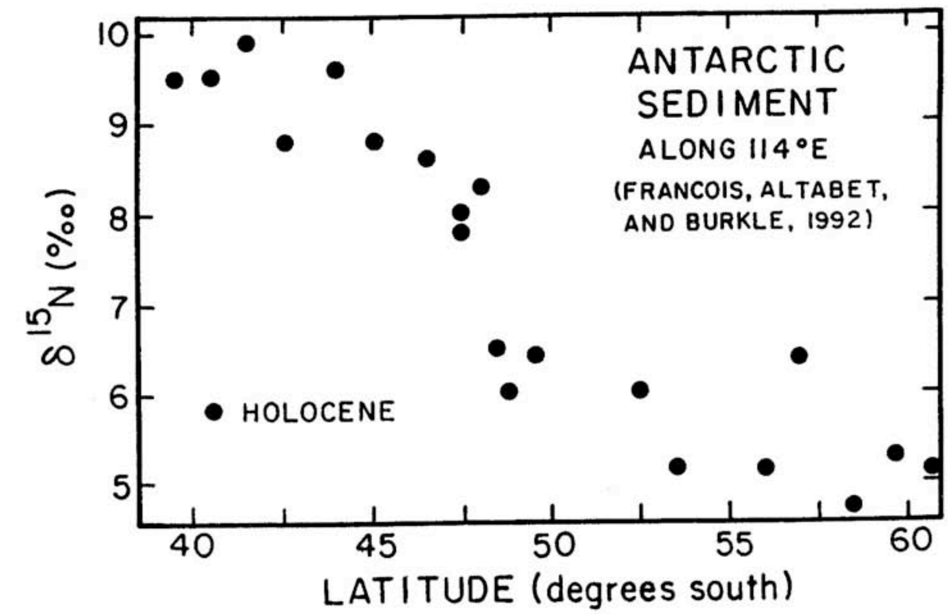
However, the actual difference in isotopic composition between the inorganic nitrogen upwelling to the surface and the organic nitrogen raining to the sea floor depends on the efficiency of nutrient utilization. Only if a very small fraction of the available NO_3^- is utilized will the full fractionation be seen. By contrast, if all the upwelled NO_3^- were utilized, there could be no difference between the isotope composition of the upwelled inorganic nitrogen and that of the sinking organic nitrogen.

Meridianal traverses of nitrogen isotopes in Holocene sediments from the Antarctic region nicely reflect the degree of utilization of nutrients in the overlying water. The ratio of ^{15}N to ^{14}N in the sediment organics is about 8‰ lower for the high latitude portion than for the low latitude portion of the traverse. Furthermore, the shape of this latitude trend is the mirror image of the concentrations of NO_3^- in the overlying surface water. This relationship is exactly as expected; close to Antarctica where the utilization efficiency is low, the full fractionation is observed, and well away from Antarctica where the nutrients are fully utilized, diatoms have a $\delta^{15}N$ value close to that for NO_3 in the deep sea. Early studies suggested that the trend of the nitrogen isotope ratios for glacial sediments from the same traverse of cores was nearly the same as for Holocene sediments. These results tell a story consistent with that told by the carbon isotope in planktic foraminifera shells. During glacial time, the nutrients in surface waters at high latitude in the Antarctic Ocean were utilized with similar efficiency as at present.

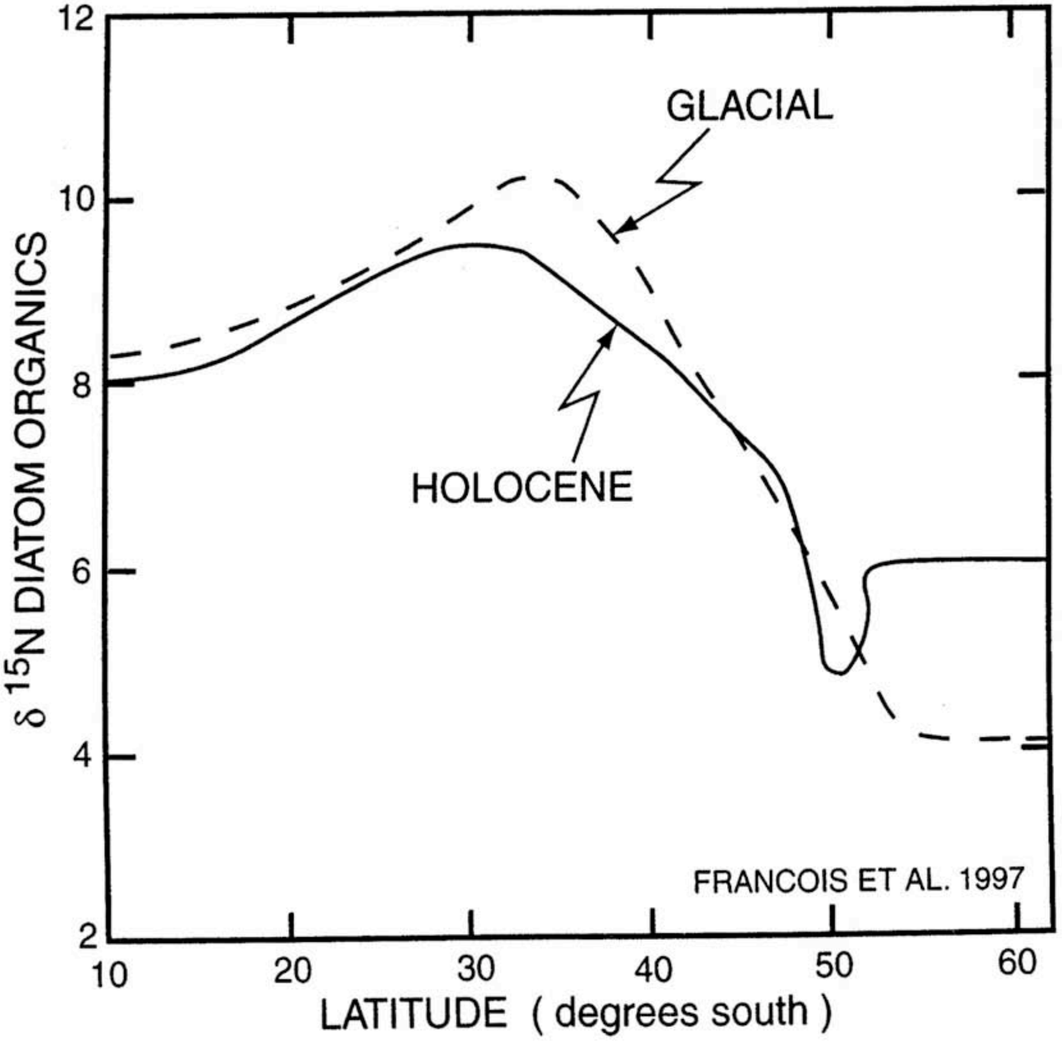
This is how things stood at the time the first edition of this book was completed. Since then a host of new results have appeared which have forced a rethinking of conditions in the glacial Southern Ocean. While ^{13}C measurements on both benthic and planktonic foraminifera confirm earlier results, new cadmium measurements suggest that Southern Ocean waters of glacial age were depleted rather than enriched in nutrients. Measurements of uranium concentrations and of ^{231}Pa to ^{230}Th ratios suggest that productivity was lower to the south of the present day position of the polar front and higher to the north. With the development of a more rigorous cleaning procedure for

NITROGEN ISOTOPE METHOD





GLACIAL TO HOLOCENE CHANGE IN $^{15}N/^{14}N$ IN DIATOM BOUND ORGANICS



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diatoms, Roger Francois and his coworkers from Woods Hole were able to show that while north of the polar front (~50°S) in the Atlantic and Indian sectors of the Antarctic, the $\delta^{15}N$ in diatom bound organic remained nearly the same, south of 50°S the values were 2‰ more negative during glacial than during interglacial time. This suggests a higher nutrient utilization efficiency then than now. These new results also suggest a major difference between the magnitude of the changes in the Pacific sector on the one hand and the Atlantic and Indian sectors on the other. All in all as of June 1998, things were in such a state of flux. Clearly what went on during glacial time in the Southern Ocean will occupy the attention of marine geochemists for the next decade. The implications of these findings to the cause of the lower than present CO_2 content of the glacial atmosphere will of course be of utmost importance!

Carbonate Ion Concentration

As we have already discussed, the CO_2 partial pressure exerted by a given parcel of sea water depends on its excess of alkalinity over ΣCO_2 concentration. Changes in this excess are reflected in the $CO_3^=$ ion concentration. To the simplest approximation

$$[CO_3^=] \cong [ALK] - [\Sigma CO_2] = \text{ALK Excess}$$

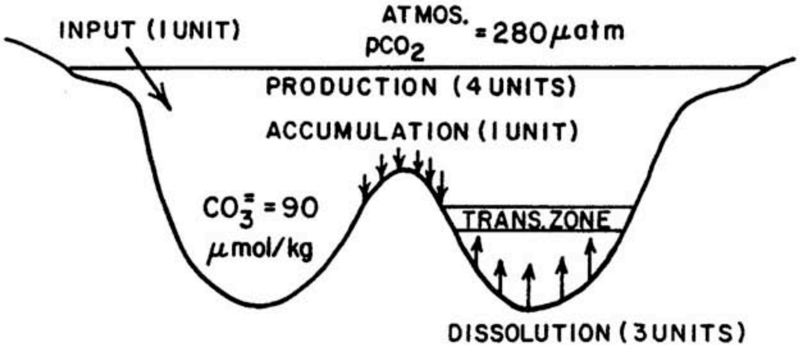
Furthermore, the CO_2 gas concentration of sea water is to the simplest approximation inversely proportional to its $CO_3^=$ concentration. Hence

$$[CO_2] \cong \frac{1}{[ALK] - [\Sigma CO_2]} =$$

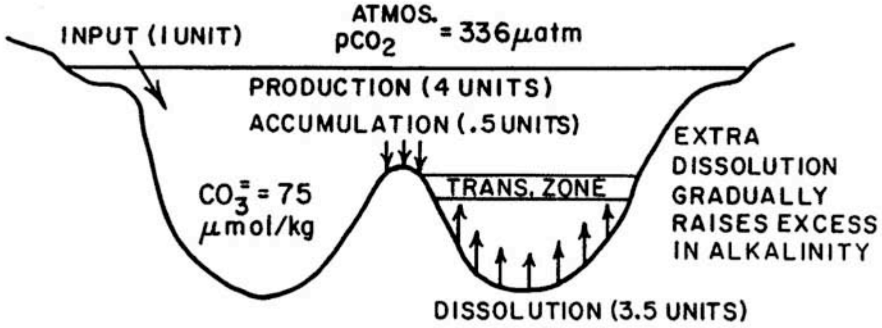
The major cause for differences in the alkalinity excess from one place to another in the sea is the production or dissolution of $CaCO_3$. This cycle is akin to that for organic material in that $CaCO_3$ is produced in the surface ocean and is destroyed at depth in the sea. However, two important differences exist. First, the generation of $CaCO_3$ raises rather than lowers the CO_2 content of sea water. The reason for this is that the alkalinity change associated with $CaCO_3$ formation is twice as great as the ΣCO_2 change. Hence, the alkalinity excess is decreased when $CaCO_3$ is manufactured by marine organisms. Second, rather than being almost completely destroyed as is organic matter, roughly one

$CaCO_3$ COMPENSATION

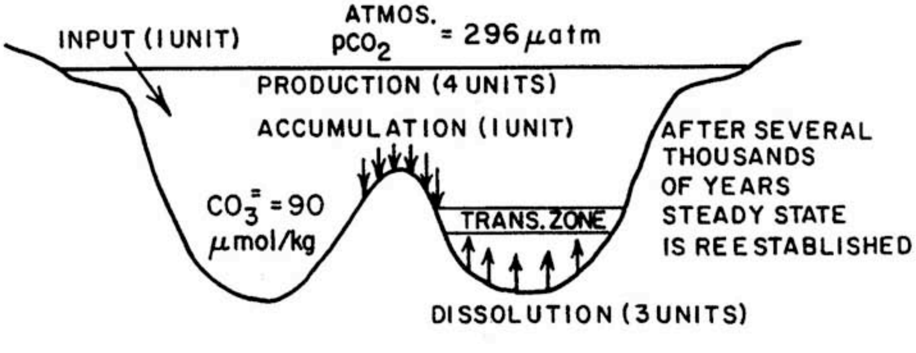
INITIAL STATE

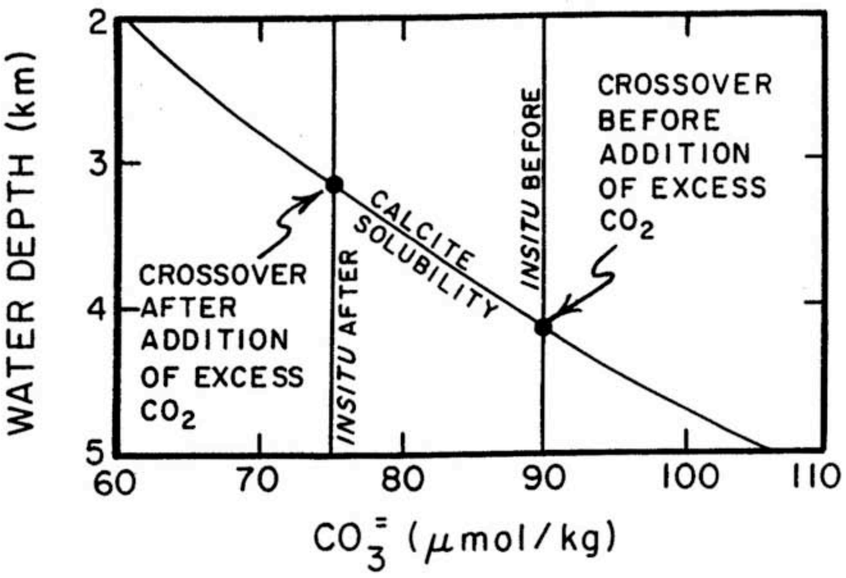


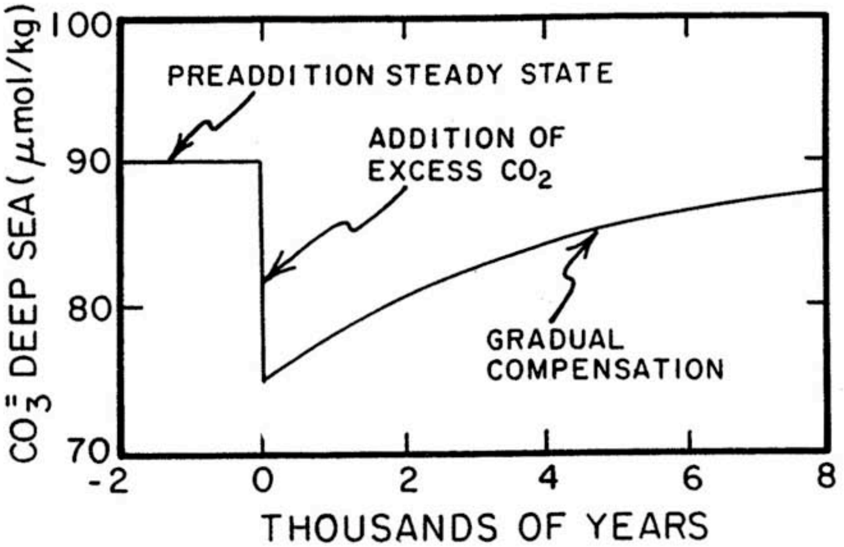
PERTURB BY ADDING WOOD-HUMUS DERIVED CO_2



AFTER COMPENSATION




WATER DEPTH (km)
2
3
4
5
60
70
80
90
100
110
$CO_3^=$ (μmol/kg)
CROSSOVER BEFORE ADDITION OF EXCESS CO_2
CROSSOVER AFTER ADDITION OF EXCESS CO_2
INSITU AFTER
INSITU BEFORE
CALCITE SOLUBILITY

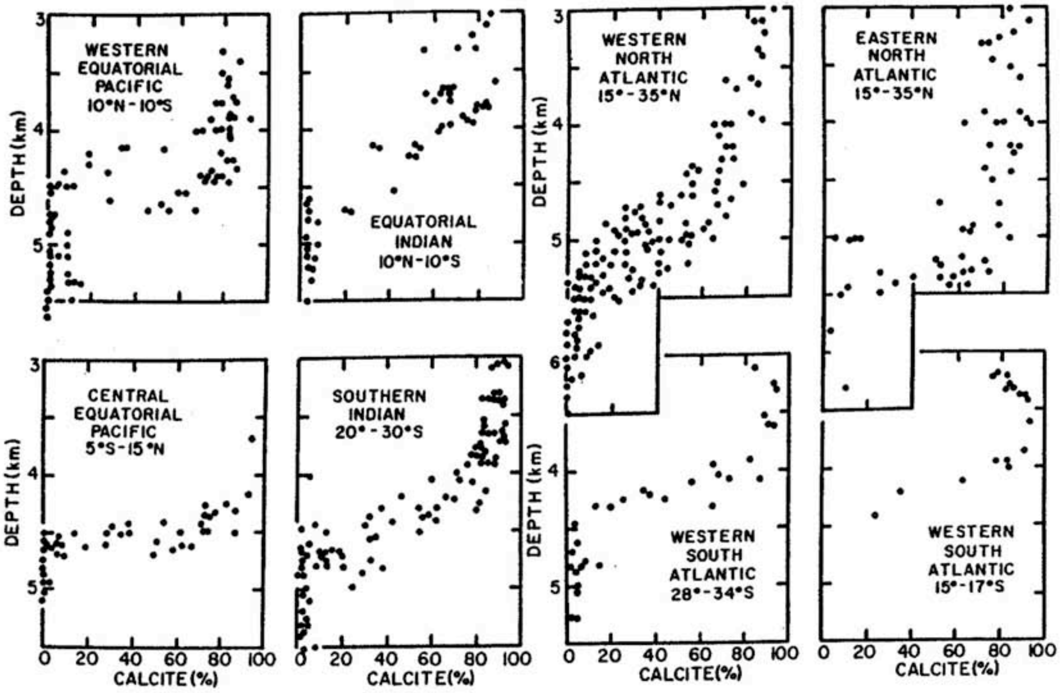

$CO_3^=$ DEEP SEA (μmol/kg)
100
90
80
70
-2
0
2
4
6
8
THOUSANDS OF YEARS
PREADDITION STEADY STATE
ADDITION OF EXCESS CO_2
GRADUAL COMPENSATION

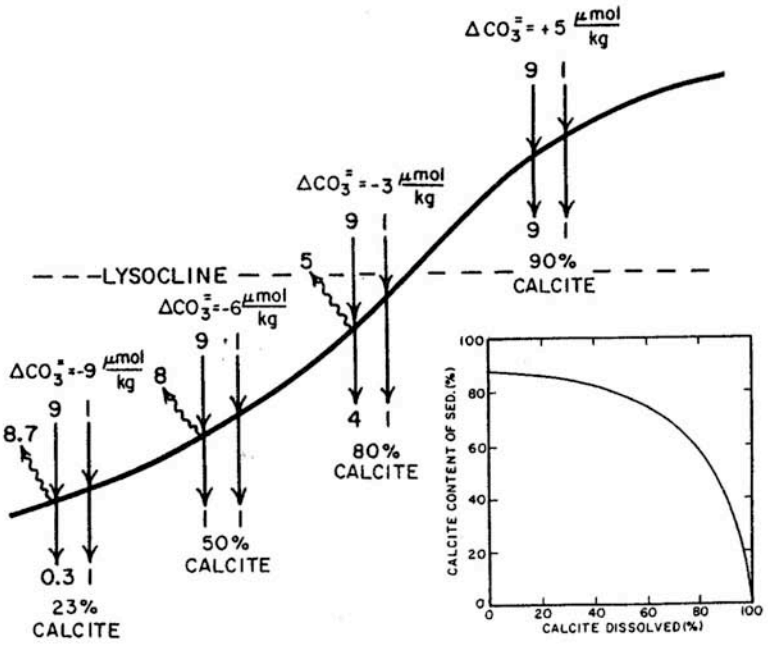
quarter of the $CaCO_3$ produced by marine organisms survives dissolution and accumulates on the sea floor.

The first point to be made is that the cycle of $CaCO_3$ sets the $CO_3^=$ ion content in the deep sea and in so doing influences the CO_2 content of the atmosphere. The basis of the control is economic: namely, unless the rate at which $CaCO_3$ accumulates in deep sea sediments just matches the rate at which the ingredients for $CaCO_3$ (i.e., CaO and CO_2) are supplied to the ocean, the ocean's chemistry will gradually change. In today's ocean, marine organisms manufacture $CaCO_3$ at a rate about four times faster than that at which the ingredients are being supplied. In order to compensate for this overproduction, the chemical composition of sea water has adjusted so that three quarters of the $CaCO_3$ produced redissolves. This compensation is accomplished by adjustments in the ratio of the area of the sea's floor bathed in waters supersaturated with respect to the mineral calcite to the area bathed in waters undersaturated with respect to the mineral calcite. As the Ca^{++} ion content of sea water is 100 times larger than that of $CO_3^=$ ion, it remains nearly uniform throughout the sea and constant over the course of a glacial cycle. Thus the tendency toward $CaCO_3$ dissolution is dictated by the $CO_3^=$ ion concentration. In particular, it is related to the ratio of the in situ $CO_3^=$ ion concentration to the saturation $CO_3^=$ ion concentration. When this ratio is less than unity, calcite tends to dissolve. Due to the pressure dependence of the solubility of calcite, the saturation concentration increases by about 18 μmol/kg per kilometer water depth. By contrast, in most parts of the deep sea, the in situ $CO_3^=$ concentration changes very little with water depth. Because of this, at shallower depths the in situ $CO_3^=$ concentration exceeds the saturation concentration and, at great depth, the reverse is true. At that depth where the saturation $CO_3^=$ concentration curve crosses the *in situ* concentration, the water is exactly saturated with respect to the mineral calcite.

This situation is clearly imprinted in marine sediments. Sediments well above the crossover are rich in calcite reflecting the fact that in most parts of the ocean the rain rate

INFLUENCE OF DISSOLUTION ON $CaCO_3$ CONTENT OF SEDIMENTS

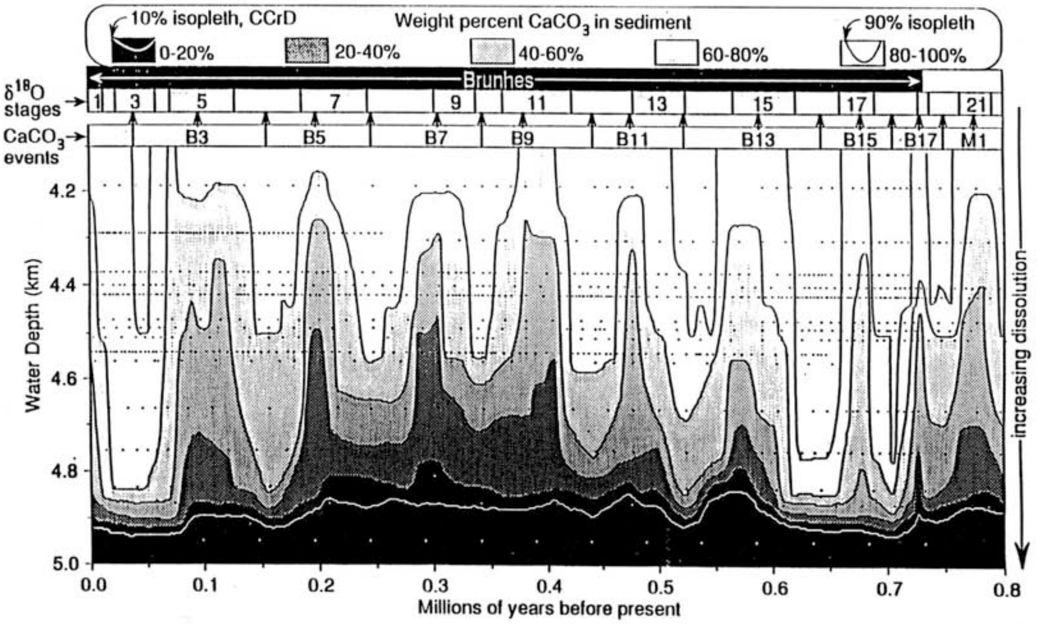


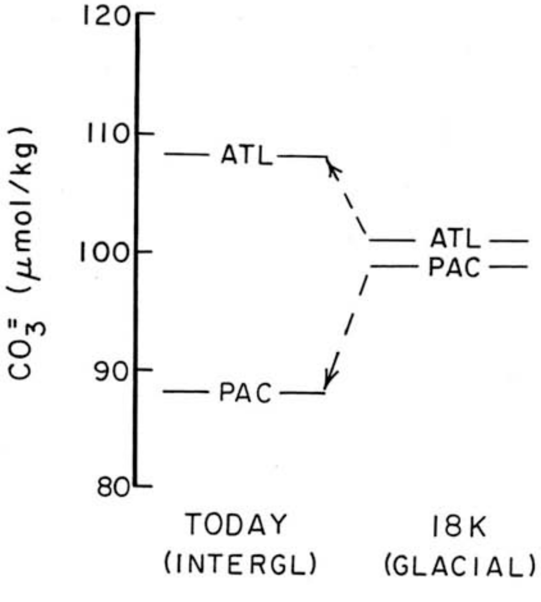


of calcite exceeds that of mineral detritus by roughly an order of magnitude. Sediments well below the crossover lose all their calcite to dissolution. If for some reason the match between ingredient supply and calcite accumulation is disrupted, then the $CO_3^=$ ion concentration in the deep sea is driven toward a new value at which accumulation once again matches ingredient supply. As the readjustment time is only several thousand years, glacial to interglacial changes in either the rate of delivery of the ingredients for $CaCO_3$ or in the production rate of $CaCO_3$ would have caused changes in the $CO_3^=$ ion content of the deep sea and hence also the CO_2 content of the atmosphere. So we have the makings of another scenario. Changes in either the rate of supply of ingredients or in the production rate of $CaCO_3$ by marine organisms offer a way to push the atmosphere's CO_2 content up and down.

Firm evidence exists for glacial to interglacial changes in the depth of the transition zone separating the realms of $CaCO_3$-rich and $CaCO_3$-poor sediments. Cores from the tropical Pacific and Indian Ocean taken within and adjacent to this transition zone reveal that during glacial time the transition zone was shifted to greater depth. In other words, dissolution during glacial time was less intense at any given water depth. For the Atlantic, the change was in the opposite direction. Dissolution was more intense during glacial time. However, as the Pacific and Indian Oceans cover a much larger area than the Atlantic, globally the average $CO_3^=$ concentration of average deep water appears to have been somewhat higher during glacial time. If so, then the CO_2 content of the atmosphere must have been correspondingly lower. The problem is that the magnitude of the $CO_3^=$ ion shift calculated from the change in the depth of the transition zone is far too small to account for the required 80 ppm lowering of atmospheric CO_2 content. In order to create a lowering of this magnitude, the $CO_3^=$ ion content of glacial deep water would have to have been about twice as high as today's. Such an increase would have deepened the transition zone separating calcite preservation and dissolution by several kilometers. As today's transition zone is centered at about 4 kilometers, this would have led to calcite

TEMPORAL CHANGES IN LYSOCLINE DEPTH





accumulation on the ocean's abyssal planes. But glacial age sediments from abyssal planes are devoid of calcite. The observed transition depth shift for the Pacific and Indian Ocean was no more than 0.8 km. When the Atlantic's opposing change is taken into account, the global shift becomes more like 0.5 km. Foiled again! Just as the carbon isotope record for Antarctic foraminifera appeared to rule out enhanced biological pumping at high southern latitudes as the cause for lower atmospheric CO_2 contents, the calcite record from the sea floor appeared to rule out a large increase in the $CO_3^=$ ion content of deep ocean water as the cause.

Our original hero, David Archer, found a way around this lysocline constraint by suggesting that under certain circumstances the tie between transition zone depth and saturation horizon could be broken. But before exploring this new idea, we must consider a couple of loose ends. The first of these has to do with the statement that the $CO_3^=$ ion concentration in the deep sea would adjust to any imbalance between $CaCO_3$ accumulation rate and ingredient supply rate on the time scale of several thousands of years. At first thought, this appears to be at odds with residence times of both ΣCO_2 and alkalinity in the sea. Based on estimates of the amount of limestone dissolved from the continents and the amount of CO_2 outgassed from the Earth's interior, the time required to replace the inorganic carbon stored in the ocean is about 10^5 years. Based on the alkalinity flux to the sea from the world's rivers, the alkalinity replacement time is also about 10^5 years. If so, how can the carbonate ion content of the sea adjust on a time scale of a few times 10^3 years? The reason is related to that depicted in the Twin Towers experiment outlined in Keeling's World. Carbonate ion content of deep sea water (~95 μmoles/kg) constitutes only about 4% of the ΣCO_2 (~2200 μmoles/kg) in deep sea water. Hence the $CO_3^=$ content responds to imbalances in the $CaCO_3$ budget 25 times faster than the ΣCO_2 content.

The other issue left unmentioned is what might induce imbalances in the $CaCO_3$ budget. One such scenario has to do with the storage of $CaCO_3$ in coral reefs. During periods of glaciation, sea level dropped to the point where the vast continental shelves were

left high and dry. This greatly reduced the habitat for corals. Then during interglacials when the sea rose and flooded across the shelves, coral reef communities were able to store away $CaCO_3$ at a rate rivaling that occurring on the sea floor. According to this hypothesis the imbalance created in this way caused a draw down of the carbonate ion concentration in the sea thereby raising the CO_2 content of the atmosphere. During low sea stands, not only was this rate of storage greatly decreased but $CaCO_3$ deposited on the shelves during the preceding interglaciation was subject to chemical erosion.

Another scenario holds that the rate of production of calcite by marine organisms may have been lower during glacial time. Perhaps conditions during glacial time were more favorable to organisms living in silica houses allowing these organisms to partially displace their calcite-housed brothers. Yet another scenario proposes that the supply of alkalinity from rivers was higher during glacial time. Perhaps increased freeze-thaw activity on the colder planet created fresh mineral surfaces accelerating chemical weathering. If so, then in order to compensate, the rate of alkalinity removal via $CaCO_3$ burial on the sea floor would have to have risen correspondingly. But as we have seen, to explain the entire atmospheric CO_2 content change, these scenarios would require that during glacial time the $CaCO_3$ transition zone deepened by several kilometers. It didn't.

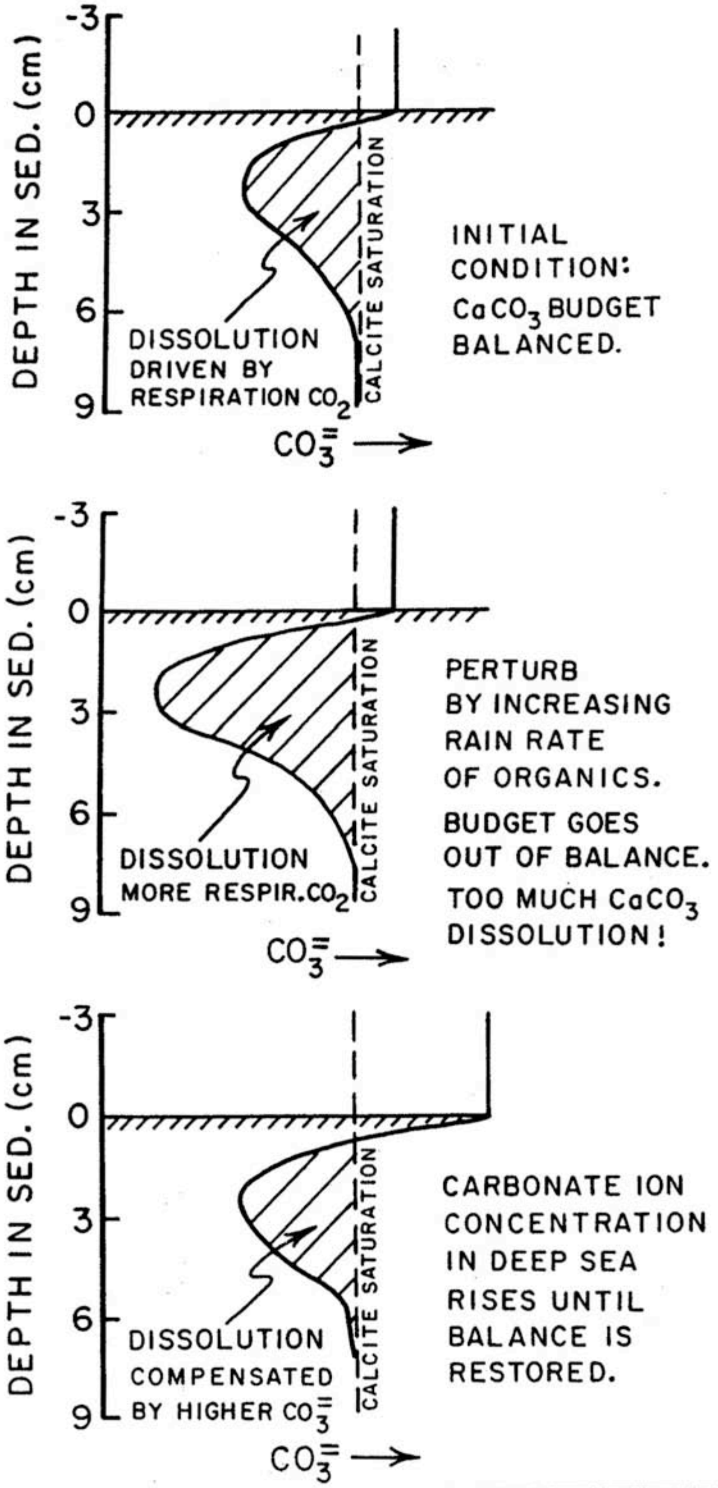
But now David Archer to the rescue! Following the lead of his mentor, Steve Emerson, Archer pursued as his Ph.D. research the role of the CO_2 released by bacterial respiration within the upper few centimeters of deep sea sediments in promoting calcite dissolution. Two observations made this avenue an appealing one. First, analyses of the material caught in deeply moored sediment traps reveals that the ratio of organic matter carbon to $CaCO_3$ carbon falling to the deep sea floor is close to unity. Hence, if the CO_2 released when the organic matter is eaten were neutralized by reaction with calcite, a near neutral addition of calcium bicarbonate would be generated;

$$H_2O + CO_2 + CaCO_3 \Rightarrow Ca^{++} + 2HCO_3^-$$

What this tells us is that respiration CO_2 has the potential to do the job. The second observation is that the geographical trend in the chemistry of deep waters in the Pacific and Indian Oceans suggests that such a titration is indeed occurring. The increases in ΣCO_2 along the pathway of deep water flow is matched by an increase in alkalinity such that the $CO_3^=$ concentration remains very nearly constant. These two observations led to the suspicion that CO_2 released by bacteria living within the upper few centimeters of deep sea sediment might be responsible for much of the $CaCO_3$ dissolution taking place on the sea floor.

In order to determine whether this was indeed the case, Archer employed micro pH and O_2 electrodes which could be inserted into the sediment from a bottom lander. What he found was that the O_2 concentration dropped sharply in the upper few millimeters of sediment in response to bacterial consumption of organic matter. As expected, he found that the respiration CO_2 drew down the pore water pH creating a minimum of ten or so centimeters below the sediment water interface. Above this minimum, the pH increased so that at the interface it matched that for bottom water. Below this minimum, it also increased eventually reaching the value corresponding to saturation with calcite. The important point is that the magnitude of the pH minimum was not as large as that predicted from the rate at which respiration CO_2 was being created (as indexed by the O_2 results). The reason is that roughly one half of the respiration CO_2 had reacted with calcite. Only about one half of the CO_2 managed to escape the pores into the overlying bottom waters. What this demonstrated was that indeed much of the sea-floor dissolution of calcite was being driven by respiration CO_2 released into the sediment pore water. It also provided a possible way around the requirement that the depth of the calcite saturation horizon closely match the depth of the top of the transition zone. Rather, dissolution commences well above the saturation horizon.

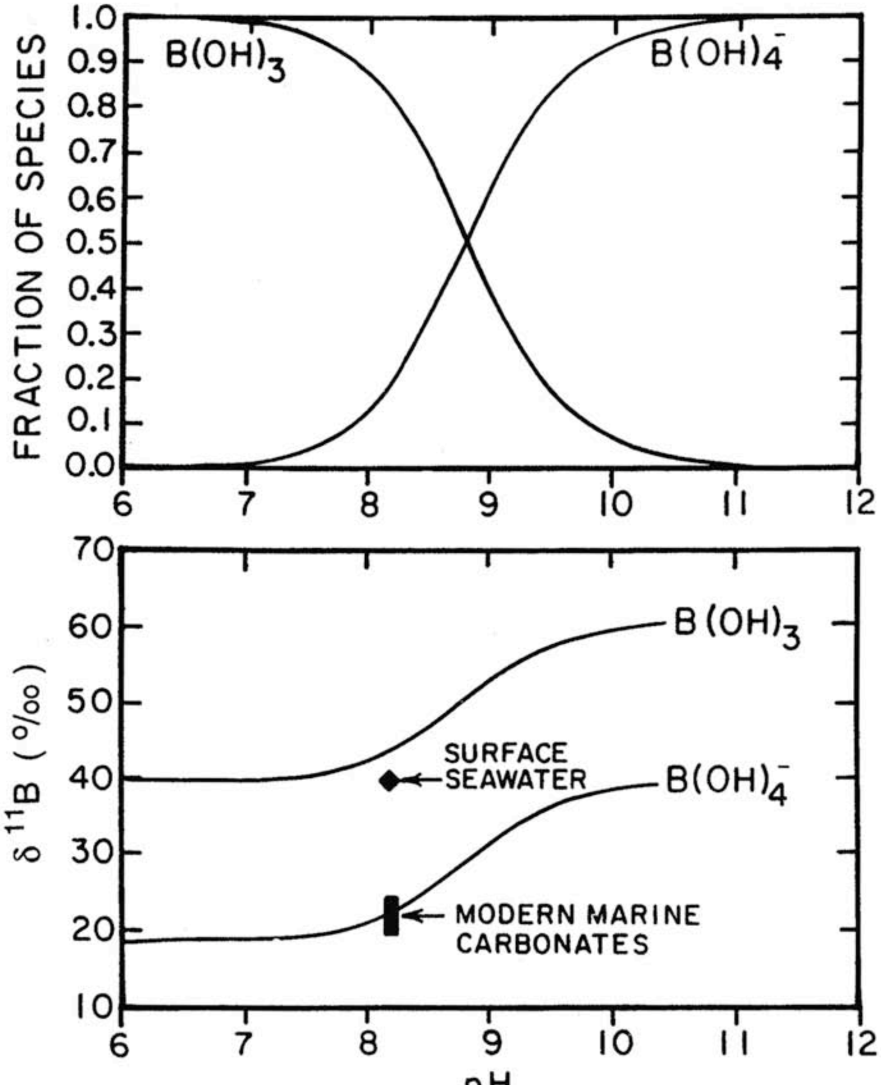
ARCHER'S SCENARIO



It is because of this upward displacement of the transition zone by respiration CO_2 that Archer saw a way to decouple the tie between transition zone depth and deep sea carbonate ion concentration. He reasoned that if, for example, the rain rate of organic carbon to the sea floor relative to that for calcite were higher during glacial time, then the amount of respiration CO_2 released by bacterial activity within the sediment column would increase and the transition zone would temporarily shift to shallower depths. This would throw the ocean's $CaCO_3$ budget out of kilter for the rate of accumulation of $CaCO_3$ would fall below the rate of ingredient supply. Hence, the ocean's $CO_3^=$ ion content would begin to climb. This climb would continue until the additional bottom water $CO_3^=$ just balanced the impact of the excess respiration CO_2. The transition zone would have moved back to its original position restoring the balance between calcite accumulation and ingredient supply. So here we have a situation where an increase in $CO_3^=$ ion content in the deep sea produces no corresponding change in the steady state depth of the transition zone!

Fortunately, a means was discovered by which Archer's scenario might be verified. It involved a paleo pH method based on measurements of the isotopic composition of the boron contained in foraminifera shells. A thermodynamic isotope separation occurs between the two species of borate present in sea water. The singly charged form, $B(OH)_4^-$, has a 20‰ lower ^{11}B to ^{10}B ratio than the neutral form, $B(OH)_3$. In today's surface water (pH =8.2), about 80% of the boron is in the neutral state and 20% is in the charged state. Were sea water to be acidified, the proportions would be shifted in favor of the neutral state. By contrast, were it to be made more basic, the proportions would be shifted in favor of the charged state. Such changes in the pH would bring about shifts in the isotopic composition of both $B(OH)_3$ and the $B(OH)_4^-$. In low pH sea water, the neutral species would have the same isotopic composition as bulk borate while the tiny fraction of remaining charged borate form would be depleted in ^{11}B by 20‰. In high pH sea water, the opposite would be found; the charged borate ions would have the same

BORON ISOTOPES AS RECORDERS OF PALEOCEAN ACIDITY



isotopic composition as bulk borate and the tiny fraction of remaining neutral species would be enriched in ^{11}B by 20‰. At that pH, where the $B(OH)_3$ to $B(OH)_4^-$ ratio was unity, the ^{11}B to ^{10}B ratio for the charged form would be 10‰ lower than that for bulk borate and the ratio for the uncharged form, 10‰ higher.

The paleo pH method assumes that the boron contained in the shells of foraminifera is built into the calcite lattice as charged borate and carries with it the isotopic composition of this species in sea water. As residence time of borate in sea water is about 20 million years, it is quite safe to conclude that on the time scale of a glacial cycle the isotopic composition of sea water borate remains constant. The hope is that the sole control on the isotopic composition of borate in the shells of foraminifera is the pH of the sea water in which they grow and, of course, that no change in isotopic composition occurs after burial in the sediment.

In the fall of 1993 when the first edition of this book was being completed, Abhijit Sanyal, a graduate student at Lamont, in cooperation with Gary Hemming, a research scientist at SUNY, Stony Brook had just completed preliminary measurements of boron isotopes in planktic and benthic foraminifera from Holocene and last glacial sediments. These measurements suggested that the glacial deep ocean had a pH 0.3 of a unit more basic than the Holocene ocean. This translates to $CO_3^=$ ion contents for deep water twice as great as today's. Because the $CO_3^=$ ion content of surface water in the sea averages about twice that of deep water, the dissolution of enough $CaCO_3$ to raise the pH of deep water by 0.3 units would raise the pH of surface waters by only one half this amount. Boron isotope measurements on planktonic foraminifera yielded as required a smaller pH shift. The exciting result is that the boron-based pH changes predict a lowering of the atmospheric CO_2 content consistent with that observed in ice cores. Confidence increased when Sanyal went on to culture the planktonic species *Orbulina universa* at the Santa Catalina Wrigley laboratory at a range of pHs. The results confirmed the predicted pH dependence of the isotope ratios for the boron incorporated into these shells.

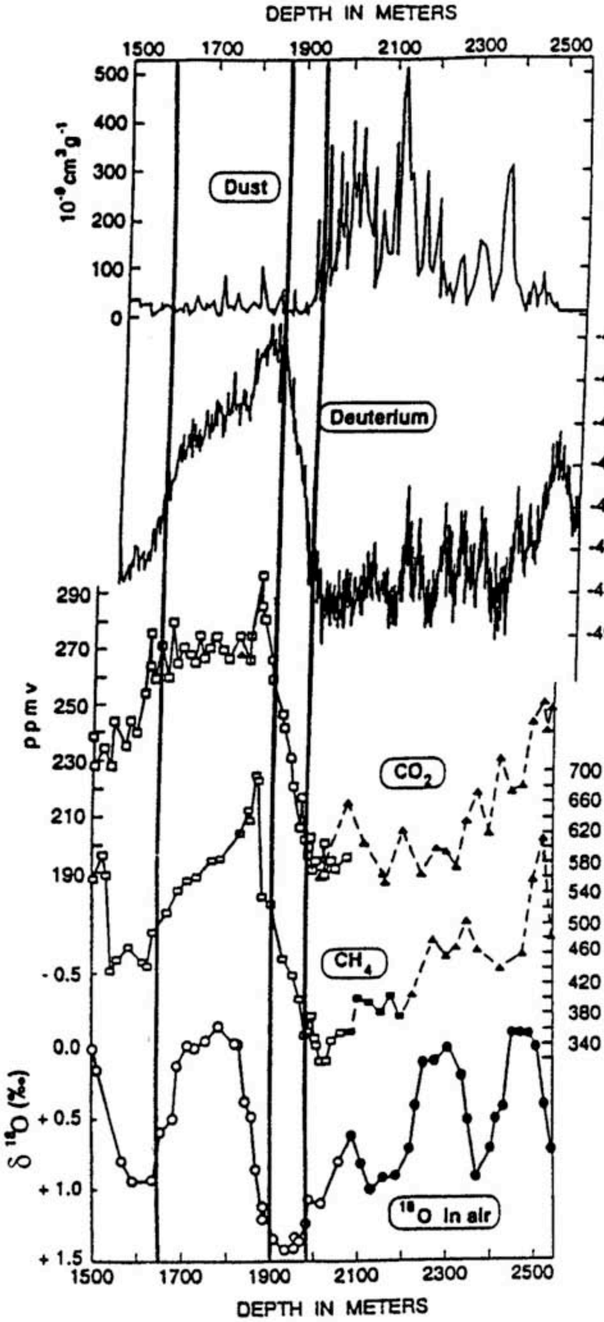
However, there remained some disquieting aspects of Archer's respiration hypothesis. First no compelling explanation appeared as to why the rain of organic matter to the sea floor was higher during glacial time. Explaining this increase proved especially difficult since its magnitude would have to have been nearly the same across the entire ocean. Were this not the case, then the topography of the glacial lysocline would have developed some very large bumps. No such bumps have been found. Second, the absence of $CaCO_3$ in the upper portion of sediments on the ocean's abyssal plains is very difficult to explain. According to Archer's scenario if during glacial time the carbonate ion content of deep sea water was twice as high as at present, then the saturation horizon would have been driven down well below the depth of the abyssal plains. The problem is that when at the close of glacial time the excess flux of organic matter to the sea floor was shut down, $CaCO_3$ would have begun to accumulate across the entire ocean floor. Only when a substantial portion of the excess $CO_3^=$ ion had been consumed as a result of this deposition would the saturation horizon have risen above the abyssal plains. At this point, a 3 cm-thick layer of $CaCO_3$-rich sediment would have accumulated acorss the entire abyssal ocean floor and would have been bioturbated into the underlying clay. It seems extremely unlikely that this $CaCO_3$ could have been completely dissolved away during the remainder of the Holocene. Yet measurements on cores from abyssal plains consistently yield $CaCO_3$ contents less than 0.2 percent.

The coup de grâce came when, using model calculations, Danny Sigman demonstrated that it was quite impossible to separate the lysocline from the saturation horizon by anywhere near the several kilometers required by the Sanyal-Hemming paleo pH reconstructions. Archer repeated these calculations and had to admit that Sigman had a point. So this beautiful scenario appears to have bitten the dust.

Iron Fertilization to the Rescue

But it seems that no sooner has one idea regarding the cause of the low CO_2 content of the glacial atmosphere paled that another arises to seek its place. Indeed,

SEQUENCE OF EVENTS SURROUNDING TERMINATION II AS RECORDED IN THE VOSTOK ICE CORE



within a year after Sigman put aside the Archer hypothesis a new idea emerged. It came into being in a rather round about way. In reexamining the Vostok Antarctica ice core record for the end of the penultimate glaciation (i.e., Termination II), Broecker and Henderson puzzled over the observation that the transition from glacial to interglacial conditions came in three distinct steps. The first was the demise of the heavy glacial dust fall onto the Antarctic ice cap. This was followed by a 7000-year period during which the air temperature over the Antarctic ice cap warmed and the CO_2 and CH_4 contents of the atmosphere increased. Only after this second step was complete did the ^{18}O content of the O_2 trapped in the Antarctic ice begin to decrease. The reason for this fall is that the ^{18}O content of sea water decreased as the ^{18}O-deficient ice cap water reentered the sea. Confirmation of the validity of the ^{18}O in O_2 proxy for ice volume came from the observation that the rain of silicate debris onto the Southern Ocean sea floor and the rise in surface water temperatures in the southern Indian Ocean led the ^{18}O shifts in benthic foraminifera (also due to the return of ^{18}O-deficient ice-cap melt water to the sea). If as seems reasonable, the ^{18}O decline in atmospheric O_2 paralleled the meltdown of the northern hemisphere ice caps, then the entire rise of CO_2 was completed before the ice caps began to melt. This eliminates any hypotheses for the CO_2 change requiring the flooding of the shelves. Also since the rejuvenation of the Atlantic's conveyor circulation occurred during the ice-melt interval, it also eliminates any hypothesis tied to the reorganization of ocean circulation.

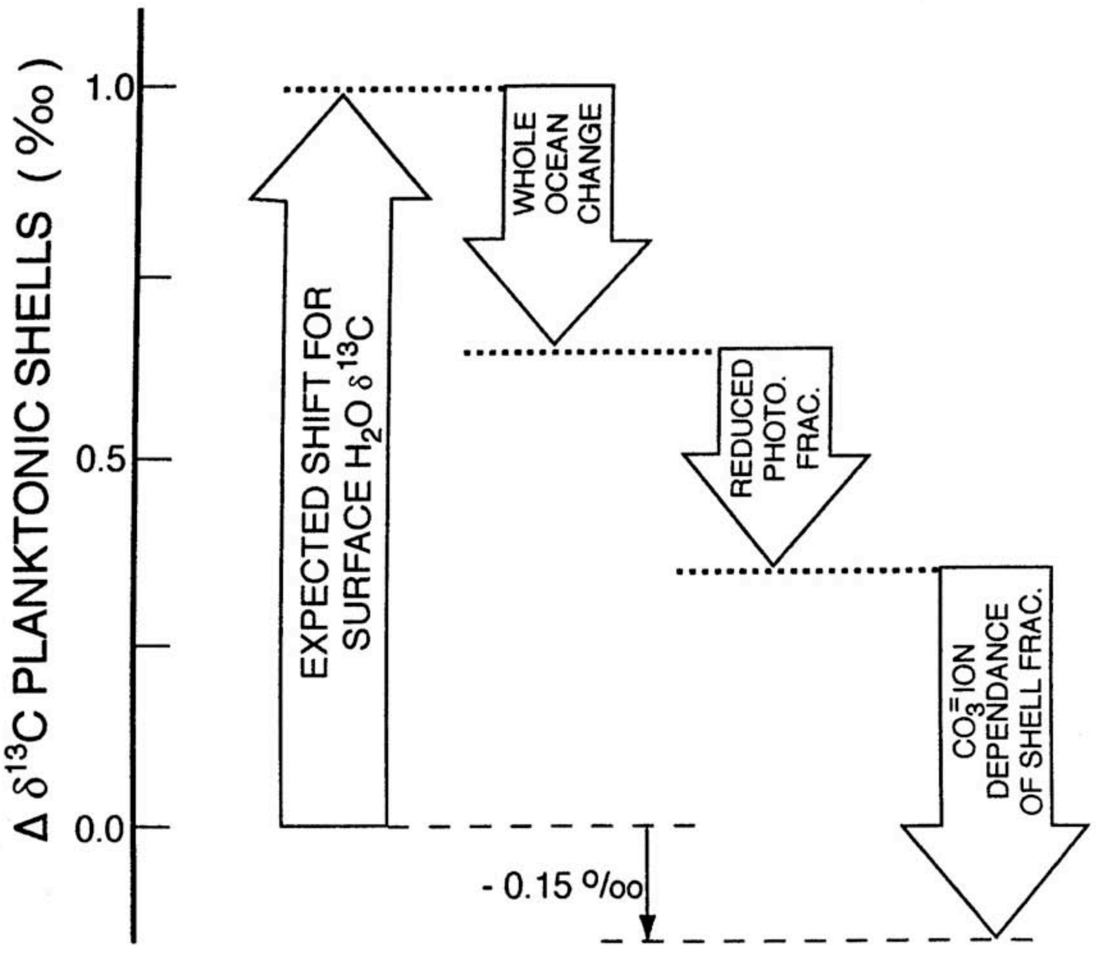
These observations led Broecker and Henderson to ponder the role of dust. Instead of thinking in terms of iron fertilization of high latitude waters, they proposed that the higher global dust fall during glacial time allowed nitrogen fixing cyanobacteria to proliferate in their subtropical habitats. These organisms are known to have a tenfold higher iron demand than other planktonic organisms. So the idea was that during glacial time the increased iron availability created by the excess dust fall led to a 40 percent increase in the oceanic inventory of NO_3. If, and its a big if, this extra NO_3 could be utilized with more or less the same efficiency as that presently in the ocean, then the biologic pump would have been correspondingly strengthened.

The residence time of fixed nitrogen in the sea (i.e., $N_2 \rightarrow NO_3 \rightarrow N_2$) is estimated to be about 3000 years. Hence, no matter where it was manufactured, the extra NO_3 produced by the cyanobacteria would become mixed throughout the entire sea. Further, when the dust fall ceased, the NO_3 decline would take several thousand years helping to explain the 7000-year-duration atmospheric CO_2 climb at the end of the penultimate glaciation.

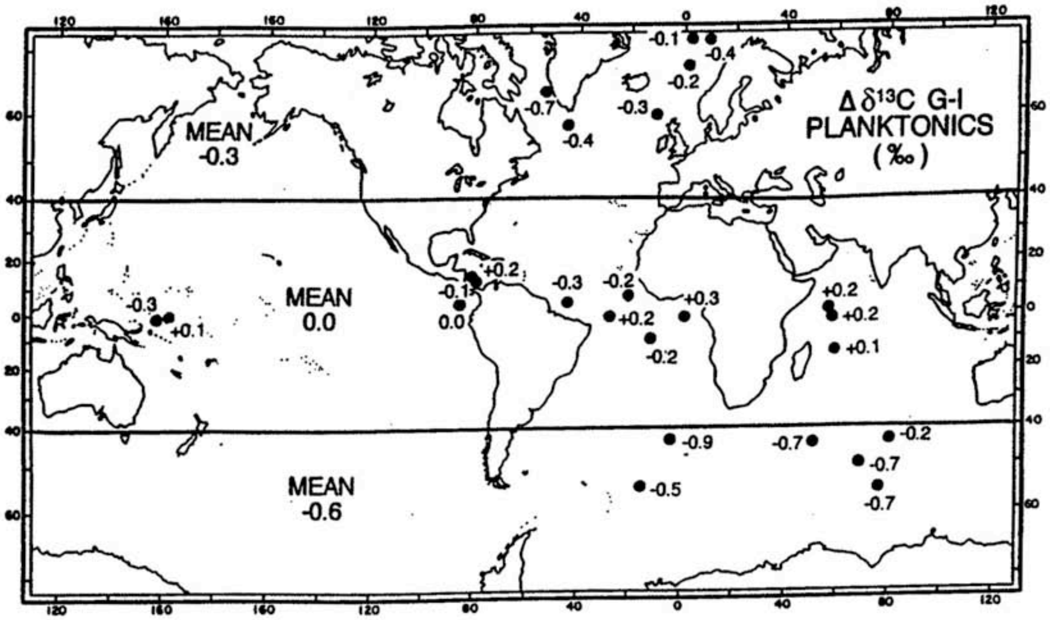
One possible drawback to this new idea is that were it to explain the entire drawdown of the atmosphere's CO_2 content, it would create a 1‰ increase in the $\delta^{13}C$ for glacial age planktonic shells. No such increase is seen anywhere in the world ocean. But easing this situation are two new findings. First, laboratory growth experiments by a group led by Howie Spiro show that there is a pH dependence on the carbon isotope fractionation for planktonic foraminifera. As the lowered glacial atmospheric CO_2 content requires that the pH of the surface ocean averaged 0.2 units higher than today's, the Spiro et al. measurements suggest that this would have lowered the $\delta^{13}C$ in planktonic foraminifera by about 0.5‰.

The other factor is that the fractionation of carbon isotopes during photosynthesis depends on CO_2 content of sea water, the lower the concentration, the lower the fractionation (as explained in the 'Walker's World' section, this dependence involves the interplay between the resistance posed by diffusion through the cell wall and that posed by the reaction with the photosynthetic enzyme). Such a reduction would decrease the contrast in $^{13}C/^{12}C$ difference between surface and deep water for any given strength of the biological pump. This would further reduce the expected $\delta^{13}C$ planktonic shells by about 0.3‰. When combined with the -0.35‰ change in the $\delta^{13}C$ for glacial ocean ΣCO_2, instead of a 1.0‰ increase in the $\delta^{13}C$ for planktonic foraminifera, an 0.15‰

^{13}C IN PLANKTONICS



GLACIAL TO INTERGLACIAL CHANGE IN $^{13}C/^{12}C$ IN PLANKTONIC FORAMINIFERA SHELLS*



*HIGH LATITUDES - *N. PACHYDERMA (L)*
LOW LATITUDES - *G. SACCULIFER*

decrease would be expected. Although not well defined, the glacial to interglacial $\Delta\delta^{13}C$ for planktonic foraminifera lies in the range 0.0 to -0.3‰.

A second drawback has to do with the phosphorus requirement of marine microplankton. Along with most geochemists, we had always assumed that the strong correlation between NO_3 and PO_4 in the sea reflected a tight-knit biochemical demand for these nutrients by marine plankton. Somehow shifts in ecology allowed nitrogen fixation to maintain the required 16 to 1 ratio. But the discovery that nitrogen-fixing bacteria are strongly limited by the availability of iron requires that this line of thinking be reexamined. Perhaps instead the close correlation between NO_3 and PO_4 reflects luxury storage of phosphorus. Certainly observations made in lakes and experiments carried out in chemostats show that these micro-organisms can function with a wide range of N to P ratios.

A third drawback is that an increase in the strength of the biological pump would increase the O_2 demand in the ocean interior. Models suggest that an 80 μatm drawdown in the atmosphere's CO_2 partial pressure would require a 40% increase in the oceanic NO_3 inventory (based on the assumption that the utilization efficiency for nutrients remained the same as today's). Other things being equal (i.e., circulation patterns, the depth profile of respiration...), this would produce a 40% increase in O_2 demand. As only roughly a third of this would be compensated by the higher O_2 capacity of colder surface waters, those parts of the deep ocean currently low in O_2 would have gone anoxic. Yet, as documented by the ubiquitous presence of benthic foraminifera, this did not occur.

Finally, this scenario is at odds with the Harvardton Bear concept which would suggest that any drawdown of the CO_2 content of warm ocean waters associated with an increased strength of the biological pump would be compensated by an inflow (via the atmosphere) of CO_2 supplied by the cold surface ocean. If so, then only the increased pumping action in the cold surface waters would contribute significantly to the CO_2

drawdown. As these waters already have large inventories of unused nutrients, it is not clear why they should benefit from a nitrate content increase.

Putting aside the problems raised in connection with the Archer hypothesis, one could argue that the increased global production of organic matter created by the excess nitrate could be responsible for the excess rain of organic matter required by this hypothesis. Of course, if, as one might expect, the production of $CaCO_3$ increased correspondingly, then this increase would be nullified.

At this point, one might ask why direct iron fertilization of the Southern Ocean is not the invoked. After all, this is the scenario suggested by this chapter's hero. The problem lies in the observation that at the time of the penultimate deglaciation, the fall of dust onto Antarctica bottomed out early in the 7000-year duration period of CO_2 rise. Were direct fertilization the answer, then as iron has a very short residence time in the sea, the CO_2 content of the atmosphere should follow directly on the heels of the decline in iron supply. It did not.

Recent studies demonstrating that the small amount of iron found in the deep sea is stabilized by an organic ligand suggest yet another scenario. The fact that the same amount of iron is found in deep Atlantic waters as in deep Pacific waters suggests that these ligands have lifetimes of several ocean mixing times (i.e., several times 10^3 yrs). If so, it is possible that the higher glacial dust rain somehow led to an increased ligand inventory. Gaia in action! This in turn would permit higher plant productivity in ocean regions currently deficient in iron. It would also prevent a rapid response to the sudden dust demise because several thousands of years would be required for the ligand inventory to drop from its glacial to its interglacial level.

Summary

This section's puzzle had to do with the mechanism responsible for the 30% reduction of the atmosphere's CO_2 content during glacial time. While a number of fascinating scenarios have been proposed, all have stumbled because they appear to violate the record kept in ocean sediments or constraints placed by models. Those scenarios involving a strengthening of the biologic pump were initially put aside because the carbon isotope record in foraminifera shells was not consistent with such a strengthening. Those scenarios involving changes in the ocean's alkalinity resulting from calcium carbonate accumulation in the shallow ocean were blocked by the observation that the depth of the transition zone separating calcite-rich from calcite-poor sediments did not deepen nearly enough during glacial time. The exciting scenario proposed by David Archer at first received strong support from the boron isotope record, but then was put into question by its requirement that a several kilometer separation existed between the depth of the saturation and lysocline horizons. But then two new findings reopened the possibility that a strengthening of the biological pump was after all responsible for the CO_2 lowering during glacial time. The first was John Martin’s discovery that in many parts of the ocean the availability of iron limits marine productivity. Coupled with the finding that planetary dust fall was several times higher during glacial time, this provided a mechanism to strengthen the biological pump. Second, a large pH dependence was demonstrated for the ^{13}C fractionation between $\sum CO_2$ and marine calcite. This latter finding removes the impasse created by the failure of the carbon isotope ratios in the shells of glacial age planktonic foraminifera to show a shift toward heavier values. So perhaps we are at last closing in on the answer to our mystery. In one way or another, the high glacial dust fall supplied the iron required to strengthen the ocean's biological pump.

Commentary on Plates in Martin's World

pg. 3

Analyses of air trapped in polar ice offers a means of reconstructing trace gas concentrations in the glacial atmosphere. Records from Antarctica representing areas of low snow accumulation and colder temperature (Vostok) and high snow accumulation rate and warmer temperature (Byrd) yield nearly the same CO_2 content for ambient glacial time. While similar results are obtained at the Dye 3 site in southern Greenland, the details differ from those for the two Antarctic sites. Specifically, during the millennia duration interstadials which punctuate the glacial portion of the Greenland record, the CO_2 content rises halfway back to the interglacial value. Matching excursions are absent in the very detailed Byrd Station, Antarctica, record. As the mean-annual CO_2 contents at the two poles can not have differed significantly, these disagreements indicate problems with the ice archive. The suspicion is that the villain is $CaCO_3$ accompanying the dust contained in the ice. The Greenland ice has at all times an order of magnitude more dust than Antarctic ice. Thus if $CaCO_3$ were the cause of the biases, then they would be expected to be far more serious in the Greenland. The electrical conductivity record reveals that during the interstadial warms the electrical conductivity jumps up from near zero value during times of extreme cold, demonstrating that unneutralized acid is present. Perhaps this acid is responsible for the dissolution of $CaCO_3$ releasing excess CO_2 gas within the ice.

pg. 8-9

Carbon isotope ratio measurements carried out on benthic foraminifera shells from deep sea sediments suggest that the ^{13}C to ^{12}C ratio in deep ocean $\sum CO_2$ was on the average about 0.35‰ lower during the peak of the last glaciation than it was during the Holocene. The most likely way such an isotope shift could be accomplished on this short a time scale (i.e., ~5000 years) would be via changes in the size of the biospheric carbon pool. To create an 0.35‰ rise in $\delta^{13}C$ at the end of the last glaciation would require that the biospheric pool increase in size by about 500 GtC. This carbon was stored not only in the trees and soils of the northern areas previously covered by the ice caps and tundra of glacial time but also in expanded tropical forests.

The cycling of this carbon back and forth between the ocean and the terrestrial biosphere would of course have changed the atmospheric CO_2 content. In the absence of any impact of this CO_2 on the sea-floor $CaCO_3$, the CO_2 content of the atmosphere would have been raised by 56 μatm during glacial intervals relative to interglacial intervals. This change is in the opposite sense to that observed in ice cores. But on the time scale of several thousand years, the ocean would partially compensate for this CO_2 change by reducing the amount of $CaCO_3$ stored on the sea floor. The CO_2 released to the ocean at the onset of a glacial period would react with $CaCO_3$ otherwise destined to accumulate in sediments.

$$H_2O + CO_2 + CaCO_3 \Rightarrow 2HCO_3^- + Ca^{++}$$

This reaction would consume CO_2 reducing the magnitude of the rise. When compensation had returned the $CO_3^=$ ion content of deep water to a new steady state value, the excess CO_2 pressure would have been reduced from 56 to 16 μatm. Nevertheless, the change in terrestrial biomass makes the problem more difficult for it shifts the atmospheric CO_2 content 16 μatm in the wrong direction.

One caveat must be given. If, as described later in this section, the boron-isotope-based 0.3 unit increase in the pH of the glacial deep ocean proves to be correct, then a corresponding correction will have to be made for a change in the carbon isotope fractionation during shell growth. This correction would more than compensate for the observed -0.35‰ shift in the $\delta^{13}C$ for glacial age benthics suggesting that the terrestrial biomass was greater rather than smaller during glacial time.

pgs. 12-13

A simple two-box abiotic ocean model consisting of a warm reservoir which occupies 80% of the surface and a cold reservoir which underlies the warm but has a polar outcrop occupying the remaining 20% of the ocean surface is employed to demonstrate the potential importance of the high latitude ocean in controlling the atmosphere's CO_2 content. As the volume of cold reservoir is assumed to be so much larger than that of the warm reservoir, its CO_2 partial pressure is immutable. Hence, regardless of what happens to the atmosphere and warm ocean, the CO_2 partial pressure for the cold sea remains pegged at 280 μatm. Water is circulated between the two reservoirs as shown. Were no transport of CO_2 through the atmosphere from the warm to the cold reservoir to occur, the CO_2 partial pressure in the warm reservoir would be raised to 790 μatm (simply because it is warmer). In this limiting case, the atmosphere would have the following CO_2 partial pressure:

$$
\begin{aligned}
pCO_2^{atm} &= 0.2\ pCO_2^{cold} + 0.8\ pCO_2^{warm} \\
&= 0.2 \times 280 + 0.8 \times 790 \\
&= 688\ \mu atm
\end{aligned}
$$

The other extreme would be the situation where CO_2 could readily move through the atmosphere from the warm to the cold reservoir. CO_2 would escape from the warm reservoir, pass through the atmosphere and be absorbed into the cold reservoir. In this way, the pCO_2 difference would be eliminated and both reservoirs would have a CO_2 partial pressure of 280 μatm. So also would the atmosphere.

Where between these extremes our simple model ocean comes to balance depends on the ratio of the rate of water circulation to the rate of CO_2 transport across the air-sea interface. The higher this ratio, the greater the CO_2 partial pressures for the warm reservoir and atmosphere. The CO_2 exchange rate is set at the ocean average given in section one of the book (i.e., 0.06 moles/μatm m^2yr) and the upwelling rate is set to yield a residence time in the deep sea consistent with that obtained based on radiocarbon measurements (i.e., an upwelling rate of 4 m/yr). In this case, for a pCO_2 partial pressure of 280 μatm, 16.8 moles of CO_2 will pass across the air-sea interface each year and for a ΣCO_2 content of the cold reservoir of 2.2 moles per m^3, 8.8 moles/m^2 of ΣCO_2 will pass upward into the warm reservoir each year. In this case, the CO_2 partial pressure for the warm reservoir will stabilize at 335 μatm and that for the atmosphere at 324 μatm. The resulting 44 μatm increase in the atmosphere's CO_2 pressure turns out to be only 11% of that which would have existed were no CO_2 transferred through the atmosphere from the warm to the cold reservoir. This is an example of the Harvardton Bear effect.

On the right hand page are shown the equations used to make this calculation. Equation 1 gives the flux of carbon, T, carried by the water upwelling into the warm reservoir (i.e., water flux per unit area x area x $\sum CO_2$ concentration). Equation 2 gives the net flux of carbon, ΔT, from the atmosphere into the cold reservoir. Equation 3 gives the ratio of these fluxes and matches it to the deficit in $\sum CO_2$ transport from the warm to the cold reservoir.

In the diagram on the left, the solution is shown graphically. The long curved line coming down from the upper right corner is the path followed the warm surface water as it loses ever more CO_2 to the atmosphere (and from there to the cold ocean). The arrows end shows the balance point.

pg. 15

In today's ocean, deep waters of nearly the same density are created in two regions: along the perimeter of the Antarctic continent and in the northern Atlantic. In the Antarctic, newly formed deep waters have a temperature close to the freezing point of sea water (i.e. -1.8°C). Because the Atlantic waters are saltier, this density is achieved at a temperature of about 4°C greater than the freezing point of sea water. During glacial time, when the northern Atlantic was surrounded by ice, the deep water formed there likely had a temperature much closer to the freezing point. If so, then the mean temperature of deep ocean water was perhaps 2°C colder than now. Were the Harvardton Bears principle to hold, this would suggest that glacial cooling caused a 20 μatm drop in the atmosphere's CO_2 content. The reason for this drop is that the equilibrium constants relating pCO_2 to $\sum CO_2$ and alkalinity change such that cooling reduces the water's CO_2 concentration and hence its CO_2 partial pressure.

pg. 16

A number of lines of evidence including direct estimates based on the depth of radiometrically-dated surface-dwelling corals retrieved from borings off-shore from the island of Barbados suggest that sea level stood about 115 meters lower during the peak of the last glaciation. The missing water was in the ice caps of glacial time. As the salt associated with this missing water remained behind, the ocean's salinity must have been about 3% (i.e., 100 x 115/3800) higher than today's. Such a rise would cause an increase of about 10 μatm in the ocean's CO_2 partial pressure. This change is caused by the effect of salinity on the equilibrium constants relating CO_2 concentration to $\sum CO_2$ and alkalinity.

pg. 18

All plants require the elements N and P. In sea water, the ratio of N (as NO_3^-) to P (as $H_3PO_4^-$) dissolved in the sea is close to 16. Over much of the surface ocean both dissolved nitrate and phosphate have been drawn down to near zero values. In these places, plant growth is limited by the rate at which these nutrient constituents are stirred up from below. Exceptions are found in high latitude waters and in regions of tropical upwelling. Here far more dissolved N and P are supplied to the surface than can be utilized by plants. This unused fertilizer caught the eyes of the Harvardton Bears who postulated that if for some reason during glacial time the nutrients upwelling at high latitude were more efficiently utilized, this could explain the reduction of the atmosphere's CO_2 content as revealed by measurements on ice cores. Our hero, John Martin, supplied a possible cause for such a glacial drawdown, namely, the increased availability of the element iron carried to the sea with the large glacial dust fall.

Shown here are maps of the distribution of phosphate in surface waters and in the deep sea (at a depth of 3 kilometers). Equivalent maps for nitrate would look much the same except the concentrations would be everywhere about 16 times higher.

pg. 20

In the polar regions, the CO_2 partial pressure of surface waters depends strongly on the efficiency with which nutrients are utilized. The reason is that for each mole of PO_4 utilized, roughly 125 moles of CO_2 are fixed into organic matter. As shown in this example in today's Southern Ocean, the partial pressure of CO_2 could range from 514 μatm were none of the nutrients to be utilized to 103 μatm were they to be completely utilized. For the present day Antarctic, roughly one third of the nutrients upwelled are utilized, giving rise to a CO_2 partial pressure near the middle of this range.

Important for paleoceanographic reconstructions is the fact that the $^{13}C/^{12}C$ ratio in surface water $\sum CO_2$ depends on the efficiency of utilization changing by 3.8‰ for the full range from 0% to 100% utilization, the greater the extent of utilization, the higher the ^{13}C to ^{12}C ratio. The reason for this dependence is that ^{12}C-bearing CO_2 molecules are fixed during photosynthesis in slight preference to the heavier ^{13}C-bearing CO_2 molecules. The organic material formed in cold water has a 30‰ lower ^{13}C to ^{12}C ratio than the $\sum CO_2$ in the water. Thus utilization of nutrients causes an enrichment of ^{13}C in the $\sum CO_2$ remaining behind in the water. As the shells of foraminifera bear a record of the ^{13}C to ^{12}C ratio in the water in which they grow, changes in the efficiency of nutrient are potentially imprinted in the planktonic shells preserved in Southern Ocean sediments.

pg. 21

Carbon isotope records from Antarctic sediments fail to show the increase in $^{13}C/^{12}C$ ratio in glacial planktonics predicted by the Harvardton Bears. Rather, glacial age sediments show a depletion in ^{13}C. However, as a comparable depletion is seen for bottom dwelling forams, one might conclude that the efficiency of utilization was nearly the same.

pg. 23

The nitrogen isotope composition for a traverse of Holocene-age sediment across the Southern Ocean is the mirror image of the NO_3^- content of overlying surface water. At high latitudes where the NO_3^- content of surface waters is high, the ^{15}N content of the nitrogen bound into the sedimentary organic matter is low. At lower latitudes where the NO_3^- is largely depleted, the $^{15}N/^{14}N$ ratio in the organic matter is several per mil higher. This difference is attributed to preferential incorporation of the light nitrogen isotope (^{14}N) by organisms. Where only a small fraction of the available NO_3^- is utilized, the full fractionation is seen. However, where nearly all the NO_3^- is consumed, there can be no difference in between the isotope composition of the sediment nitrogen and that of the nitrate upwelled to the surface.

pg. 24

Traverse with latitude obtained by Roger Francois and his colleagues of the difference in the isotopic composition of the nigrogen bound in diatoms from glacial and from Holocene sediments in the Atlantic and Indian Ocean sectors of the Southern Ocean. While north of 50°S the differences are small, south of this latitude the glacial age forams have $\delta^{15}N$ values closer to that for today's oceanic NO_3 suggesting that nutrient utilization was more efficient during glacial time.

pg. 26-27

The production of calcite by marine organism exceeds by several fold the supply of the ingredients required for the manufacture of this mineral. In order to compensate, the carbonate ion concentration in deep ocean water adjusts itself (through a chemical feedback loop) to that value where dissolution forces accumulation on the sea floor into balance with ingredient supply. If this balance between ingredient supply and calcite burial is disrupted by the introduction to the ocean of CO_2 from the destruction of biomass, the $CO_3^=$ ion concentration would be driven to lower values causing excess dissolution which in turn would cause both the alkalinity and ΣCO_2 concentrations in sea water to rise. However, the alkalinity would rise twice as fast as the $\sum CO_2$ and hence the $CO_3^{=}$ ion content of sea water would increase. The rise would continue until the $CO_3^{=}$ ion content of deep water had returned to that value where accumulation of calcite on the sea floor once again matched the supply of the ingredients for calcite.

The tendency toward calcite dissolution always increases with depth in the sea. The reason is that the solubility of calcite increases with pressure (because the volume occupied by the Ca^{++} and $CO_3^{=}$ ions is smaller when they are in solution than when they are in a mineral lattice). In the deep sea, the saturation $CO_3^{=}$ ion content increases by about 18 μmol/kg per kilometer. As the $CO_3^{=}$ ion content in the deep sea is nearly uniform with depth, this leads to a crossover of the *in situ* concentration profile and the solubility profile. The depth of this crossover is related (but not identical) to the top of the transition zone which separates the realm of calcite ooze from that of red clay. If the $CO_3^{=}$ ion concentration in sea water is decreased, the depth at which this crossover occurs will become shallower and area of sea floor on which dissolution occurs will be correspondingly increased.

Important to understanding temporal trend of the glacial to interglacial change in atmospheric CO_2 content is the time required for compensation to occur. It turns out that the half-response time is on the order of only several thousand years. This is fast enough to permit a role for the $CaCO_3$ cycle in the rapid glacial to interglacial transitions in atmospheric CO_2 content.

pg. 29

All ocean sediments on ridge crests and plateaus are rich in $CaCO_3$. By contrast, those on the abyssal planes are devoid of $CaCO_3$. This difference reflects the saturation state of the deep waters. At a depth of 2.5 kilometers, the ocean is everywhere supersaturated with respect to $CaCO_3$. At a depth of 5.0 kilometers, it is everywhere undersaturated. The depth and shape of the transition zone separating the realm of

$CaCO_3$ preservation from that of complete dissolution depends on the depth profile of $CO_3^=$ concentration and on the rain rate of $CaCO_3$ to the sea floor.

While the $CaCO_3$ content of sediments is a handy index of the extent of dissolution, as illustrated in the lower part of this plate, the relationship between extent of dissolution and $CaCO_3$ content is highly non linear.

pg. 31

Variations with time of the water depth at which sediments in the eastern equatorial Pacific achieve a given $CaCO_3$ content. As can be seen, the horizons of equal $CaCO_3$ content are deeper during times of glaciation (i.e., odd numbered ^{18}O stages) than during times of interglaciation (i.e., even numbered ^{18}O stages). These depth excursions are largest for the high $CaCO_3$ content contours than for the low $CaCO_3$ content contours. In no case, do they exceed about 600 meters.

Based on studies similar to this in other parts of the ocean, it is possible to reconstruct the glacial lysocline in the three major oceans. If the offset between the saturation horizon and the lysocline were roughly the same during glacial time as it is today, then these depth changes can be used to reconstruct the $CO_3^=$ ion concentrations in the deep glacial ocean (see lower portion of plate). Keep in mind however, that if Archer and Maier-Reimer hypothesis is correct, then the offset between the lysocline and saturation horizon was far greater during glacial time.

pg. 35

Much of the dissolution of calcite on the sea floor occurs within the upper several centimeters of the sediment column. It is driven by CO_2 respired by bacteria as they devour organic matter. This CO_2 can either diffuse out of the sediment into the overlying water or it can react with calcite in the sediment to form bicarbonate:

$$CO_2 + H_2O + CaCO_3 \Rightarrow Ca^{++} + 2HCO_3^-$$

Bacterial respiration produces a CO_2 maximum and hence a $CO_3^=$ minimum several centimeters below the sediment-water interface. Above this depth, the CO_2 content drops because it diffuses out to the overlying sea. Below this depth, the availability of organic matter decreases rapidly reducing the rate of bacterial production of CO_2. Also the respiration CO_2 is neutralized by the result of reaction with the surrounding calcite. Deeper in the sediment, the $CO_3^=$ content stabilizes at the saturation value.

If during glacial time the rain rate of organic carbon to the sea floor were greater than today's, the magnitude of the respiratory bulge would have been greater. So also would be the extent of calcite dissolution within the upper sediment. This would shift the transition zone to greater depths creating too rapid a rate of dissolution (in other words, the rate of accumulation of calcite would dip below the rate of supply of the ingredients). This would cause the $CO_3^=$ ion content in deep water to increase. As the $CO_3^=$ concentration increased, the negative bulge in $CO_3^=$ concentration would shrink. Eventually its size would return to that at which dissolution once again matched the over-production of calcite. The interesting aspect of this scenario is that, while it leads to a large increase in the $CO_3^=$ ion content of deep sea water, it does not produce a large deepening of the transition zone. Thus it offers a way around the constraint placed by the observation that the deepening in the transition zone during glacial time was too small to be consistent with any $CaCO_3$-based hypotheses purporting to explain the low glacial CO_2 content. Unfortunately, as shown by Danny Sigman, the required large separation between the saturation horizon and the transition zone cannot be maintained.

pg. 37

Like that of ΣCO_2, the speciation of borate dissolved in sea water changes with pH. At high pHs, the charged borate species dominates and at low pHs, the neutral species dominates. The two species are equal in abundance at a pH of 8.8. The isotopes of boron are not distributed uniformly between these two chemical forms. Rather, the heavy isotope, ^{11}B, is enriched by about 20‰ in the neutral species relative to the charged species. As it is the charged borate which becomes incorporated into marine calcite, its isotopic composition is preserved in the sedimentary record. The isotopic composition of this species depends on pH. The higher the pH, the closer this value will be to the isotopic composition of bulk borate in sea water. It is for this reason that the boron isotopic record in foraminifera offers a means to test the idea that it was a higher rain rate of organic matter to the sea floor during glacial time which caused the atmosphere's CO_2 content to drop. The higher $CO_3^=$ ion content of deep sea water required by this scenario would be accompanied by a higher pH and hence a higher ^{11}B to ^{10}B ratio in the shells of benthic foraminifera.

pg.40

Records of dust content of the ice, D/H ratio in the ice, of the CO_2 and CH_4 contents of the air trapped in the ice, and of the $^{18}O/^{16}O$ ratio in the O_2 trapped in the ice for the Vostok Antarctica ice core. Note that the depth scale for the gases has been shifted upward by 40 meters with respect to that for the properties measured in the ice itself. Although the initial offset is about 80 meters (i.e., the firn depth), at a depth of 2000 meters, models for the Antarctic ice cap suggest that each layer has thinned (through lateral spreading) by about a factor of two.

Note the sequence of the changes associated with the end of the penultimate glacial period (i.e., marine isotope stage 6). The heavy glacial dust fall comes to an end. Then, the D/H ratio, CO_2 content and CH_4 content begin rises which take about 7000 years to be completed. Only then does the $\delta^{18}O$ in the O_2 begin its decline. If, as we believe, this decline closely follows the return to the sea of the isotopically 'light' water stored in the stage 6 ice, then the melting of these ice sheets did not begin until the Antarctica had warmed, the ocean's biological pump had weakened and the area of methane producing swamps had been expanded (and perhaps warmed).

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Expected $\Delta\delta^{13}C$ between glacial and interglacial planktonic foraminifera if the NO_3 content of the glacial ocean were 1.5 times higher than now and if its utilization efficiency remained the same as today's. Putting aside the three corrections, if half again as much CO_2 were extracted from surface waters by plants, then the surface to deep $\Delta\delta^{13}C$ should have increased from 2‰ to 3‰. From this must be subtracted -0.35‰ decrease in the $\delta^{13}C$ of ocean ΣCO_2 (based on the measured glacial to interglacial $\delta^{13}C$ difference for benthic foraminifera). Also, a correction must be made for the reduction in the fractionation between plant tissue and surface ocean ΣCO_2 caused by the drop in the CO_2 content of surface waters. As this reduction in CO_2 content brings about a 10 percent fractionation reduction, the surface to deep water $\Delta^{13}C$ drops by 0.3‰ (i.e., from 3.0 to 2.7‰). Finally, the pH dependence of the carbon isotope fractionation between ΣCO_2 and the shells of planktonic foraminifera must be taken into account. The atmospheric pCO_2 drop of from 280 to 200 μatm must have been accompanied by an increase in the $CO_3^=$ ion concentration in warm surface waters from 200 to 280 μmol/kg. As recently documented by Spero and his colleagues through laboratory calcification experiments, this would have led to a drop of 0.5‰ in the shell $\delta^{13}C$. After these three corrections have been applied, the expected glacial to interglacial $\Delta^{13}C$ becomes -0.15‰ and hence is consistent with the observation (i.e., 0.0 to -0.3‰).

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Map showing sites at which the glacial to interglacial difference in the ^{13}C to ^{12}C ratio in the shells of planktonic foraminifera has been determined.

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Part III

WALKER'S WORLD

CO_2, CHEMICAL TRAFFIC CONTROLLER?

CONTENTS

WALKER'S WORLD:

CO_2, CHEMICAL TRAFFIC CONTROLLER?

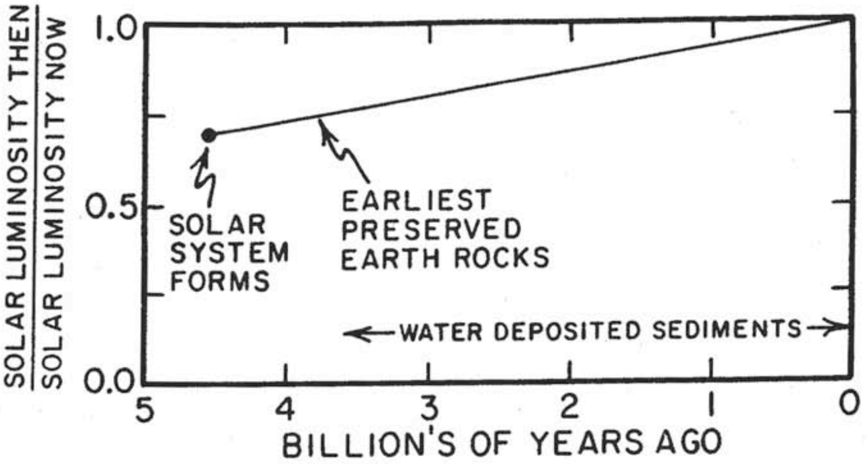
This section's hero is James C.G. Walker, a space physicist at the University of Michigan. In 1981, together with his colleagues P.B. Hays and J.F. Kasting, he published a paper which lays out in beautiful simplicity the role of atmospheric CO_2 *as the chemical policeman controlling the flow of continental weathering products to the sea, and thereby maintaining a balance between the rate of outgassing of* CO_2 *gas from our planet's interior and the rate of* CO_2 *removal to sea floor sediments as calcite. The important consequence of this police action is its influence on Earth climate. Walker and his colleagues pointed out that early in the Earth's history the tendency toward cooler temperatures related to the faintness of the young Sun was most likely compensated by higher atmospheric* CO_2 *contents. In an attempt to explain the cooling of the Earth over the last 100 million years, the role of Walker's mechanism was subsequently expanded by Berner, Lasaga and Garrels who postulated that the cooling was driven by a decrease in the planetary outgassing rate related to a progressive slowing of plate motions. This suggestion was met with wide interest and became known as the BLAG hypothesis in honor of its creators. In the enthusiasm to explore all the aspects of BLAG, the earlier contribution of Walker tended to be forgotten. Hopefully, in naming this section, we will help to return the credit for the* CO_2 *policing concept to its originator, James C.G. Walker.*

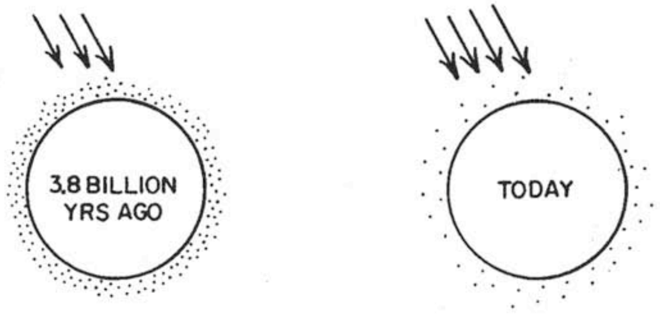
Our third puzzle has to do with the proposal that a tie exists between tectonics and climate. It is well documented that the temperature of the Earth has drifted back and forth between conditions cold enough to support polar ice caps and warm enough to allow forests to flourish in these regions. It is tempting to call on changing CO_2 content of the Earth's atmosphere as the driving force behind these changes. As we have already learned, the CO_2 molecules residing in the atmosphere-ocean reservoir are currently being replaced on the time scale of about 10^5 years. Because this residence time is so short, the amount of CO_2 present in the atmosphere will be sensitive to both fluctuations in the rate of addition of CO_2 through outgassing from the Earth's interior and to the rate of removal of CO_2 to sediments (as $CaCO_3$ and organic matter). Earth degassing is influenced by the motions of the great crustal plates (i.e., tectonics) and $CaCO_3$ accumulation in marine sediments by the rate at which the element calcium is made available through chemical weathering (a process influenced by climate). This section's hero, Jim Walker, proposed a self-regulating mechanism by which Earth surface temperature (via the atmosphere's CO_2 content) is tied to the rate of CO_2 outgassing. He suggested that the atmosphere's CO_2 content serves as a policeman controlling the flow of the elements carbon and calcium through the ocean-atmosphere reservoir. The validity of this proposal has been debated for more than a decade. The jury is still out. However, regardless of the verdict, the beauty of the logic behind Walker's idea makes it worth our consideration. To see why, let us first consider the early history of out planet.

Compensating for the Faint Young Sun

The geologic record tells us that liquid water has existed on the planet continuously for at least 3.8 billion years. We know this because representing all epochs are sediments deposited beneath liquid water in river deltas and on seafloors. By contrast, deposits left behind by glaciers appear only sporadically in the record and were with two possible exceptions restricted to land masses residing at high latitudes. At first thought this is not surprising, for to cool the tropics to the freezing point, would require either a large reduction in the Sun's energy output or in the Earth's greenhouse shielding. However, it is surprising when one takes into account calculations carried out by astrophysicists which reveal that the Sun's energy output must have steadily increased and is now about 30 percent greater than it was in the beginning (4.6 billion years ago). Thus at the onset of the preserved geologic record, 3.8 billion years ago, about 25 percent less sunshine reached us than now. The reason for this increase is that the Sun's

WALKER'S WORLD





LESS SUNSHINE	MORE SUNSHINE
MORE ATM. CO_2	LESS ATM. CO_2
TROPICAL TEMP.	TROPICAL TEMP.
>0°C	~25°C

nuclear furnace has steadily fused hydrogen into helium, gradually reducing the number of atomic nuclei flying about in its hot interior. This, in turn, has reduced the thermal pressure holding back the forces of gravity. In order to maintain a balance between the gravitational tendency to collapse and the thermal tendency to expand, the rate of energy production in the Sun's nuclear furnace has steadily risen compensating for the decrease in the number of nuclear entities. The current rate of energy release from the Sun tells us how many hydrogen mergers occur each year. Based on this conversion rate, astrophysicists can calculate how the Sun's helium to hydrogen ratio has evolved and hence how its energy output must have increased in order to compensate for this change. The bottom line is that, early on, the amount of energy reaching us from the Sun was not large enough to maintain equatorial temperatures on our planet (at least with an atmosphere like the present one) above the freezing point. Thus, in order to account for the presence of liquid water on the planet at that time, something must have compensated for the dearth of sunshine. That something was very likely extra greenhouse gases in the atmosphere: CO_2 being the top candidate.

The Earth's Anti-Freeze

The Earth has a built-in thermostat which prevents freezing. The active element of this thermostat is CO_2 gas. Roughly a tenth of a gigaton of carbon escapes from the planet's interior each year in the form of CO_2 gas. In a period of several thousand years, this flux brings to the surface an amount of CO_2 equal to that currently present in the atmosphere. But the CO_2 content of the atmosphere is not becoming larger. For this to be the case, the carbon atoms contained in this CO_2 must be removed to sediments (as calcite and organic matter) at approximately the same rate as they are being gained from the Earth's interior through outgassing.

Let us consider what would happen if Kurt Vonnegut's ice-nine catastrophe were to strike the Earth. In the absence of liquid water, no further $CaCO_3$ or organic residues would be formed. However, the release of CO_2 from the Earth's interior would chug along virtually unchanged, for outgassing is driven by heat produced by the radiodecay of the ^{40}K, ^{235}U, ^{238}U and ^{232}Th contained in the Earth's mantle. Considering that interior temperatures are measured in thousands of degrees, a change in the temperature of a few tens of degrees at the surface would go unnoticed by the Earth's mantle. So, were the Earth's surface to freeze, the outgassing would continue and CO_2 would accumulate in the atmosphere. No pathway for removal would be available. After ten or so million years, the atmosphere's CO_2 partial pressure would approach one atmosphere! Of course long before this level was achieved, the warming induced by the extra greenhouse insolation would bring about a thaw. As at any one time only a tiny fraction of the Earth's carbon resides in the atmosphere as CO_2, no chance exists that the supply from the interior would ever have been so measly that the Earth was at risk of becoming permanently ice bound. Our planetary twin, Venus, with its 100-fold larger atmosphere of nearly pure CO_2 and greenhouse supported surface temperature of 450°C stands witness to the potential power of this blanket.

A potential flaw has been found in this argument. Jim Kasting, a co-author on the 1981 Walker paper, and his Penn State colleague, Ken Caldeira, point out that were the Earth ever to have become 'white', the supposed savior might instead have sealed its doom. It is possible that before CO_2 had built up to the point where the Earth's ice cover could melt, this gas would condense to form globe straddling ice clouds. The reflection of sunlight from these clouds would have so starved the planet of solar heat that it would forever remain in its frozen state. Were this to have happened, Earth and Venus would have stood as twin sentinels, one bearing witness to a CO_2-driven runaway cooling and the other to a CO_2-driven runaway warming!

Evidence from carbon isotope ratios has led Harvard's Paul Hoffman and his colleagues to suggest that at least twice the Earth did freeze over and that both times it was bailed out by a build up of CO_2. Following up on reconstructions by Kirshvink which suggest that two major late Proterozoic glaciations (one at about 740 and the other at about 550 million years ago) reached well into the tropics. Further, as these glaciers extended to sea level, it is difficult to explain their existence unless the Earth had become one large snowball. It has long been known that the tills laid down by these glaciers are immediately overlain by limestones referred to as 'cap carbonates'. Hoffman et al. provide a fascinating explanation for this sequence. Once frozen over, no mechanism would exist to deposit the CO_2 escaping from the Earth's interior either as $CaCO_3$ or as organic debris. Hence the CO_2 content of the atmosphere would steadily increase. Eventually, the greenhouse warming created by the CO_2 buildup would overcome the massive cooling created by the snowball's ability to reflect away the sun's rays. At this point, the ice cover would begin to retreat progressively darkening the planet's surface. A runaway warming would ensue eliminating all the planet's ice cover and thereby flooding the low-lying portions of the continents. Weathering of the newly exposed land surface would supply the calcium required to precipitate the great excess of CO_2 in the atmosphere and oceans. The result would be to produce the limestones which now cap these glacial deposits. As the CO_2 disappeared the Earth would cool.

Hoffman et al. point to the carbon isotope ratios in the cap carbonates as evidence in support of their proposal. Instead of the near zero $\delta^{13}C$ values which have characterized most of geologic time, these limestones have quite negative values ($\delta^{13}C$ -5‰). The important point is that this value is equal to that for our estimate for average Earth carbon. Thus, the isotopic composition of the limestone carbon is entirely consistent with the idea that it is the product of an enormous buildup of mantle-derived CO_2.

Directing Chemical Traffic

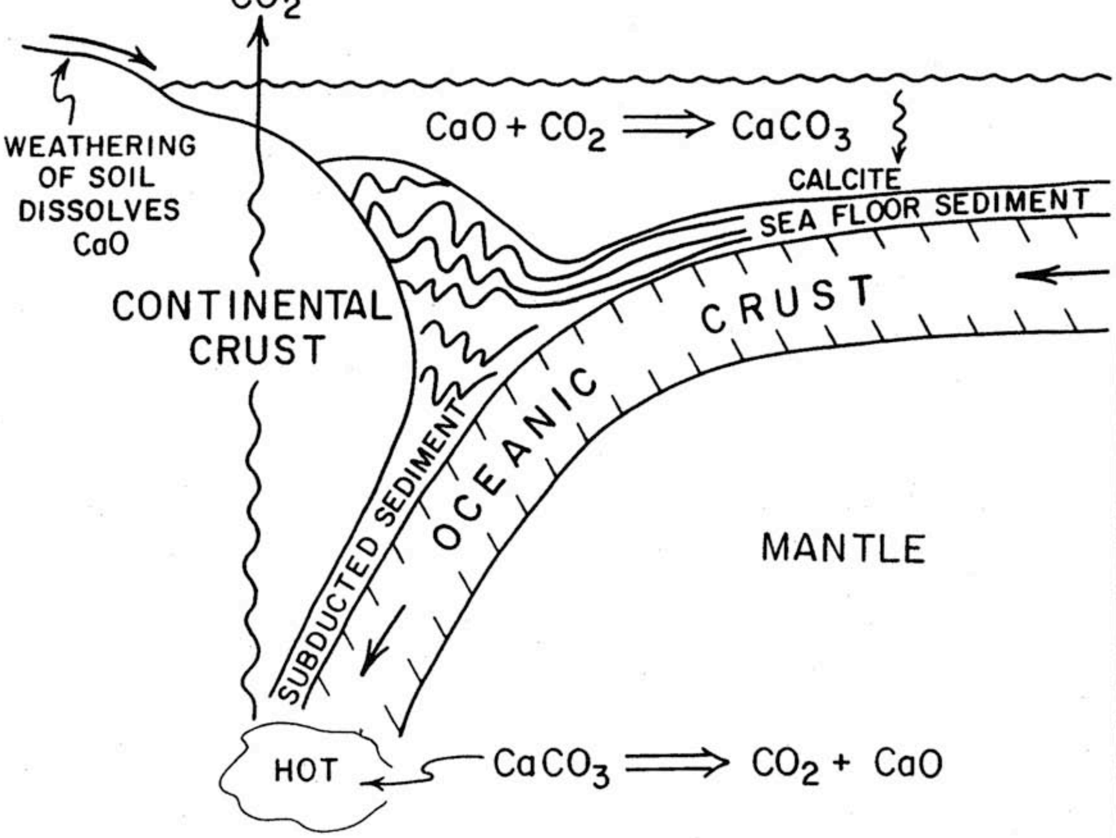
Not only has CO_2 stood guard against an Earth freeze-up but, as Walker proposed, it may have exerted an active influence on the climate. This can be seen by carrying the above logic one step further. To do so, let us consider the hypothetical planet X made of only two minerals, CaO and $CaCO_3$. The temperature in this planet's interior is high enough to thermally decompose $CaCO_3$ to CaO and CO_2. The CO_2 generated in this way migrates to the surface where it accumulates in the atmosphere maintaining temperatures sufficiently high to allow water to exist in liquid form. Water evaporates from the planet's ocean and falls on its continents as rain. CaO dissolves from the planet's soils and is carried to the sea by rivers. The sea becomes supersaturated with respect to $CaCO_3$, allowing CO_2 to mate with CaO. The calcite formed by this union falls to the sea floor producing a sedimentary blanket. In this way, the CO_2 escaping from the planet's interior is returned to solid form.

Now, if for some reason the supply of CO_2 from the interior were to temporarily exceed the supply of CaO from rivers, then the mateless CO_2 molecules would be forced to accumulate in the atmosphere and the planet would warm. This warming would drive up the chemical weathering rate to rise (more rain and faster chemical kinetics). The warming would continue until the dissolution rate of CaO once again matched the rate at which CO_2 was being supplied from the planet's interior. Because of this, the planet's chemical system would be self regulating. If CO_2 were outgassed faster than CaO was eroded, the atmosphere's CO_2 content (and consequently also Earth's temperature) would rise until balance was reestablished. Or, on the other hand, if CaO were dissolved from the continents faster than CO_2 escaped from the interior, the atmosphere's CO_2 content and (consequently Earth's temperature) would fall until the balance was reestablished.

Even on this simple planet, the temperature at which a balance between CO_2 outgassing and CaO erosion was achieved need not have remained constant. For example, as its radioactive isotopes decayed away, the planet's interior would cool and the rate of outgassing of CO_2 would ebb. Less matching CaO would be required and hence surface temperatures would fall.

But the Earth is not a ball of CaO and $CaCO_3$. Nor do its rates of continental weathering and oceanic calcite precipitation follow the simple rules postulated for planet

CHEMICAL CYCLE ON PLANET X

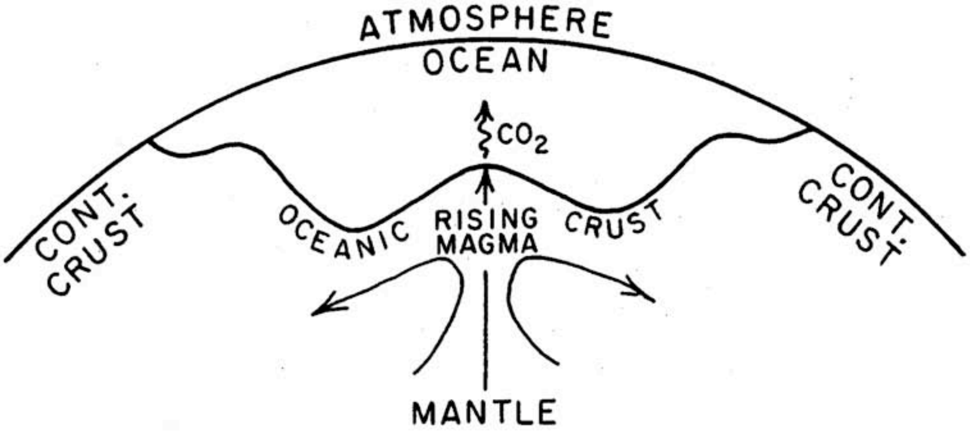


X. However, a feedback loop similar to that for planet X very likely operates. As CO_2 resides in the ocean-atmosphere reservoir for only a hundred thousand or so years, a control mechanism must exist which forces a balance between CO_2 loss to sediments and CO_2 supply from the interior. The difference is that Earth chemical cycles are far more complex than those for planet X. These complexities offer many more possibilities for shifts in the temperature at which the balance between CO_2 loss matches CO_2 gain. Changes in the rate of plate motion, in the height of mountain belts, in the freeboard of continental blocks, in the physiology of terrestrial plants and in the habitat of $CaCO_3$ precipitating marine organisms, all have the potential to change the temperature at which CaO supply balances CO_2 outgassing.

The BLAG Scenario

In a paper which attracted much interest to this subject, Berner, Lasaga and Garrels (BLAG) treated the Earth much as if it were planet X. They assumed that the rate of CO_2 release from the Earth's interior is proportional to the rate of sea-floor spreading and that the main factor perturbing the Earth's CO_2 budget over the last 100 million years was the gradual slowdown in this rate as first postulated by marine geologists Pitman and Hays. If so, then following Pitman and Hays' suggestion that 100 million years ago sea floor spreading rates were twice today's, the rate of CO_2 outgassing must also have been roughly twice today's. As the Earth-surface CO_2 budget is balanced on the time scale considerably less than one million years, the delivery rate of CaO to the sea as the result of the chemical weathering of silicate rocks must also have been twice as great at that time. The major factor controlling the chemical weathering rates is assumed by BLAG to be soil temperature. As chemical reaction rates rise by about a factor of two for each 10°C warming, in order for the CaO supply to have been twice its present values, the Earth would have to have been 10°C warmer 100 million years ago. BLAG assumes that this extra warmth was maintained by a higher atmospheric CO_2 content. Simulations carried out in general circulation models suggest that for each doubling of the

BLAG'S WORLD



100 MILLION YEARS AGO

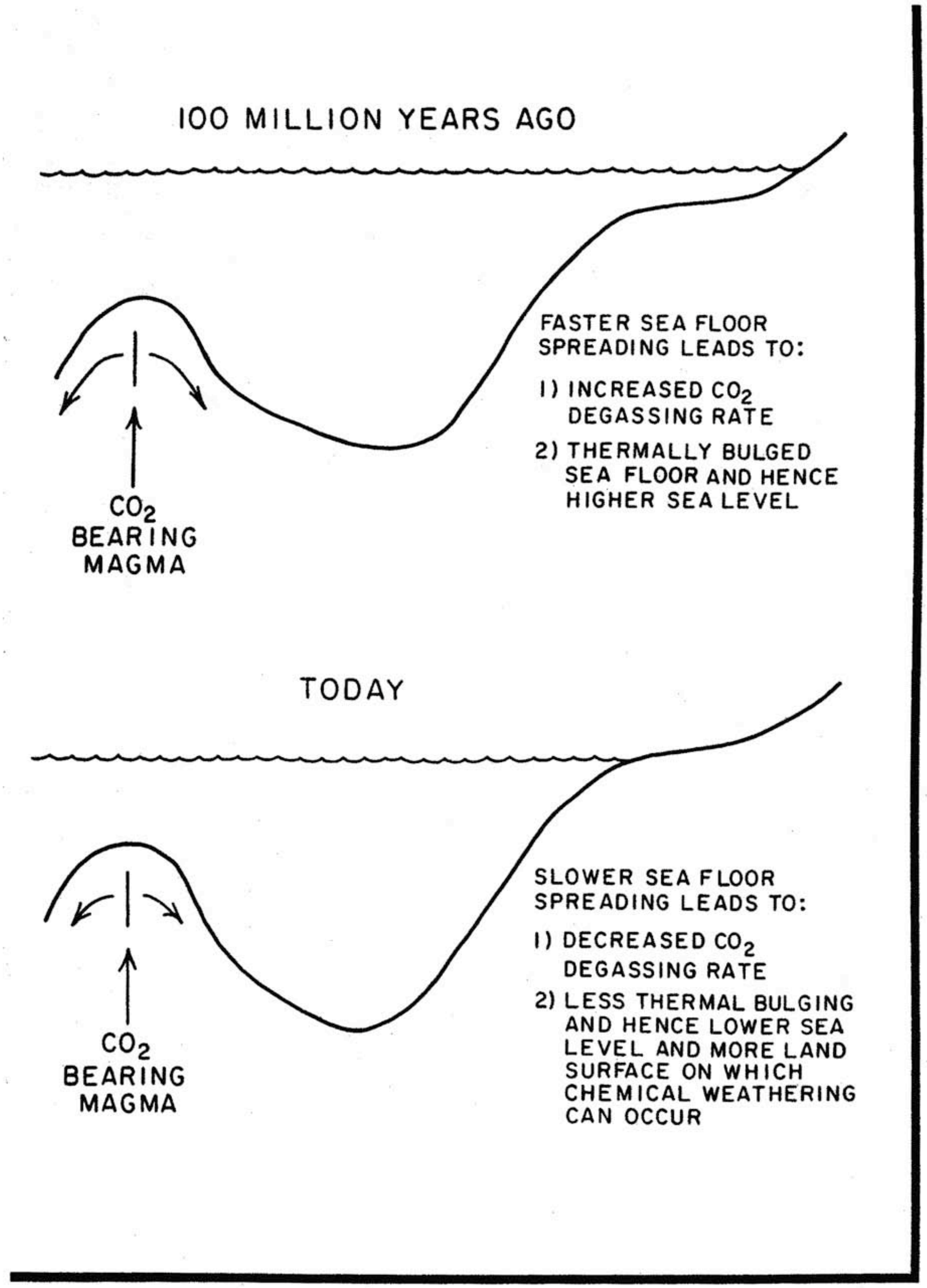
$\frac{\text{SEA FLOOR SPREADING RATE}}{\text{TODAY'S}} = 2$

$\frac{CO_2 \text{ OUTGASSING RATE}}{\text{TODAY'S}} = 2$

$\frac{\text{ATMOSPHERIC } CO_2 \text{ CONTENT}}{\text{TODAY'S}} = 8$

EARTH SURFACE TEMPERATURE COMPARED TO TODAY'S +10 °C

$\frac{\text{CHEMICAL WEATHERING RATE}}{\text{TODAY'S}} = 2$


100 MILLION YEARS AGO
FASTER SEA FLOOR SPREADING LEADS TO:
1) INCREASED CO_2 DEGASSING RATE
2) THERMALLY BULGED SEA FLOOR AND HENCE HIGHER SEA LEVEL
CO_2 BEARING MAGMA
TODAY
SLOWER SEA FLOOR SPREADING LEADS TO:
1) DECREASED CO_2 DEGASSING RATE
2) LESS THERMAL BULGING AND HENCE LOWER SEA LEVEL AND MORE LAND SURFACE ON WHICH CHEMICAL WEATHERING CAN OCCUR
CO_2 BEARING MAGMA

atmosphere's CO_2 content the temperature rises about 3.3°C. Hence a 10°C warming would require an eight fold increase in the atmosphere's CO_2 content. We know from measurements on air trapped in ice cores that, over the last 250,000 years, the CO_2 content of the atmosphere has averaged about 250 ppm. If the BLAG reconstruction is correct, then the CO_2 content of the atmosphere must have been about 2000 ppm 100 million years ago. The fact that oxygen isotope evidence demonstrates that the earth's polar regions were considerably warmer at this time has been taken as a confirmation of BLAG scenario.

Since the publication of BLAG, much discussion has occurred concerning the details of their argument. Did sea floor spreading rates really drop by as much as a factor of two over the last 100 million years or, as other reconstructions suggest, has the extent of slowdown been much smaller? Do the chemical weathering rates for silicate minerals really depend primarily on temperature, or as some have suggested, do other factors such as mechanical breakup or plant enzymes play important roles? Does Earth climate change only as the result of fluctuations in the CO_2 content of the atmosphere, or as some have suggested, has it been more strongly influenced by the geography of continents and oceans? While these and other uncertainties cast doubt on the specific conclusions of BLAG, the concept has stood the test of time.

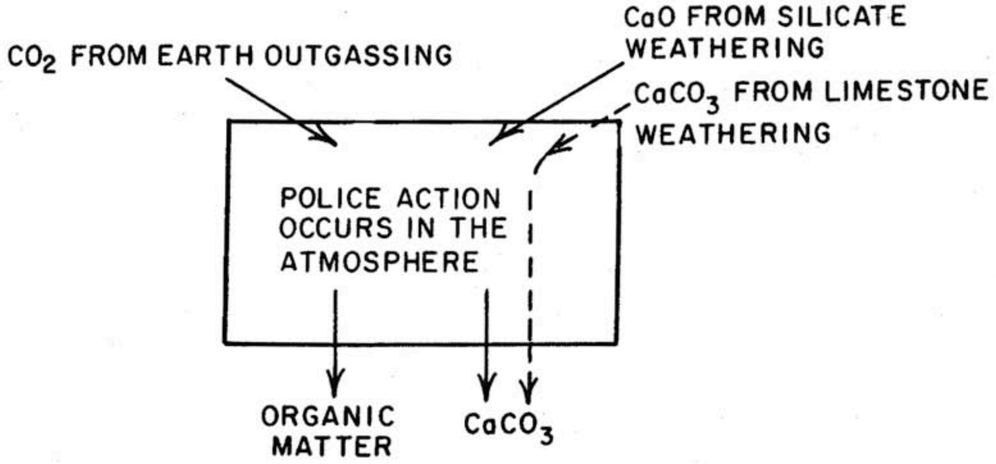
But Might the Policeman Reside in the Ocean?

While the most attractive candidate for chemical traffic director is the CO_2 content of the atmosphere, other choices exist. The assumption that the sole fate for the CaO released by the weathering of continental silicate rocks is deposition as $CaCO_3$ on the sea floor is open to challenge. Perhaps the supply of calcium is in excess of what's needed to match the CO_2 being degassed from the Earth's interior. In this case, the excess calcium would have to be taken up in silicate minerals. One pathway would be into minerals forming on the sea floor. Unfortunately, minerals formed by this so-called "reverse weathering" process are not present in nearly the abundance expected if they

BLAG *vs.* GALB

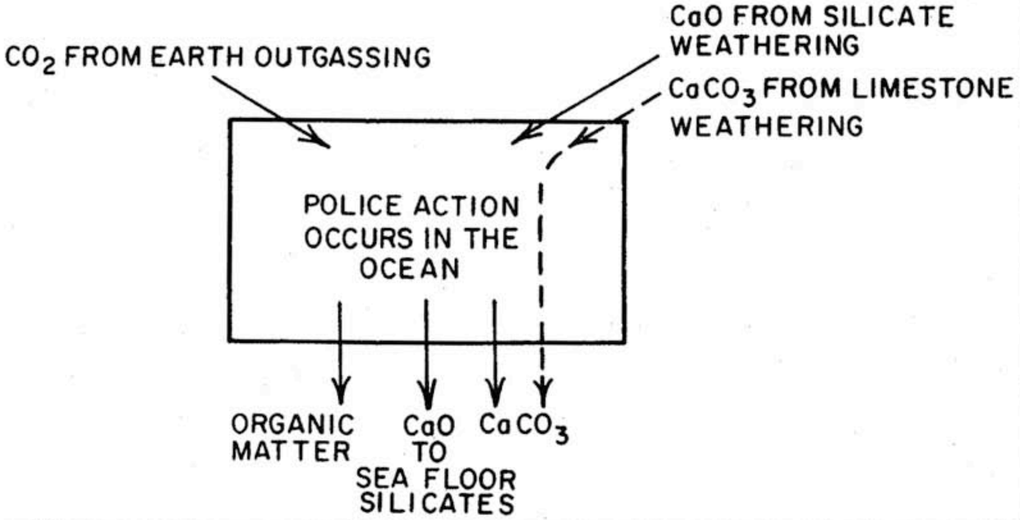
BLAG CaO SUPPLY = CO_2 SUPPLY

ATMOSPHERIC CO_2 CONTENT IS DRIVEN TO THAT VALUE WHERE SOIL TEMPERATURES ALLOW SILICATES TO WEATHER AT SUCH A RATE THAT THE SUPPLY OF CALCIUM IONS TO THE SEA JUST MATCHES THE SUPPLY OF CO_2 FROM EARTH OUTGASSING.



GALB CaO SUPPLY > CO_2 SUPPLY

OCEAN pH (OR OCEAN Ca CONCENTRATION) ADJUSTS TO THAT VALUE WHERE THE REMOVAL OF THE CALCIUM THROUGH THE FORMATION OF SEA FLOOR SILICATE MINERALS MATCHES THE EXCESS OF CALCIUM DELIVERY FROM THE CONTINENTS OVER CO_2 DELIVERY BY EARTH OUTGASSING.



were to constitute a calcium sink comparable in magnitude to that of marine calcite which makes up about half of presently forming open ocean sediment. If the silicate route is an important one, the product must be hidden from view either in basins adjacent to continental margins where the rate of deposition of detrital material is very rapid or in the basalts which lie beneath the blanket of open-ocean sediment. While little support exists that the former hiding place is important, the chemical signature of hydrothermal waters issuing forth from the ridge crests clearly demonstrates that extensive alteration of the underlying basalt is occurring. Hence if significant amounts of calcium are being removed into silicate minerals, this is likely occurring in sea floor basalts. But, at least close to the centers of sea floor spreading, calcium is being released rather than taken up. The effluent from ridge-crest geothermal vents contains on the average about twice as much calcium as does sea water. The major reaction appears to be a replacement of calcium in the basalt by magnesium carried into the hot crust with the circulating sea water. So, if calcium is being removed, it must be as a result of lower temperature reactions occurring away from the spreading centers.

We shall refer to this alternate scenario as GALB. For BLAG the policeman resides in the atmosphere; for GALB he resides in the sea. For BLAG calcium supplied to the sea is removed almost entirely as $CaCO_3$. For GALB silicate minerals, formed on the sea floor, constitute a major additional sink for calcium. For BLAG the flow of CaO through the system is closely tied to that of CO_2. For GALB, the control is most likely the pH of deep sea water. The higher the pH the more rapidly CaO is removed.

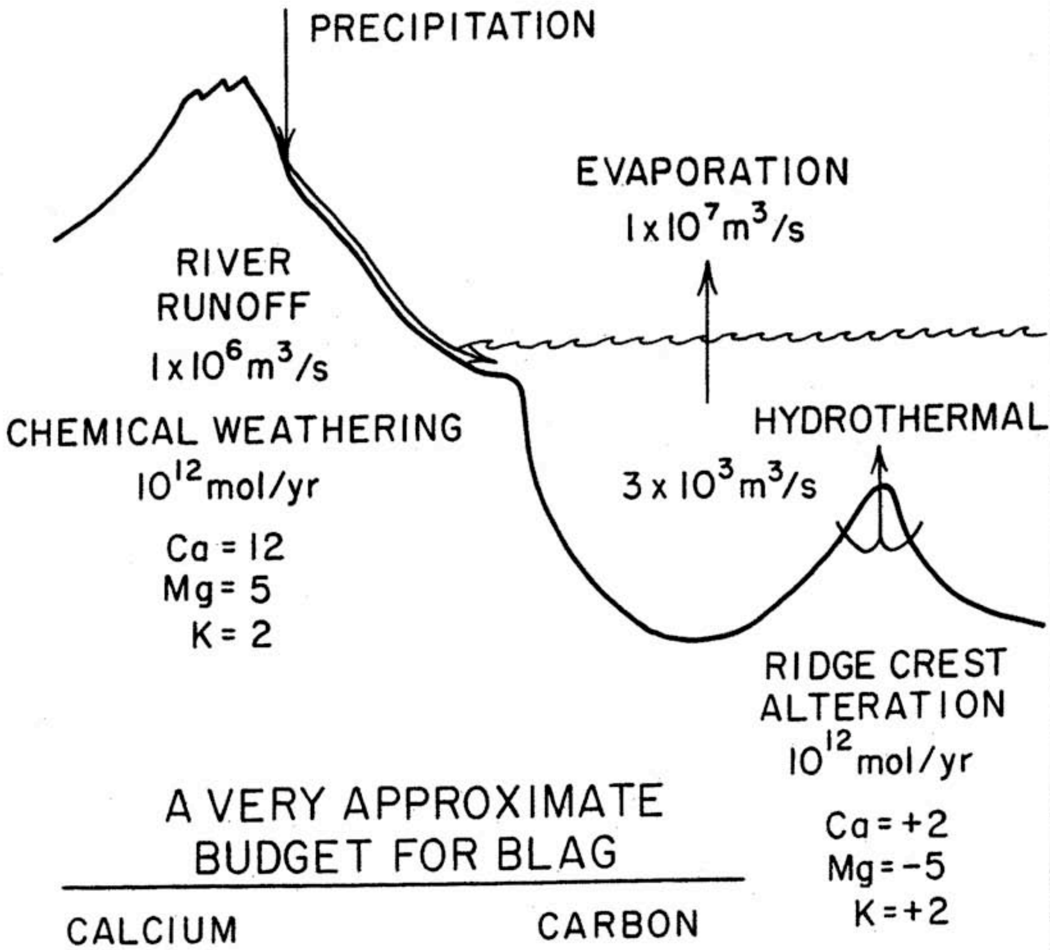
The Rates of CO_2 Degassing and Ca Supply From Silicates

First let us put aside an obvious strategy for distinguishing between the BLAG and GALB scenarios. It involves measurements of today's rates of input of CaO and CO_2 to the ocean-atmosphere reservoir. If such studies were to reveal that the rate of delivery of CaO derived from the chemical weathering of silicate minerals closely matched the rate of outgassing of CO_2 from the Earth's interior, then the case for BLAG would be strengthened. On the other hand, if the delivery of silicate-derived CaO proved to be significantly higher than that of CO_2, the finger would point toward GALB. But this strategy proves to be impractical. The reason is that to be successful these fluxes would have to be measured with an accuracy of better than ±15%. We are hard pressed to achieve even a factor of two.

These endeavors are bedeviled by a common problem; the erosion of limestone dominates the supply of both CaO and CO_2 to the sea. This greatly diminishes the value of the two fluxes we can measure with a fair degree of accuracy, i.e., the accumulation rate of calcite on the sea floor and the supply rate of calcium by the world's rivers. As both fluxes are dominated by the recycling of limestone (dissolved from the continents and redeposited on the sea floor), it is not possible to separate out the lesser contribution made by the weathering of silicate minerals. One might conclude that such a separation is not necessary, for if the rate of removal of calcium to the sea floor as calcite exactly matched the rate at which calcium is supplied to the ocean from rivers and sea floor hydrothermal activity, then we could be assured that no excess remained for the formation of silicate minerals in the basaltic crust or sediment column. However, as the recycling of limestone dominates the fluxes of calcium and carbon to the sea, the two rates would have to be known to a very high degree of accuracy. It has been estimated that only about one quarter of the calcium eroded from the continents is derived from silicates. If so, then a 25% uncertainty in the estimate of river flux of calcium could create a factor of two uncertainty in the amount of CaO available for matching the CO_2 added by mantle outgassing. Unfortunately, it is not possible to determine either the river flux or input of calcium to better than 20%. Hence, this approach does not offer a means of distinguishing between BLAG and GALB.

One of the complications associated with any attempt to use today's river fluxes has to do with the dependence of chemical weathering rate on climate. We live in the

GLOBAL CHEMICAL CYCLES



A VERY APPROXIMATE BUDGET FOR BLAG

CALCIUM 10^{12} mol/yr	
RIVERS	
LIMESTONE	+9
SILICATE	+3
HYDROTHERM	+2
TOTAL INPUT	**+14**
$CaCO_3$ OOZE	−14
TOTAL LOSS	**-14**

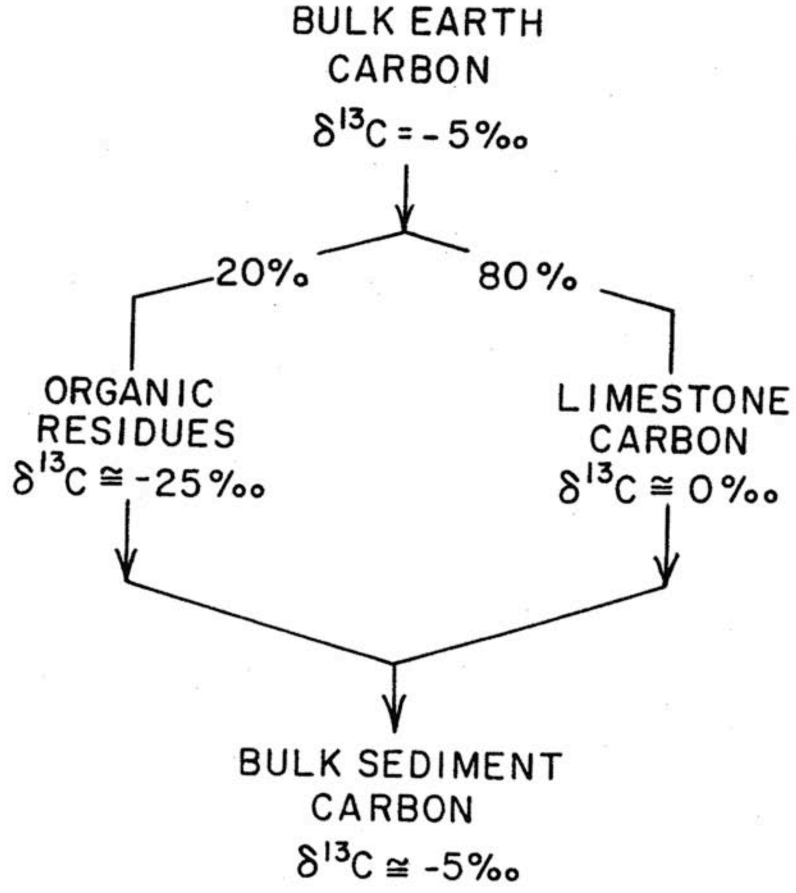
CARBON 10^{12} mol/yr	
RIVERS	
LIMESTONE	+9
OUTGASSING + ORGANICS	+8
TOTAL INPUT	**+17**
$CaCO_3$ OOZE	−14
ORGANICS	−3
TOTAL LOSS	**-17**

warm phase of one of a long series of 100-thousand-year duration glacial cycles. As these intervals of warmth constitute only about ten percent of each climate cycle, the chemical weathering rates that we compute from today's river discharge may not typify the entire cycle. The situation is further complicated by anthropogenic impacts on river chemistry. Plowing, irrigation, acid rain... have all accelerated the release of exchangeable ions bound in soils. Thus the chemical load of many of the world's rivers is not even typical of interglacial climates. Frustration!

The failure of this obvious approach leaves us with the more difficult one of separately determining the rates of CO_2 degassing and silicate weathering. In the case of CO_2, we know that sea-floor spreading centers are major conduits for CO_2 emanating from the Earth's interior. The reason is that basalt glasses dredged from mid-ocean ridge crests have CO_2-bearing inclusions (which often burst when brought aboard oceanographic vessels, giving rise to the term 'popping rocks'). The ratio of CO_2 gas to solid in these glasses offers a means of estimating the amount of CO_2 carried to the surface with basaltic magmas. We know reasonably well the rate of sea floor spreading and hence the amount of basalt formed each year. Ultimately all the CO_2 brought up with the basalt magma escapes into the overlying ocean. CO_2 is also released from zones where plates are subducted and from zones of continental metamorphism. These contributions currently defy quantification. Hence the likelihood that the aggregate CO_2 flux from all three sources can be adequately quantified is remote.

An additional complication in the CO_2 budget is that only part of the carbon removed from the ocean-atmosphere reservoir becomes calcite. The rest becomes bound into organic residues. Hence, in order to estimate the required supply rate of CO_2 destined to become $CaCO_3$, the amount of carbon going into organic residues must be subtracted from the amount of CO_2 being outgassed. Fortunately, we have a means to assess the magnitude of this correction. It is based on carbon isotope ratios measured in marine carbonates. From a knowledge of the approximate isotope composition of bulk

WHOLE EARTH CARBON ISOTOPE BUDGET



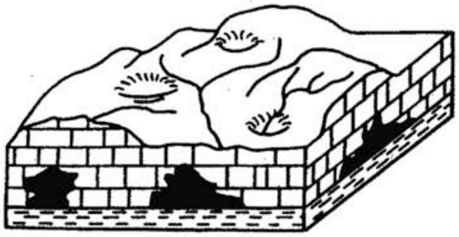
$$0.2 \times -25‰ + 0.8 \times 0‰ \equiv 1.0 \times -5‰$$

Earth carbon ($\delta^{13}C$=-5‰) and of the difference between the carbon isotope ratio in plant carbon and in marine calcite carbon ($\Delta\delta^{13}C$= -25‰), we can use the isotopic composition record for marine carbonate to tell us how the carbon output has been divided between organic residues and calcite. For example, if the $\delta^{13}C$ for marine $CaCO_3$ of a given age is close to 0‰, then mass balance requires that at that time 80% of the carbon went into limestone and 20% into organic residues. The results of thousands of carbon isotope measurements on marine $CaCO_3$ of all ages suggest that the fraction of carbon going into organic residues has remained small. For the last 100 million years, it has been in the range 20±5% of the total. But organic matter cannot be written off as a minor player. The reason is as follows. Since only about one quarter of the calcium delivered to the sea is derived from the weathering of silicate minerals, organic matter accounts for the removal of roughly half of the CO_2 supplied by Earth outgassing (and oxidation of recycled organics).

An alternate approach would be to estimate the contribution made by the chemical weathering of silicate rocks to the dissolved Ca^{++} carried in rivers. One means by which this might conceivably be done is through measurements of the carbon isotope ratios in river water $\sum CO_2$. The plus charges on cations derived from silicates are balanced by minus charges on bicarbonate ions derived from soil CO_2 ($\delta^{13}C$=-26‰). The plus charges on cations derived from carbonate rocks are also matched by minus charges of bicarbonate ions. But, in this case half the carbon atoms are from the carbonate rocks ($\delta^{13}C$=0‰) and half from soil CO_2 ($\delta^{13}C$=-26‰). Together they would yield a $\delta^{13}C$ value of -13‰. Were the situation simple, then the $\delta^{13}C$ for bicarbonate would be expected to lie somewhere between -13‰ for streams draining limestone terrane and -26‰ streams draining silicate terrane. For example, were the $\delta^{13}C$ for the HCO_3^- of average river water -20‰, then one could conclude that about half the cations were derived from the weathering of limestone and about half from the weathering of silicate rocks. Unfortunately, the situation is far more complex. First, the

CARBON ISOTOPES IN CHEMICAL WEATHERING CYCLE

RIVERS DRAINING LIMESTONE TERRANE

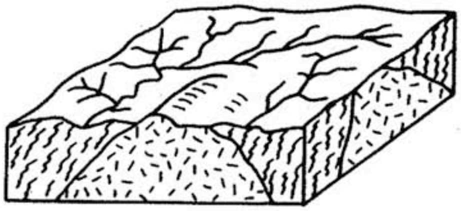


$$\overset{\text{SOIL GAS}}{CO_2} + \overset{\text{LIMESTONE}}{CaCO_3} + H_2O$$

$$\Longrightarrow 2HCO_3^- + Ca^{++}$$

$$\delta^{13}C_{HCO_3^-} = \frac{1}{2}(-26)^* + \frac{1}{2}(0) = -13‰$$

RIVERS DRAINING SILICATE TERRANE

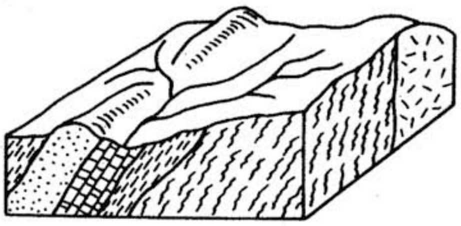


$$2\,\overset{\text{SOIL GAS}}{CO_2} + \overset{\text{CALCIUM BEARING SILICATE MINERALS}}{CaSiO_3} + 3H_2O$$

$$\Longrightarrow 2HCO_3^- + Ca^{++} + H_4SiO_4^0$$

$$\delta^{13}C_{HCO_3^-} = -26‰^*$$

ALL RIVERS

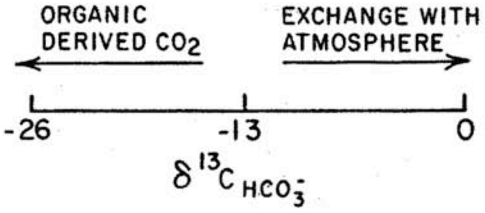


ADDITION OF EXCESS ORGANIC DERIVED CO_2

$$\delta^{13}C_{HCO_3^-} \rightarrow -26‰^*$$

EXCHANGE WITH CO_2 IN ATMOSPHERE

$$\delta^{13}C_{HCO_3^-} \rightarrow 0‰$$



* FOR C-4 PLANTS SUBSTITUTE -10‰

bicarbonate in rivers exchanges CO_2 in the overlying with atmosphere driving the $\delta^{13}C$ for river bicarbonate toward 0‰. Second, the decomposition of organic matter within the river drives the carbon isotope ratio toward the -26‰ value characterizing organic material. Finally, in the soils where weathering occurs, there is a large excess of soil CO_2 gas carrying the organic carbon isotope ratio. Again, this CO_2 drives the carbon isotope ratio in soil water bicarbonate toward -26‰. As no means exists to assess the relative strengths of these tendencies, the carbon isotope approach also proves futile.

A better approach is chemical. It involves the use of the concentrations of Na^+, K^+ and SiO_2 in river water as a means to assess the contribution of silicate weathering. But as the results obtained in this way depend strongly on the composition of the material being weathered as well as on the composition of the residues left behind in the soil, this approach has its own set of problems. Various authors have pondered relative contributions of silicate and carbonate. Most conclude that only about one-quarter of the calcium carried to the sea by rivers comes from the weathering of silicates.

The Marine Strontium Isotope Record

Which kind of world do we live in: one where chemical balance is maintained through a feedback loop involving atmospheric CO_2 content or one where balance is maintained by feedback loops involving the chemistry of sea water? Events of the last 60 million years send us some confusing messages. As is well documented by the $^{18}O/^{16}O$ ratios measured in benthic foraminifera, polar climates steadily cooled over this time interval. According to BLAG, this cooling was driven primarily by a decreasing supply of CO_2 from the Earth's interior which was matched by a corresponding decrease in chemical weathering rates on the continents. But this message is not straight forward. The problem is that oxygen isotope measurements on planktonic foraminifera suggest that tropical temperatures remained more or less constant over the past 50 or so million years. Hence the isotope record seems to be telling us that the temperature gradient from equator to poles has steepened. One possible explanation for this change is that there has

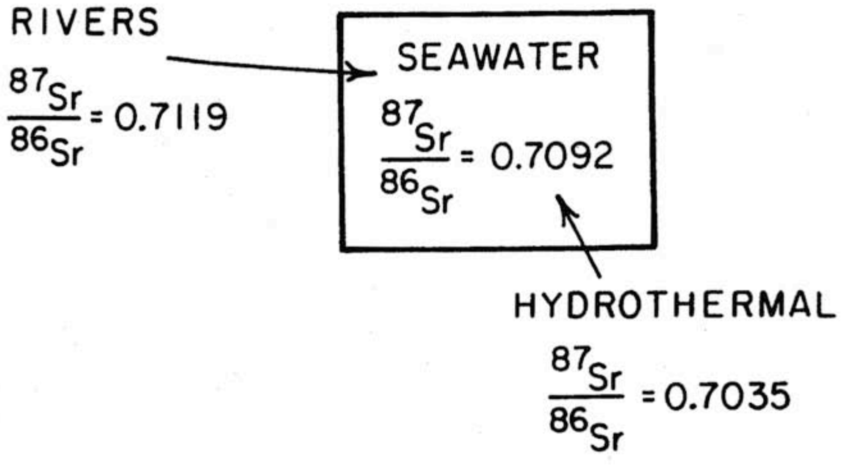
THE STRONTIUM ISOTOPE RECORD

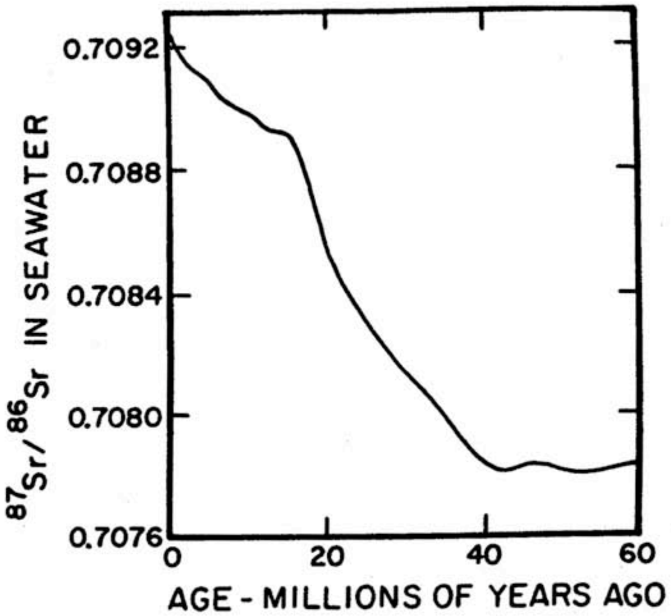
THE ELEMENT STRONTIUM HAS FOUR STABLE ISOTOPES: ^{84}Sr ^{86}Sr ^{87}Sr AND ^{88}Sr.

ONE OF THEM, ^{87}Sr, IS BEING STEADILY GENERATED BY THE DECAY OF THE LONG-LIVED RADIOISOTOPE, ^{87}Rb. HENCE ITS ABUNDANCE RELATIVE TO THOSE OF ITS ISOTOPIC BROTHERS IS SLOWLY INCREASING.

BUT THE RADIOGENIC ^{87}Sr ATOMS ARE NOT UNIFORMLY DISTRIBUTED AMONG EARTH ROCKS. BECAUSE MUCH OF OUR PLANET'S RUBIDIUM HAS BEEN SEGREGATED TO THE CONTINENTAL CRUST, ITS STRONTIUM IS THE MOST RADIOGENIC.

THE STRONTIUM DISSOLVED IN THE SEA IS A MIXTURE OF CONTINENTAL STRONTIUM DELIVERED TO THE SEA BY RIVERS, AND SEA FLOOR STRONTIUM DELIVERED BY RIDGE-CREST HYDROTHERMAL SYSTEMS. IN TODAY'S SEA:





TODAY

	$^{87}Sr/^{86}Sr$		Sr FLUX RATIO
RIVER	0.7119	0.0027	$\frac{\text{RIVER}}{\text{HYDRO}} \alpha \frac{57}{27} \sim 2$
SEA	0.7092	0.0057	
HYDRO	0.7035		

40 MILLION YEARS AGO

END MEMBER SCENARIOS

RIVER	0.7119*	0.0041	$\frac{\text{RIVER}}{\text{HYDRO}} \alpha \frac{43}{41} \sim 1$
SEA	0.7078	0.0043	
HYDRO	0.7035		

OR

RIVER	0.7099	0.0021	$\frac{\text{RIVER}}{\text{HYDRO}} \alpha \frac{43}{21} \sim 2$*
SEA	0.7078	0.0043	
HYDRO	0.7035		

* NO CHANGE BETWEEN THEN AND NOW

been a decrease in the efficiency of poleward heat transport (by air and sea). As the polar area is small compared to that of the tropics, such redistributions of heat would lead to larger changes in polar temperature. By contrast, the warming generated in atmospheric models when CO_2 is increased are not limited to high latitudes; it is global. However, whatever its origin, this cooling should according to BLAG have been accompanied by a decrease in chemical weathering rate.

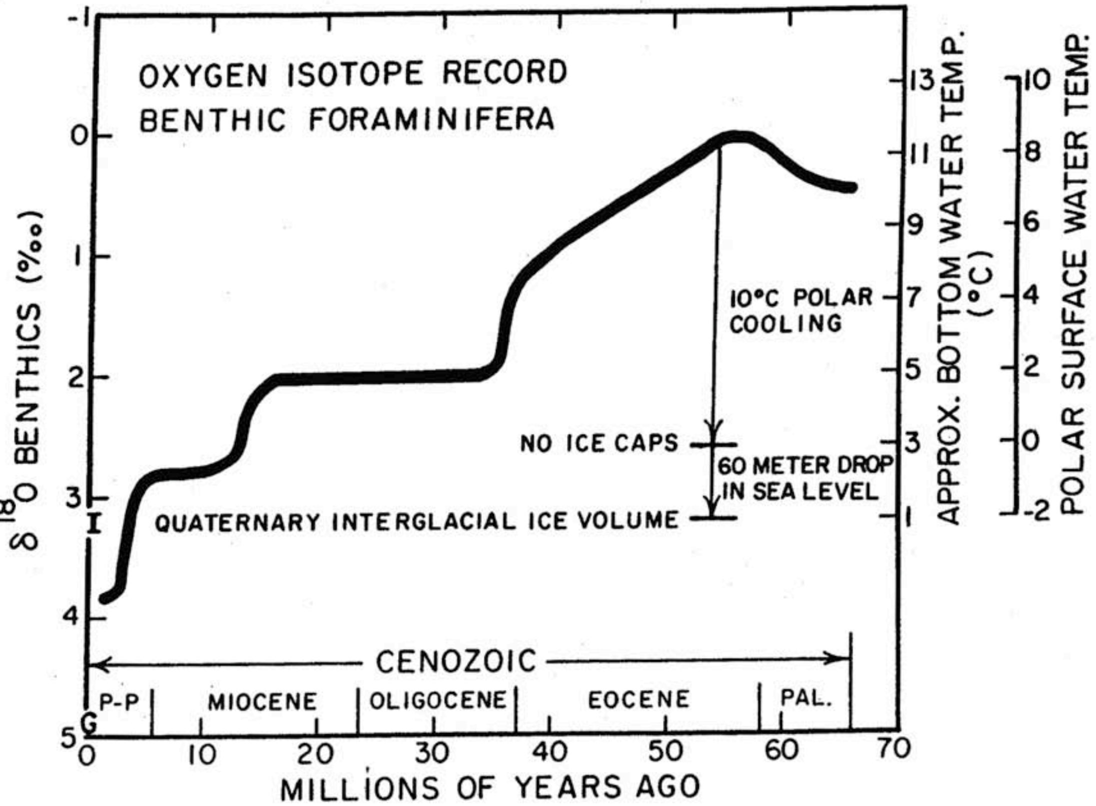
But the record of the strontium isotopic composition of sea water kept by the foraminifera preserved in deep sea sediments seems to be telling us that chemical weathering rates have been increasing over the last 40 million years. The logic is as follows. The strontium supplied to the sea through continental weathering is richer in radiogenic ^{87}Sr (derived from the decay of radioactive rubidium-87) than strontium supplied through the hydrothermal alteration of sea floor basalts. The $^{87}Sr/^{86}Sr$ of strontium dissolved in sea water lies between that for these two end members, giving the appearance that it is a mixture of about two parts strontium from rivers and one part strontium from ridge crest hydrothermal systems. As the average strontium atom resides in the sea for several million years before being removed to sediments, the strontium added to the sea from these two sources has become so well mixed that no measurable difference in isotopic composition exist from one place in the sea to another. Thus the strontium incorporated into the shells of foraminifera records the average isotopic composition of the strontium delivered to the sea over the previous several million years. Hundreds of Sr isotope analyses on foraminifera from many sea floor borings yield a detailed record of the evolution of the strontium isotopic composition of sea water over the last 100 million years. While nearly uniform during the first half of this time interval, the record reveals that an increase in the amount of radiogenic ^{87}Sr commenced 40 million years ago and has continued right up to the present. The most obvious explanation for this increase is that the supply of strontium derived from the chemical weathering of continental rocks has been on the increase. However, another explanation exists, namely, that the content of radiogenic strontium in continental-derived strontium has been increasing. Indeed, this alternative explanation has become the leading contender. The advocates of this view look to the collision with Asia of the northward-moving Indian subcontinent which took place just prior to 40 million years ago as the villian which initiated the ^{87}Sr increase. The thrusting of one continental block beneath another led to the creation of the Himalayan mountain belt and the Tibetan Plateau. Contained in this collision zone are igneous bodies, referred to by petrologists as leucogranites, whose feldspars contain strontium particularly rich in ^{87}Sr. So radiogenic is the strontium in the rivers draining the Himalayas that it alone could be responsible for the observed change in the oceanic strontium isotope ratio.

Were the BLAG reconstruction correct, then one might have expected the opposite trend in the isotopic composition of oceanic strontium. As soils cooled, the supply to the sea of continental weathering products would have decreased causing the ocean's strontium to become less radiogenic. But this need not have been the case for the rate of hydrothermal activity responsible for the release of strontium from ridge crest basalts would also have dropped in proportion to the rate of sea floor spreading. These two changes might well have compensated for one another and there would be no tendency for the isotopic composition of strontium in sea water to change. Less strontium would reach the sea but its isotopic composition would remain unchanged. Thus BLAG supporters would have to maintain that the observed increase is primarily the result of the input of highly radiogenic strontium from rivers draining the Himalayas. Viewed from this perspective, one would have to conclude that the strontium isotope record in sea water, while not lending support to BLAG, cannot be taken as evidence that the BLAG concept is incorrect.

The Influence of Mechanical Breakup on Chemical Weathering Rates

Now as already mentioned, the defenders of BLAG point to the observation that the Earth has cooled and therefore postulate that chemical weathering rates should have

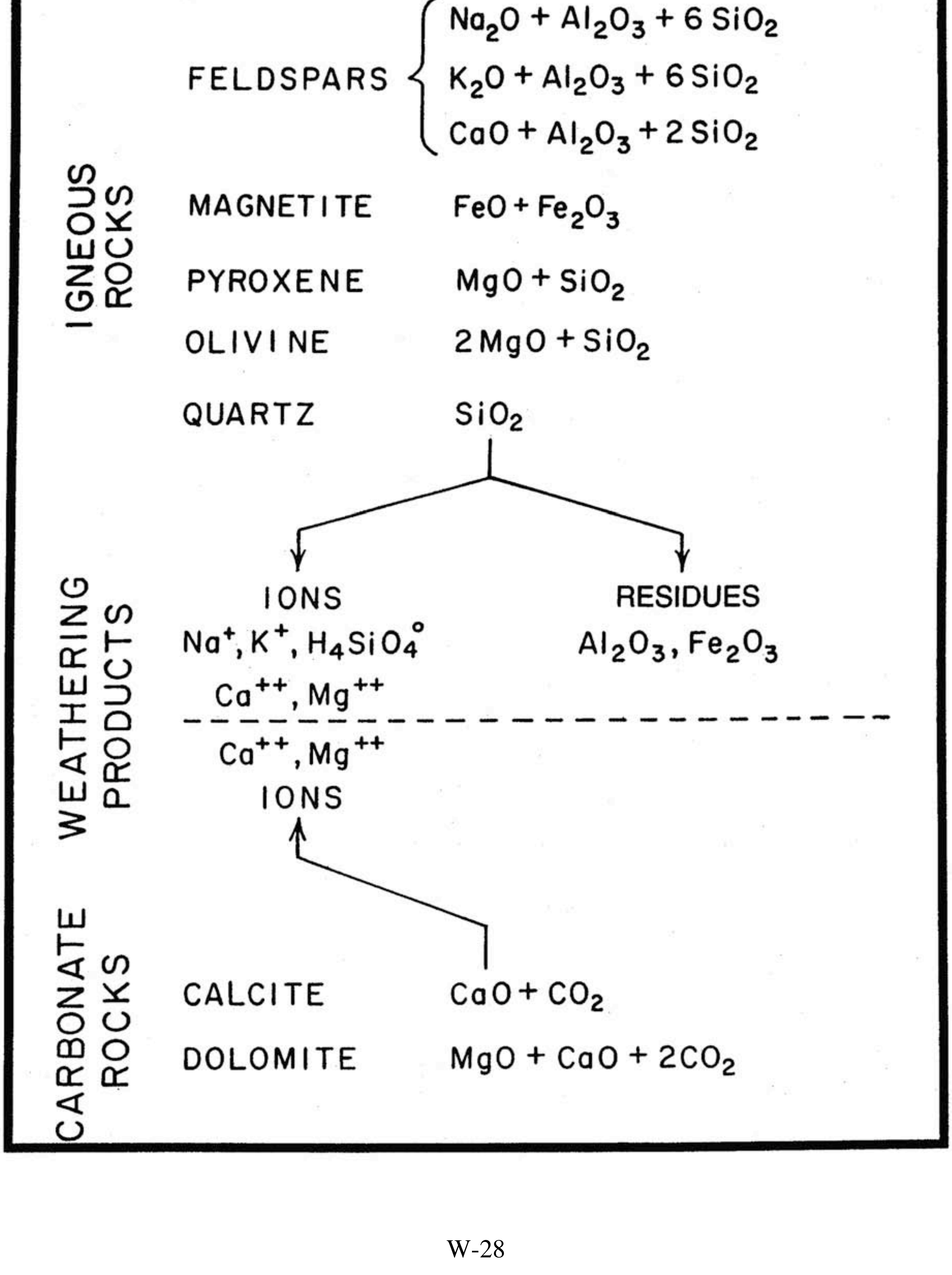
POLAR OCEAN TEMPERATURE RECORD



decreased. Cooler temperatures mean slower chemical reaction rates in soils and less precipitation to carry away dissolution products. But this way of looking at things is built on the assumption that the rate-limiting step for silicate dissolution is chemical. As pointed out by MIT's John Edmond, this need not be the case; the rate limiting step could equally well be mechanical. Chemically reactive surfaces are created when rocks are broken. Freeze-thaw cycles are powerful agents of mechanical breakup. Were the rate-limiting step mechanical rather than chemical, the dependence on climate might be the reverse. The progressive cooling during the last 60 million years has surely led to an increase in the continental area experiencing freeze-thaw cycles. Perhaps the increased rate of production of grist for the chemical mill has more than compensated for the drop in soil temperature. As a consequence, the cooling may have speeded the rate of chemical weathering! Indeed, Edmond has shown that Siberian rivers draining silicate terrain carry to the sea as much calcium (per acre draine) as does the Amazon River. In the Amazon, a thick mantle of cation-depleted material presently shields the underlying fresh rock from chemical attack. No such mantle is present in Siberia. Not only do freeze-thaw cycles break up the rock but the runoff during fierce spring melts allows the chemically weathered material to be sluiced away.

As might be expected, Edmond's suggestion that the rate of chemical weathering may decrease rather than increase with rising Earth temperature has met with considerable resistance. Where are the Siberian clay minerals which must be a byproduct of the weathering of primary igneous minerals? Instead, could the calcium in Siberian rivers be derived from limestone units as yet undiscovered in this poorly mapped terrain? These critics also point out that while the Amazon, because of its immensity, dominates today's tropical weathering, this low-lying and very flat region cannot typify the tropics of the distant past. Because of the drift of continents and the uplift of mountain ranges, the tropics of earlier time very likely had higher relief and hence a less complete mantle of chemically-depleted debris than does today's Amazon jungle.

THE PRODUCTS OF CHEMICAL WEATHERING



IGNEOUS ROCKS

FELDSPARS	$Na_2O + Al_2O_3 + 6\,SiO_2$ $K_2O + Al_2O_3 + 6\,SiO_2$ $CaO + Al_2O_3 + 2\,SiO_2$
MAGNETITE	$FeO + Fe_2O_3$
PYROXENE	$MgO + SiO_2$
OLIVINE	$2MgO + SiO_2$
QUARTZ	SiO_2

WEATHERING PRODUCTS

IONS	RESIDUES
$Na^+, K^+, H_4SiO_4^\circ$ Ca^{++}, Mg^{++}	Al_2O_3, Fe_2O_3

Ca^{++}, Mg^{++}

IONS

CARBONATE ROCKS

CALCITE	$CaO + CO_2$
DOLOMITE	$MgO + CaO + 2CO_2$

Increased rock breakup as the result of freeze-thaw cycles is not the only mechanism by which mechanical weathering might be increased. The topographic relief generated by mountain uplift is also important. Steep slopes accelerate mechanical erosion and also allow chemically spent material to be sluiced away exposing the fresh underlying material. Just as the rate of CO_2 emission from the Earth's interior is expected to decrease with the rate of sea floor spreading, so also is the rate of mountain building. So one might ask, wouldn't the Earth have been even more mountainous 100 million years ago if, at that time, the plates were moving faster? Perhaps, but in the case of mountain building, an important stochastic element exists; rare headon collisions between major continental blocks can lead to exceptional high and extensive mountain belts.

About forty million years ago such an event took place. India collided with Asia creating the Himalayan mountain chain. Pelted by monsoonal rains, this small highland region is currently responsible for about 16% of the world's chemical weathering. MIT's Maureen Raymo contends that increased chemical weathering from the Himalayas negates the BLAG hypothesis. True, at a time when CO_2 outgassing was apparently decreasing, one would expect global weathering rates to have been on the decrease. Raymo's argument rests on an interpretation of the strontium isotope record for the last 40 million years which calls on increasing continental weathering rates. But as we have seen, it is not necessarily the case. The rise in ^{87}Sr content of marine strontium may be due entirely to the more radiogenic character of the strontium derived from the Himalayas. Defenders of BLAG would claim instead that the increase in calcium supply related to the Asian uplift was compensated by a small decrease in chemical weathering rate in the rest of the world (brought about by an additional atmospheric CO_2 drop and the consequent cooling). Looked at this way, the rise in the Himalayas would according to BLAG cool the planet!

Possible Proxies for Atmospheric CO_2 Contents of the Distant Past

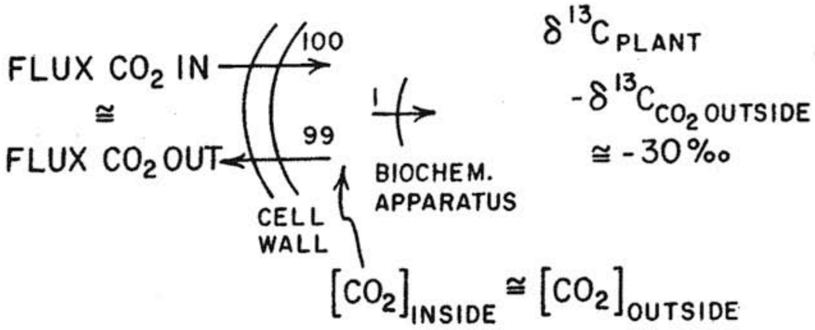
We have yet to mention the most obvious means by which BLAG might be verified. It predicts that 100 million years ago the CO_2 content of the atmosphere was substantially higher than today's. Is there a way by which we might reconstruct the CO_2 content of the atmosphere far, far beyond the record kept in ice cores? Two approaches are currently being explored. Both are based on carbon isotope measurements. In one case these measurements are made on organic residues from marine sediments and in the other on caliche from paleosoils.

Carbon isotope ratios in marine organic matter

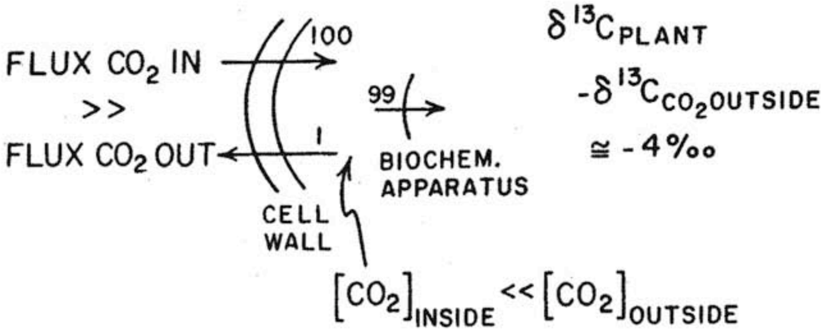
The marine organic approach is based on the observation that the magnitude of carbon isotope separation during photosynthesis in marine plants depends on the CO_2 concentration in sea water; the higher the concentration, the larger the separation. The physics behind this dependence is understood. It has to do with the fact that CO_2 molecules destined for photosynthesis have to pass two barriers. The first involves the transport of CO_2 across the membrane which separates the cell's interior (where the biochemical apparatus is located) from the surrounding water and the second involves the hook-up of CO_2 molecules to the enzyme (rubisco) where the actual chemical conversion to sugar takes place. In both steps $^{12}CO_2$ molecules outstrip their heavier $^{13}CO_2$ brothers. But the lighter isotope's advantage is ten times larger in the case of the biochemical conversion than in the case of the membrane transit. Were the membrane transit the sole resistance (i.e., if all the CO_2 molecules passing into the cell were converted to organic matter) then the $^{13}C/^{12}C$ ratio in the organic matter would turn out to be about 4‰ lower than that in the dissolved CO_2 outside the plant. On the other hand, if the biochemical conversion step constituted the sole resistance (i.e., if only a small fraction of the CO_2 entering the cell were utilized) then the $^{13}C/^{12}C$ ratio in the organic material would be about 30‰ lower than that in the CO_2. The idea is that, other things being equal, the higher the CO_2 concentration outside the cell the less important

BASIS FOR CARBON ISOTOPE BASED PALEO CO_2 PROXY

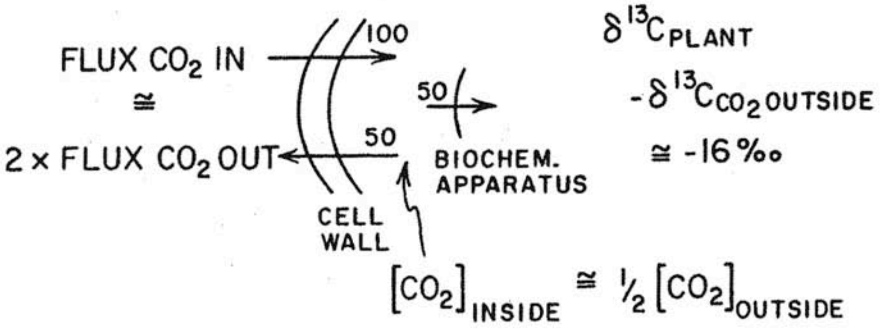
CASE #1 RESISTANCE POSED BY BIOCHEMICAL APPARATUS DOMINATES



CASE #2 RESISTANCE POSED BY CELL WALL DOMINATES



CASE #3 RESISTANCES COMPARABLE

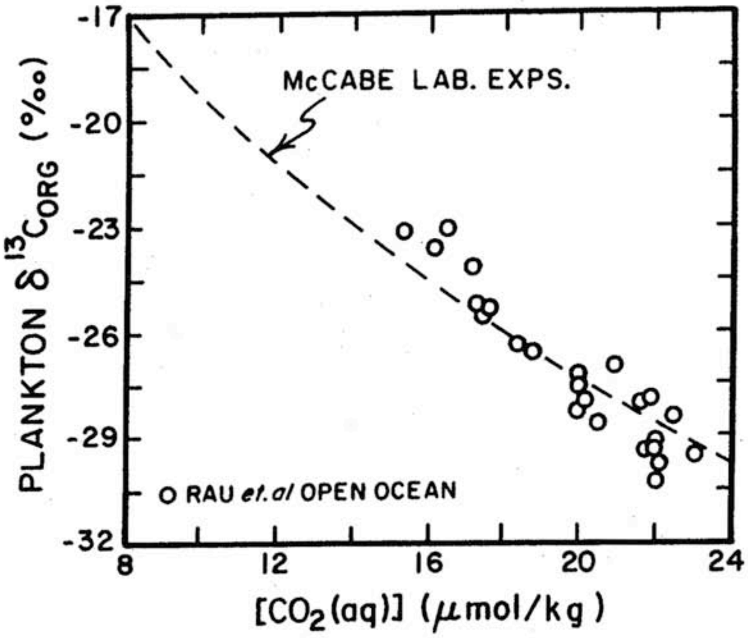


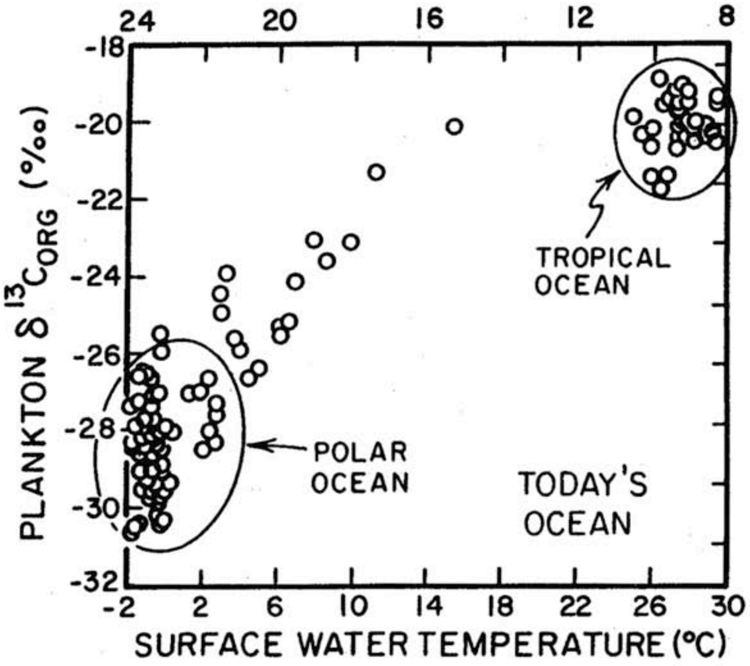
the resistance posed by the cell membrane and hence the greater the ^{13}C depletion in the plant matter. Indeed algae cultured in the laboratory over a range of CO_2 concentrations show this trend. This proves to be the case for the ocean as well. Organic matter formed in the cold and hence higher CO_2 concentration waters found in the Southern Ocean are more depleted in ^{13}C than organic matter grown in the lower CO_2 concentrations of tropical surface waters. Thus both in the lab and in the sea, at low CO_2 gas concentrations, the extent of isotope separation is shifted toward the smaller value associated with diffusion through the cell membrane.

Attempts to apply this method must take into account that the relationship between the CO_2 concentration in surface water and the CO_2 partial pressure in the atmosphere overlying the sea water is strongly dependent on temperature. At the same partial pressure, the coldest polar waters contain about three times more CO_2 than warmest tropical waters. Thus even if the ^{13}C to ^{12}C ratio in organic residues were to yield reliable paleo CO_2 concentrations for the ocean water in which they grew, the conversion to an atmospheric CO_2 pressure would require that the temperature of the water in which the plant grew be known.

The idea behind the paleo CO_2 indicator is that a universally applicable tie exists between CO_2 content of sea water and the isotope separation between the dissolved inorganic carbon content of sea water and that in the organic matter formed by marine organisms. In other words, given the CO_2 concentration in the water, the magnitude of isotope separation is uniquely determined. But this is a bit much to hope for. While the expected trend in isotope separation with CO_2 content will always exist, the position between the two limiting situations will almost certainly depend on factors other than just the CO_2 concentration. The reason is that the degree of isotope separation is controlled by the competition between two opposing forces. Diffusion across the cell wall tends to keep the CO_2 concentration in the cell fluid equal to that in the surrounding water. Photosynthesis tends to draw down the CO_2 content of the cell fluid well below

^{13}C IN MARINE ORGANICS
A PALEO CO_2 PROXY?



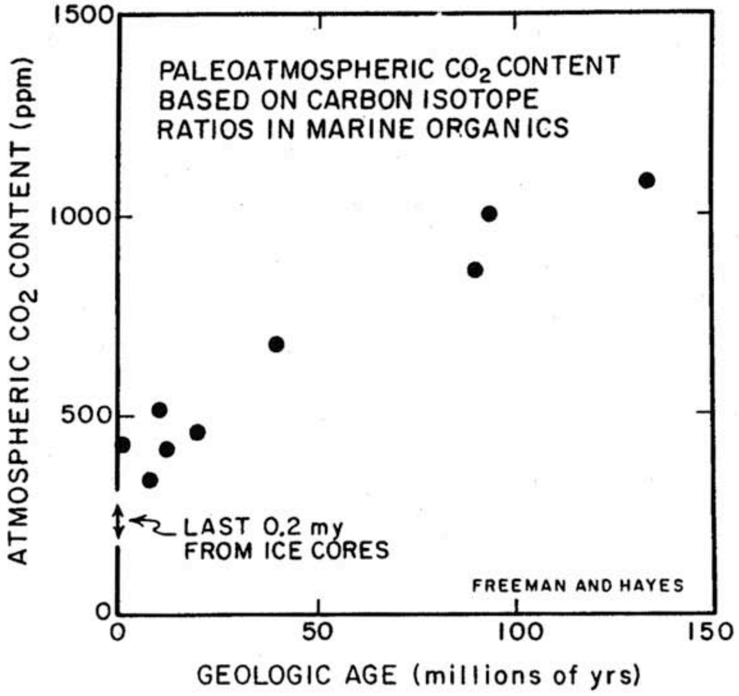


that in the surrounding sea water. The isotope separation reflects the balance between these two opposing tendencies. If, for example, the CO_2 content of the cell fluid were to be drawn down to half the value characterizing the surrounding sea water, then the isotope separation would lie half way between the limiting values. The point is that the balance between these opposing forces must be influenced by factors other than the CO_2 concentration. For example, it has been shown that the magnitude of the isotope separation is also dependent on growth rate (as measured by the frequency of cell division). The faster the growth the more important the resistance posed by the cell wall and hence the smaller the isotope separation. This being the case, the magnitude of the fractionation will depend on the availability of nutrients and of light. Finally, other factors being equal (CO_2, nutrients, light...), each species of plant has its own cell structure and photosynthetic capability.

Indiana University's John Hays, who with his students and post docs has pioneered this field, has come up with an innovative means of coping with two of these potential problems. First, instead of analyzing bulk organic material, he separates out specific compounds formed by only select groups of marine plants. Early work was done with porphyrins because they are derivatives of chlorophyll and hence represent the primary plant material. More recent efforts have concentrated on alkenones which are produced by a specific plant group. This latter approach has enormous potential for not only does it ease complications associated with the inclusion of carbon from the animals and bacteria which feed on the primary plant matter, but also complications associated with differences in physiology among plant groups. Second, it has been shown that the ratio of alkenones of different carbon number produced by certain marine plant types depends on growth temperature. If this proves to be a reliable paleotemperature method, then the combination of the chemical ratio and carbon isotope ratio measured on the same sample will give the partial pressure of CO_2 in the water in which the plant grew!

PALEO CO_2 ESTIMATES BASED ON ^{13}C / ^{12}C IN MARINE ORGANICS

Age 10^6 years	Paleo latitude	SST °C	$\delta^{13}C$ ‰		CO_2 µmol/kg	pCO_2 µatm
			Porphyrin	CO_2		
1	28°N	20.3	-22.0	-7.8	13.7	430
8	33°N	20.1	-20.1	-7.5	10.9	340
11	21°N	23.9	-21.8	-7.0	14.8	510
13	32°N	21.9	-20.9	-7.0	13.0	420
20	22°N	20.0	-20.0	-7.0	15.0	460
40	62°N	12.3	-27.0	-7.6	27.2	670
91	40°N	25.0	-27.3	-8.0	25.2	890
91	40°N	25.0	-26.5	-7.7	23.7	830
94	31°S	27.5	-25.8	-5.8	29.4	1100
94	31°S	27.5	-24.4	-5.8	24.3	910
134	38°N	26.8	-27.0	-7.3	28.3	1040
134	38°N	26.8	-27.6	-7.3	30.9	1130
154	53°S	18.9	-25.2	-6.6	24.6	730
154	53°S	18.9	-29.1	-6.6	40.8	1220



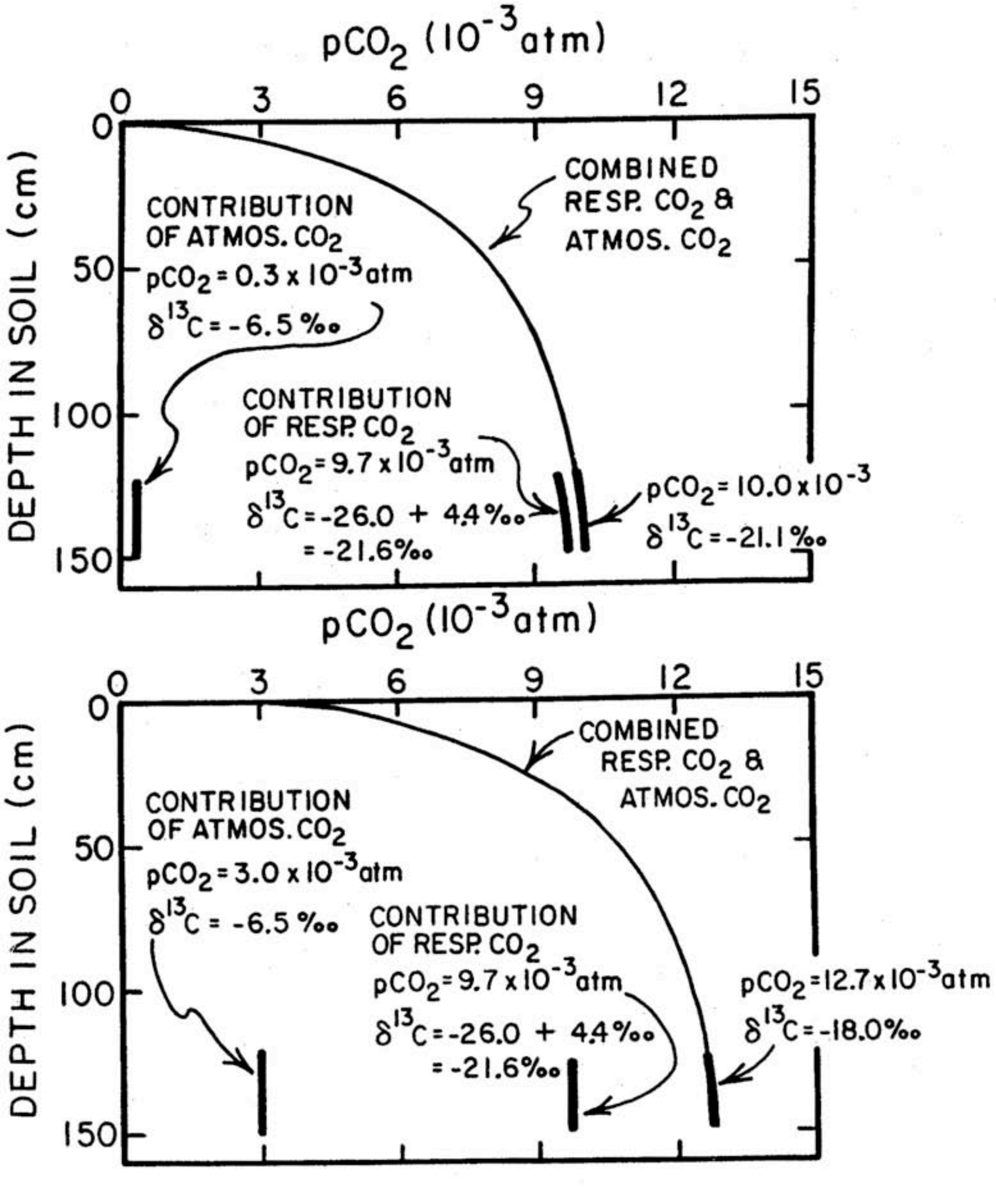
FREEMAN AND HAYES

A first try at applying this method to organic material from sediments covering the last 150 million years, does suggest that in accord with BLAG the CO_2 content of the atmosphere has been steadily decreasing. Measurements on porphyrins made in John Hays' lab suggested that the atmospheric CO_2 partial pressure 100 million years ago was about 1000 μatm. However, until hundreds of such samples have been run it will not be clear whether this trend is real or whether it reflects differences in growth conditions. A convincing case will require the analysis of samples covering a wide geographical area from a series of time slices. Only if for each time slice do these results point to similar atmospheric CO_2 values will the paleoclimate community take them seriously.

Carbon isotope ratios in soil caliche

The second carbon isotope-based paleo-CO_2 method involves measurements of the difference between the carbon isotope composition of coexisting $CaCO_3$ and organic matter in paleosoils. Cerling, its originator, has demonstrated that in today's soils the isotopic composition of the CO_2 is, as would be expected, closely related to that of organic matter growing in the soil. But, as $^{12}CO_2$ diffuses a bit faster than $^{13}CO_2$, it escapes more quickly from the soil. Hence, at steady state, soil CO_2 is enriched in ^{13}C by 4.4‰ with respect to respiration CO_2. The $CaCO_3$ found in soils consists of CaO leached from soil minerals and CO_2 from soil gas. Because of the fractionation between air phase CO_2 and $CaCO_3$ precipitated from soil waters, the isotopic composition of the caliche is about 10‰ heavier than that in soil CO_2. The important point is that in today's situation, the contribution of atmospheric CO_2 is too small to significantly influence the isotopic composition of soil gas CO_2. For example, were the excess CO_2 pressure in the soil 9700 μatm, the overlying air (with its CO_2 pressure of only 300 μatm) would make up only 3 percent of the soil's CO_2. As atmospheric CO_2 and respiration CO_2 differ in isotopic composition by about 15‰, the isotopic shift created by the presence of this small amount of air CO_2 would be only about 0.5‰. By contrast, if at some time in the past, the CO_2 content of the atmosphere were ten times higher than today's (i.e., 3000

CERLING'S CALICHE METHOD: PALEO CO2 FROM CARBON ISOTOPE RATIOS IN SOILS CALICHE



μatm) and if the soil to atmosphere difference in CO_2 partial pressure were the same as today's (i.e., in our example ~9700 μatm) then the atmosphere-induced isotope shift would be 15 x 3000/(3000 + 9700) or 3.5‰. Cerling hopes to use the magnitude of this atmospheric CO_2-induced shift in isotope composition of $CaCO_3$ in paleosoils to determine whether or not CO_2 pressures were significantly higher in the past.

An ingenious method, but will it work? The shift upon which Cerling's method is based is quite small (a few ‰); therefore, close attention must be given factors which might bias the isotopic composition of soil $CaCO_3$. Cerling points out several.

1. As the magnitude of the fractionation between soil CO_2 and soil $CaCO_3$ changes by 1‰ per 10°C, a temperature correction must be made.

2. The ^{13}C to ^{12}C ratio in atmospheric CO_2 depends on both the temperature and the ^{13}C to ^{12}C ratio for surface ocean water. Measurements by Shackleton on marine $CaCO_3$ suggest that the ^{13}C to ^{12}C ratio in surface ocean ΣCO_2 was 1 to 2‰ higher 20 million years ago than today. Further, the warmer temperatures at that time would have reduced the air-sea carbon isotope difference and thereby raised the atmosphere's $^{13}C/^{12}C$ ratio by a bit more. It must be kept in mind, however, that the influence of the atmosphere's isotope composition shift is diminished by the ratio $p_{CO_2}^{air}/p_{CO_2}^{respiration\ excess}$. So even if, as in the above example, the $p_{CO_2}^{atm}$ were ten times higher, a 2‰ difference in the isotopic composition of atmospheric CO_2 would cause only a 0.7‰ shift in the soil $CaCO_3$ isotope composition.

3. It must be demonstrated that the original ^{13}C to ^{12}C ratio in paleosoil $CaCO_3$ has not been altered by subsequent diagenesis.

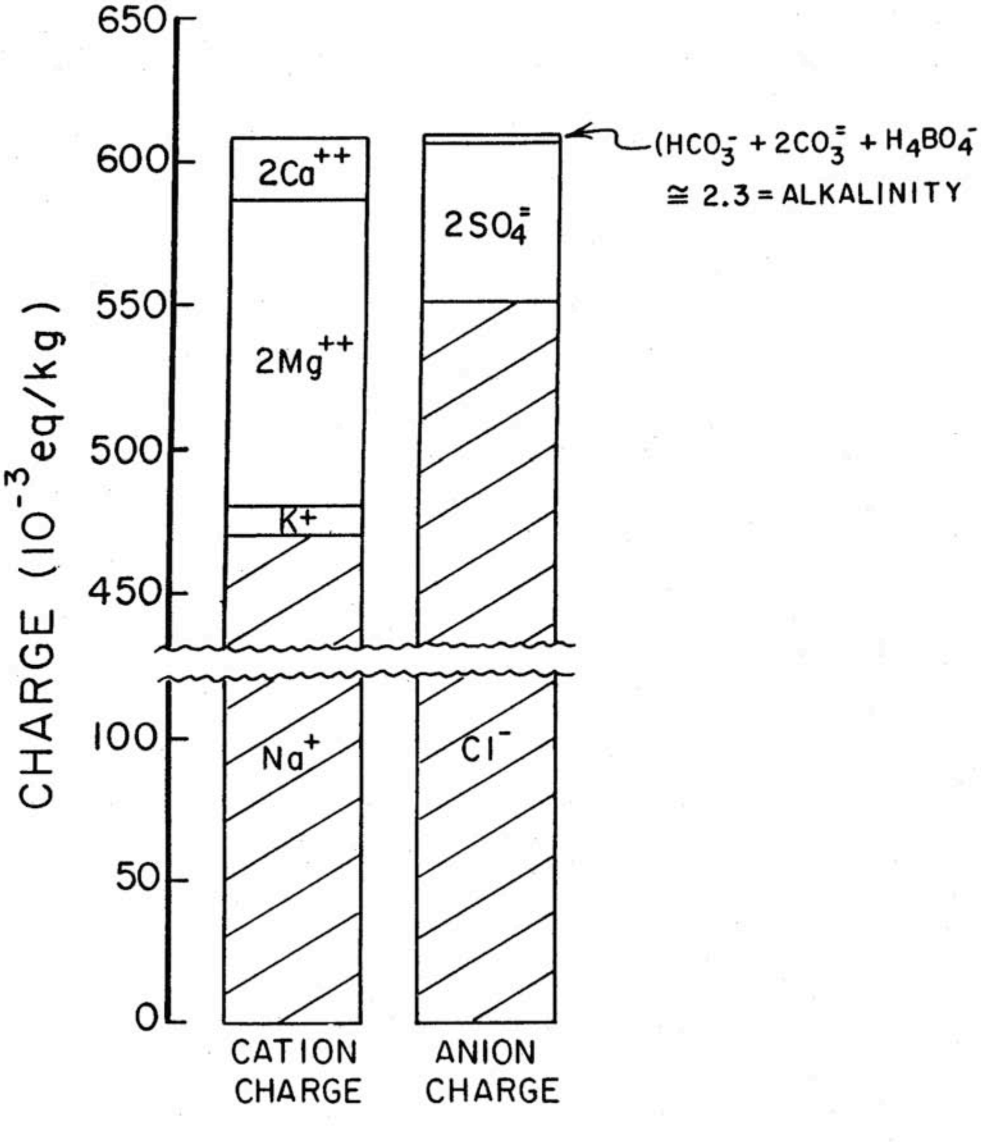
Another problem faced by Cerling is that his method is not a direct index of atmospheric CO_2 pressure. Rather, it is a measure of the ratio of atmospheric CO_2 pressure to soil CO_2 pressure. Modern soils show a wide range of CO_2 pressures reflecting both differences in plant productivity (and hence the rate of production of CO_2 by respiration) and in porosity (and hence in residence time of CO_2 in the soil before escape to the overlying atmosphere). Cerling would like to believe that the range of respiration CO_2 contents of soils is relatively small and that its mean has not changed over time. The only way he has to assess whether this is the case is to run samples from many geographic localities for each time interval of interest. Cerling is currently seeking to carry out this test. At the time of this revision, he and a PhD student were writing up hundreds of such analysis.

Ocean Chemistry

For BLAG there is no need to define the mechanisms responsible for the control of the ocean's chemistry. One only has to assume that the CaO and CO_2 which arrive there are mated to form $CaCO_3$. We have already seen that in today's ocean this mating goes smoothly; marine organisms produce $CaCO_3$ several times faster than its ingredients are supplied to the sea. In order to compensate for this overproduction, the horizon separating supersaturated from undersaturated water rises and falls insuring that a balance between input of the ingredients is matched by the accumulation of $CaCO_3$ in the sediment. As we shall see, paleolysocline reconstructions tell us that overproduction of calcite by organisms has been the rule throughout the last 100 million years. Nevertheless, it is of interest to consider how the chemistry of the ocean might have evolved over this period.

One might ask whether we can restrict our inquiry to species directly involved in the cycles of carbon and calcium, or must we deal with the salt matrix with which these species interact. Four ions, Na^{+}, Cl^{-}, Mg^{++} and $SO_4^{=}$, dominate the seas' salt. Only the first two of these have such long replacement times that they can be viewed as unchangeable on a 100 million year time scale. The other two, Mg^{++} and $SO_4^{=}$, turn over on the time scale of 10 to 15 million years. Hence their concentrations are subject to change on the time scale of interest here. But as these changes are of only secondary importance to the cycles of carbon and calcium of interest to us, we shall not ponder what they might have been.

MAJOR PLAYERS IN THE IONIC MAKEUP OF SEAWATER



For our purposes, the concentrations of five ions must be fixed: H^+, Ca^{++}, CO_2, HCO_3^- and $CO_3^=$. Three chemical equilibria relate the concentrations of these species:

1) $CO_2 + H_2O \Leftrightarrow H^+ + HCO_3^-$

$$K = \frac{[H^+]\,[HCO_3^-]}{[CO_2]}$$

2) $CO_2 + CO_3^= + H_2O \Rightarrow 2HCO_3^-$

$$K = \frac{[HCO_3^-]^2}{[CO_2]\,[CO_3^=]}$$

3) $Ca^{++} + CO_3^= \Leftrightarrow CaCO_{3\ solid}$ (at depth of lysocline)

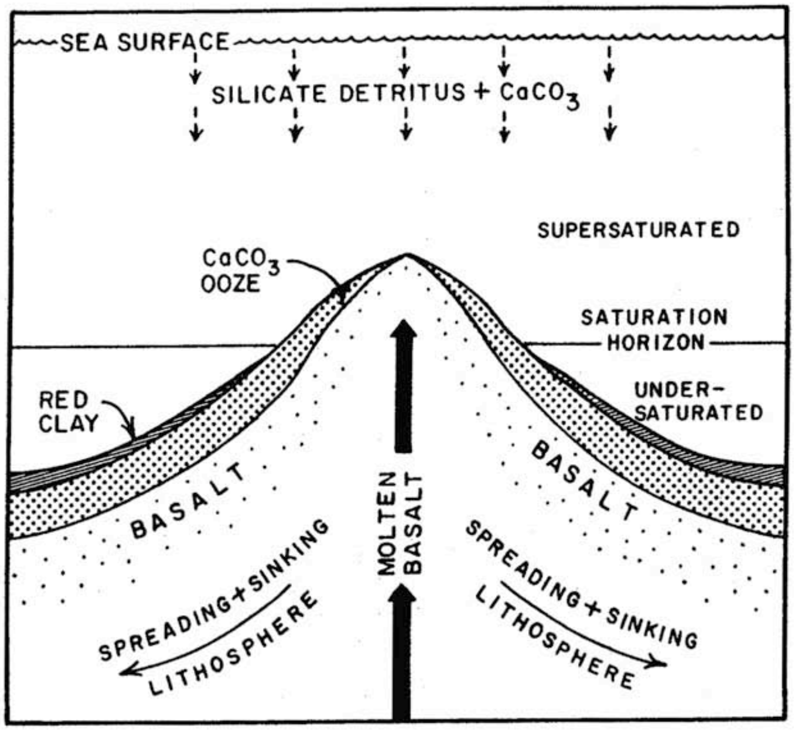
$$K = [Ca^{++}]\,[CO_3^=]$$

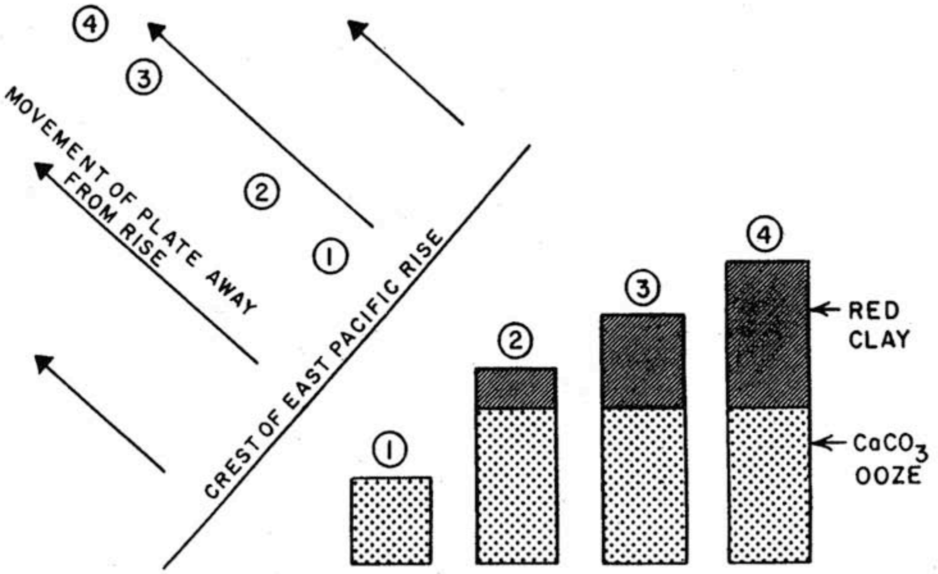
Hence if the concentrations of two of these five species are fixed, those of the other three are uniquely determined. Once the concentrations of the five ions are set, so also are both the ΣCO_2 content and alkalinity (assuming the concentration of borate has remained unchanged). For BLAG, the atmosphere's CO_2 pressure is set to yield the proper flow of CaO to the sea. Hence the CO_2 content of sea water is also fixed, leaving only one other concentration to be set. This remaining constraint could be set by an exchange reaction between Ca^{++} and Mg^{++} or between H^+ and Na^+. One complication remains, i.e., establishing the difference between the compositions of surface waters and deep waters. As we have seen, the ocean cannot be treated as a single well-mixed reservoir.

Paleolysocline Depth

As we saw in "Martin's World", the depth of the transition zone separating sediments rich in calcite from those devoid of calcite potentially carries information regarding the deep sea's carbonate ion concentration. Ideally, the top of this zone (referred to by marine geologists as the lysocline) should correspond roughly to the depth

THE SEDIMENTARY RECORD OF LYSOCLINE DEPTH



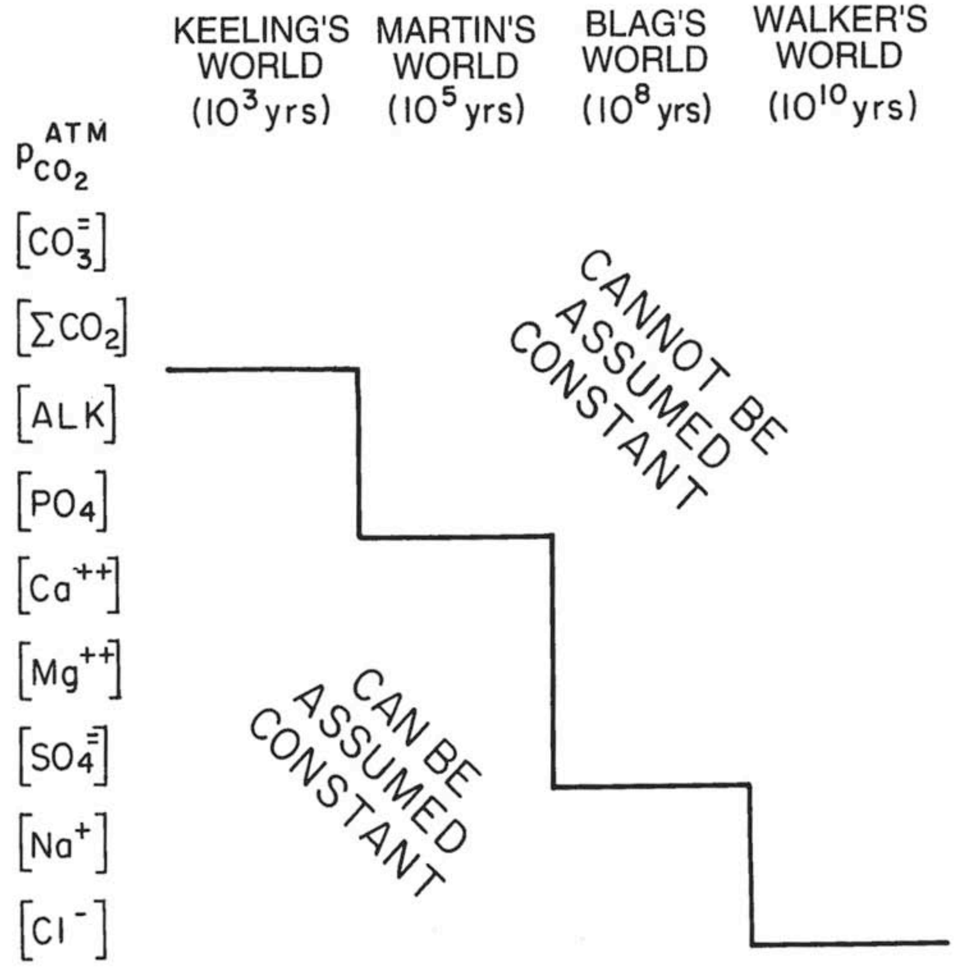


where sea water is just saturated with respect to the mineral calcite. The greater the depth below the saturation horizon, the stronger the undersaturation and hence the stronger the tendency for calcite to dissolve. The base of the transition from calcite-rich to calcite-poor sediment lies at that depth where calcite dissolves just as fast as it rains to the sea floor, leaving none to accumulate in the sediment. As the solubility of calcite increases about twenty percent per kilometer, the depth of this transition zone is a very sensitive indicator of the product of the Ca^{++} and $CO_3^{=}$ concentrations in the deep sea.

It turns out that a means exists to reconstruct the depth of the lysocline at times in the past. This is done by studying the sediment from holes drilled through the sea floor sediment column at water depths beneath the present-day calcite transition zone. Although the material in the upper portion of these sediment columns contains no $CaCO_3$, at some depth in the hole, sediments rich in $CaCO_3$ appear. This sedimentary horizon marks that point in the history of the sinking sea floor when it dropped far enough beneath the saturation horizon that the raining calcite completely dissolved. The age of this event is recorded by the fossils contained in the uppermost calcite-bearing sediment. Because the subsidence of the sea floor is ongoing, the depth below sea surface at which this transition is found does not correspond to that of the paleolysocline. But as the rules regarding the rates of subsidence have been firmly established (it is driven by cooling of the lithosphere), a correction can be made allowing the water depth at the time of deposition to be established.

By drilling many, many such holes, it has been possible to reconstruct how the depth of the transition zone has varied over the last 100 million years. This record tells us that the transition depth has not changed by very much. It has remained in the range 4000 ± 800 meters. As the solubility of calcite increases by only about 20 percent per kilometer, this suggests that the product of $Ca^{++} \times CO_3^{=}$ in the deep sea has not changed very much during this time period. If this result could be interpreted as indicating a constancy in carbonate ion concentration it would prove to be an extremely valuable

THE GROWING LIST OF POTENTIALLY CHANGING PROPERTIES



piece of information. But a problem exists. This conclusion requires that Ca^{++} concentration in the ocean has remained constant. As Ca^{++} has a residence time in the sea of about one million years, on the time scale of glacial to interglacial changes it is safe to assume that its concentration remained unchanged. However, as in this chapter we are dealing with a time interval of 10^8 rather than 10^5 years, there is no guarantee that the Ca^{++} content of sea water has remained unchanged. So the constancy of the transition zone depth really tells us only that any changes in Ca^{++} concentration were accompanied by reciprocal changes in $CO_3^=$ concentration. The reason for the near constancy of the lysocline depth has to do with the fact that the overproduction of calcite by marine organisms must be compensated by dissolution. The steeply inclined margins of the sea floor dictate that the boundary between $CaCO_3$ rich and poor sediments lie in the depth range bounded by the ridge crests (~2.5 km depth) and the abyssal planes (~5.0 km depth). Therefore, as long as calcite production by marine organisms exceeds the supply of calcite's ingredients, it is not surprising that the depth of calcite transition zone has remained in the range 2.5 to 5.0 km.

Surface Ocean to Deep Ocean Carbon Isotope Difference

One other paleoclimate indicator holds promise in our attempt to reconstruct the difference in ΣCO_2 between surface and deep water. It is the difference between the $\delta^{13}C$ for nutrient depleted warm surface water and that for average deep water. This difference depends on the carbon to phosphorus ratio in the organic matter falling from the sea surface (i.e., $C/P)_{org}$), the ratio of the PO_4 to ΣCO_2 in the ocean as a whole and magnitude of the photosynthetic fractionation of carbon isotopes between surface ocean ΣCO_2 and the organic matter produced by marine organisms (i.e., Δ^{photo}). The relationship is as follows:

$$\Delta\delta^{13}C_{s\text{-}d} = \Delta^{photo} \,.\, C/P)_{org} \,.\, [PO_4]/[\Sigma CO_2]$$

By reconstructing $\delta^{13}C$ difference between foraminifera formed in surface and those formed in deep water at times in the past, it should be possible to place limits on how the

PALEO ΣCO_2 INDICATOR

TODAY

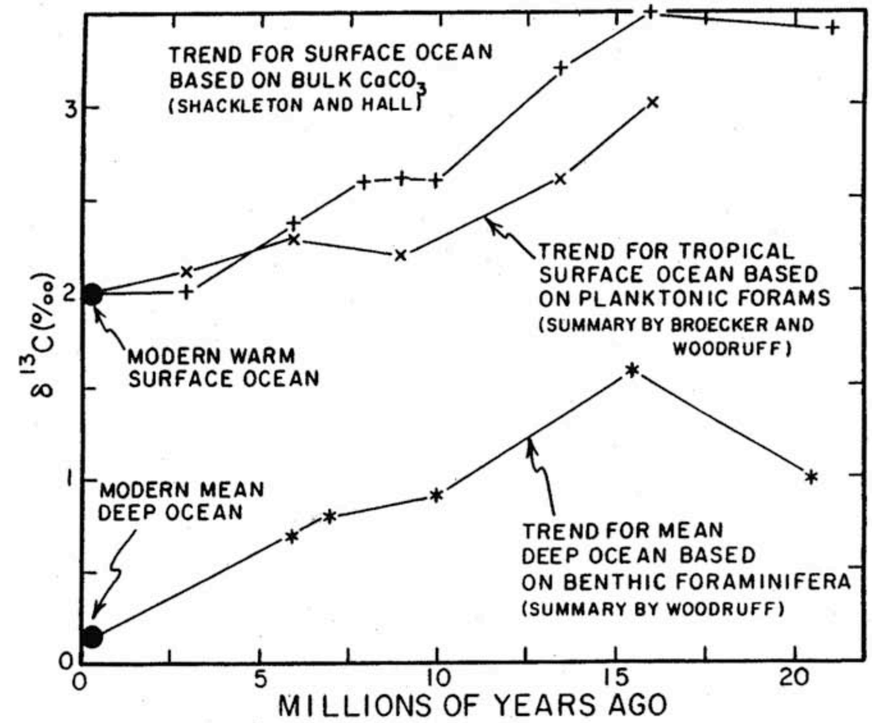
$$\Delta\ [PO_4] = 1.8\,\mu mol/kg \begin{cases} [PO_4]_{WARM\ SURFACE} = 0.2\,\mu mol/kg \\ [PO_4]_{MEAN\ DEEP} = 2.0\,\mu mol/kg \end{cases}$$

$$\Delta\,\delta^{13}C = 1.8\,‰ \begin{cases} \delta^{13}C_{WARM\ SURFACE} = 2.0\,‰ \\ \delta^{13}C_{MEAN\ DEEP} = 0.2\,‰ \end{cases}$$

$$\Delta\,\delta^{13}C = \Delta\,\delta^{13}C_{PHOTOSYN.} \times \left.\frac{C}{P}\right)_{ORG.} \times \frac{\Delta[PO_4]}{[\Sigma CO_2]_{MEAN\ OCEAN}}$$

$$= 18 \times 125 \times \frac{1.8}{2250}$$

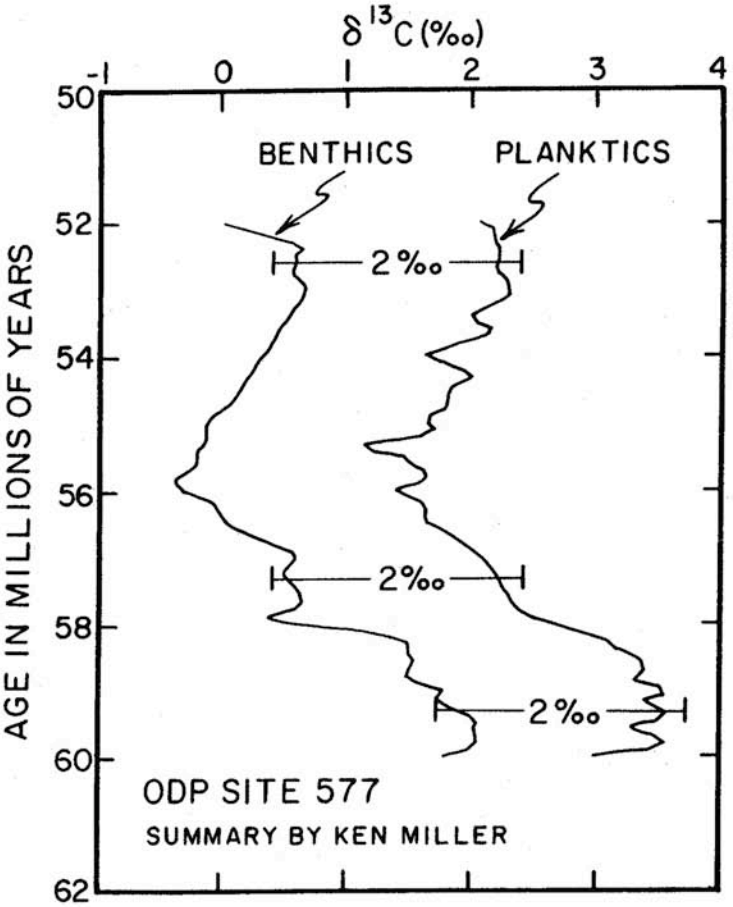
$$= 1.8\,‰$$



ΣCO_2 content of sea water has changed with time. However, to do this it is necessary to get some handle on how the other three factors (i.e., Δ^{photo}, $C/P)_{org}$, $[PO_4]$) may have changed.

But first let us examine the reconstructions of the surface to deep $\delta^{13}C$ difference. Measurements covering the last 20 million years suggest that this difference has remained more or less constant. A less complete record obtained for the Pacific Ocean extending from 50 to 62 million years suggest that the difference was similar at that time as well. Keeping in mind that were the atmospheric CO_2 content higher, the photosynthetic isotope fractionation factor must have been larger; this suggests that either the ocean's ΣCO_2 content was somewhat higher or its nutrient content somewhat lower during the early Cenozoic. If we could come up with an independent means of estimating how the nutrient content of the ocean changed with time, then we would get a handle on how the ΣCO_2 content has changed. Even a "fluffy" constraint on this quantity would be of great help in our quest to understand the chemical history of the ocean. To see why this is the case consider the following scenario. First, we will accept the Freeman and Hayes estimate that the CO_2 content of the atmosphere was about three times higher than now 55 million years ago. Second, as the planktonic-benthic $\delta^{13}C$ results suggest, the PO_4 to ΣCO_2 ratio was about two thirds today's value. Are these two pieces of chemical information self consistent? The answer is yes. Were the atmosphere's CO_2 content three times higher than today's, then under almost any scenario, the ocean's ΣCO_2 would also have been higher. For example, were the Ca^{++} content to have been the same as today's, then the near constancy of the lysocline depth would require that the $CO_3^{=}$ ion content would also have been the same. Chemical equilibria among CO_2, $CO_3^{=}$, and HCO_3^- would require that the HCO_3^- content would have increased by the square root of the factor by which the CO_2 content increased. This would give a bicarbonate ion concentration of about $\sqrt{3}$ or 1.7 times today's. As HCO_3^- is the dominant species, the ΣCO_2 concentration would also have been about 1.7 times higher. Were PO_4 to have

$\Delta\delta^{13}$C RECORD



55 MILLION YEARS AGO

$p_{CO_2}^{ATMOS.} \cong 750\,\mu atm$

INCREASE DUE TO HIGHER ATMOSPHERE CO_2

$\Delta\delta^{13}C_{PHOTOSYN.} = 18 + 6 = 24$

$C/P)_{ORG.} = 125$ (*I.E.* SAME AS NOW)

$\Delta^{13}C_{PLANK.-BENTH.} \sim 1.6‰$

$$\frac{PO_4/\Sigma CO_2)_{THEN}}{PO_4/\Sigma CO_2)_{NOW}} \cong \frac{18}{24} \times \frac{1.6}{1.8} \cong 0.67$$

remained the same, then the 1.7 fold increase in $\sum CO_3$ would have dropped the $\Delta\delta^{13}C$ difference between planktonic and benthic foraminifera from its present day value of 1.8‰ to 1.1‰. However, the higher CO_2 content of the surface ocean would have increased the photosynthetic fractionation from 18 to 24‰ and hence the $\Delta\delta^{13}C$ from 1.1‰ to 1.4‰, a value consistent with Miller's measurements.

But what about the PO_4 content of sea water? Might it have changed? PO_4 is replaced on a 10^5-year time scale. Thus its ocean content must also be subject to some sort of feedback control. As outlined in the section which follows, the content of PO_4 in the sea is very likely tied to the amount of O_2 in the atmosphere.

Paleocean Oxygen Content

While we have no proxy for the amount of oxygen in the Earth's atmosphere, we do have a paleo indicator regarding the state of oxygenation of the deep sea. Benthic foraminifera can survive only in oxygenated waters. As the shells of these organisms are ubiquitous in the Cenozoic marine sediments, we can infer that the deep waters of the major ocean basins have remained oxygenated over the past 65 million years. In one sense, this is puzzling. Waters below 1500 meters in today's North Pacific have dangerously low O_2 contents (6-15% of the saturation value). Yet no where in the deep sea does O_2 disappear altogether. True, a few small anoxic pockets exist in the so called 'shadow zones' of the main thermocline. These zones which lie along the eastern oceanic margins are equatorward of the temperate gyres and poleward of the equatorial current systems. Therefore, they are ventilated only sluggishly putting their O_2 supply in danger of being depleted by the rain of organic debris. But these regions constitute only a very small fraction of the ocean's volume. But as a sizable fraction of the deep sea currently appears to be poised on the brink of anoxia, one might ask why there weren't periods in the past when it slipped over the edge into anoxia causing benthic foraminifera to be excluded from vast regions of the sea floor. But viewed through the glasses of geochemical theory, the continued existence of finite amounts of O_2 in deep sea water is not surprising. Just as some feedback loop must control the flow of carbon through the ocean-atmosphere reservoir, so also must there be one which controls the flow of electrons. The number of electrons leaving the ocean-atmosphere reservoir must match the number entering. Stated in chemical terminology, the aggregate oxidation state of the sea's outputs must match that of its inputs. If this match is not met, then the O_2 content of the atmosphere will take up the slack and in so doing generate a feedback loop that forces the flow of electrons back into balance.

An example will help to explain how this loop works. Consider a simplified planet on which the only substances of importance are calcite, organic matter, water, and oxygen gas (no outgassing of CO_2 occurs). These materials are recycled on the planet's surface. The inputs to this planet's ocean-atmosphere reservoir are CO_2 derived from the oxidation of previously buried organic matter and $CaCO_3$ generated by chemical weathering of the planet's continents. The output is plant residues and marine shells which accumulate in marine sediment. For the system's electron flow to be in balance, the amount of carbon leaving the system as new organic residues would just match the amount of carbon entering as the result of oxidation of old residues. In this situation, the amount of O_2 created as a byproduct of the production of new residues would just balance that consumed by the oxidation of old residues and the O_2 content of the planet's atmosphere would remain unchanged. However, if for some reason this balance were temporarily disrupted by an anoxic condition and more new residues were buried than old residues were being oxidized, then the planet's O_2 content would rise. As it rose, the planet's anoxic environments would gradually be reduced in size, thereby increasing the likelihood that a given organic residue would be 'eaten'. The rise would continue until the balance was restored.

In the real ocean, the element sulfur plays an important role. This element can exist in two oxidation states: +6 in sulfate and -2 in sulfide. Eight electrons must be traded if a sulfur atom is to go from one of these oxidation states to the other. Sulfide

OCEAN - ATMOSPHERE ELECTRON BALANCE

ELECTRONS IN MUST EQUAL ELECTRONS OUT

INPUTS		OUTPUTS
CARBON - BEARING SED MIN $CaCO_3, CaMg(CO_3)_2$	C^{+4}	CARBON - BEARING MIN $CaCO_3$ .....
ORGANIC RESIDUES KEROGEN, COAL	$C^{0\ TO\ -4}$	ORGANIC RESIDUES
IRON-BEARING SED MIN $Fe(OH)_3$	Fe^{+3}	IRON-BEARING SED MIN $Fe(OH)_3$ .....
IRON-BEARING IGN MIN Fe_2SiO_4	Fe^{+2}	
SULFUR-BEARING EVAP MIN $CaSO_4$	S^{+6}	SULFUR-BEARING EVAP MIN $CaSO_4$
SULFUR-BEARING ORE MIN FeS, ZnS, PbS	S^{-2}	
SULFUR-BEARING SED MIN FeS	S^{-2}	SULFUR-BEARING SED MIN FeS .....
OXIDES MgO, CaO, H_2O	O^{-2}	OXIDES MgO, CaO, H_2O .....
ATMOSPHERIC OXYGEN O_2	O^{0}	ATMOSPHERIC OXYGEN O_2

TAKES UP SLACK

O_2 PRODUCTION DONATES ELECTRONS

O_2 CONSUMPTION CONSUMES ELECTRONS

O_2 POLICES THE FLOW OF ELECTRONS !

OXIDATION - REDUCTION BALANCE IN THREE HYPOTHETICAL OCEANS

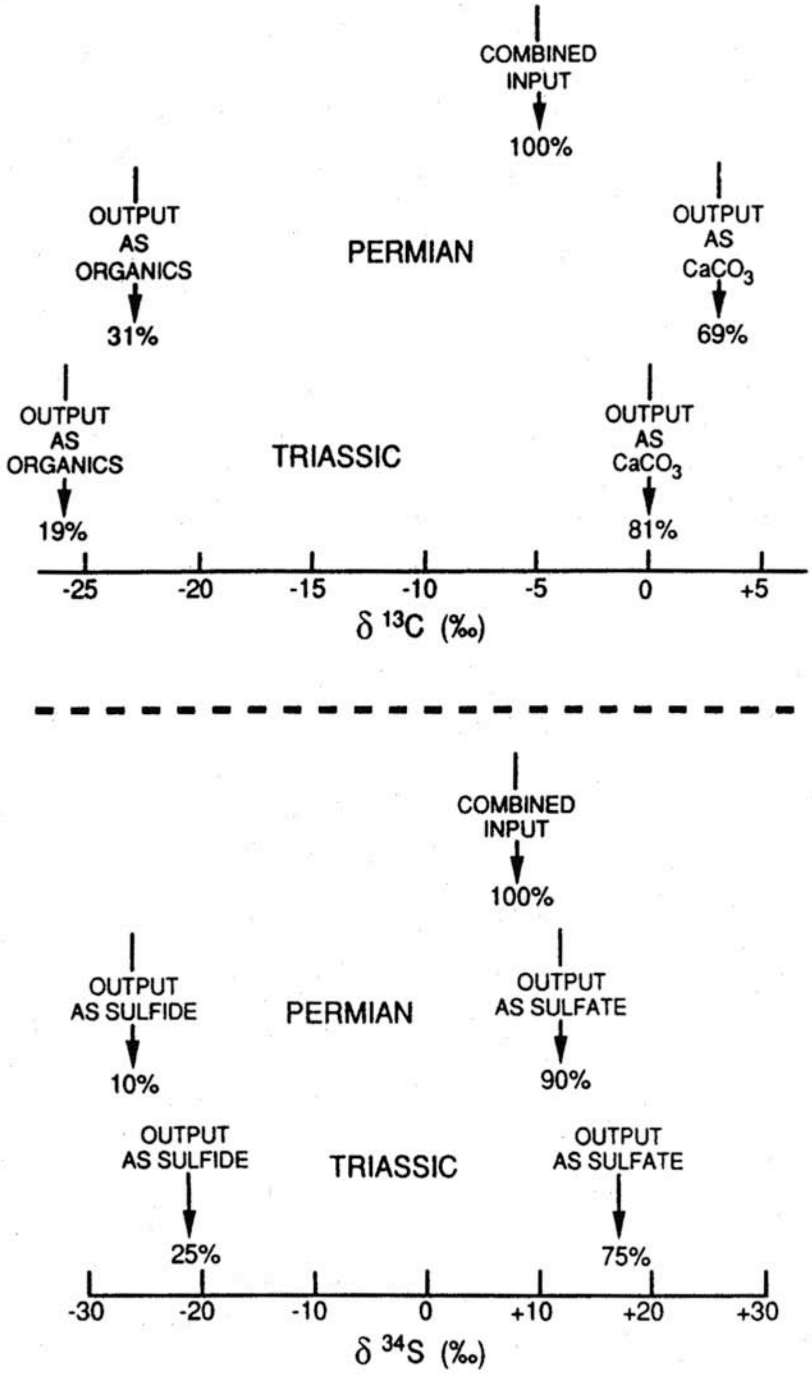
UNITS = $10^{12}\ \frac{mol}{yr}$		OCEAN#1		OCEAN#2		OCEAN#3	
		IN	OUT	IN	OUT	IN	OUT
COMPOUNDS	FeO	2	3	2	6	4	0
	FeS	4	3	4	0	4	8
	$CaSO_4$	4	5	4	8	4	0
	CO_2	4	0	4	0	4	0
	CaO	3	0	6	0	2	0
	$CaCO_3$	14	16	14	16	14	20
	C	2	4	2	4	2	0
	O_2	0	0	6	0	0	6
ELEMENTS	Fe	6	6	6	6	8	8
	Ca	21	21	24	24	20	20
	C	20	20	20	20	20	20
	S	8	8	8	8	8	8
	O	71	71	86	86	72	72
ELEC.	S	-8		-32		+32	
	C	+8		+8		-8	
	O	0		+24		-24	
	Σ	0		0		0	
		OXYGEN NULL		OXYGEN CONSUMED		OXYGEN CREATED	

minerals are eroded from the continents and sulfide minerals form in the anaerobic pore waters of sediments. Sulfate minerals are eroded from ancient evaporite deposits and sulfate minerals form in isolated hypersaline arms of the sea (and perhaps in ridge crest hydrothermal systems).

With this background in mind, we can understand why it is unlikely that the deep ocean was anoxic at any time during the last 100 million years. The important point is that the survival probability of organic matter is thought to be greater if it falls into an anoxic environment. For each mole of carbon preserved in this way, one mole of O_2 is added to the atmospheric pool. The logic is as follows. The bacteria which make their living in anaerobic environments by using NO_3^- and $SO_4^=$ as oxidants likely lack the combined destruction efficiency of the much wider range of organisms which inhabit oxygenated environments. Further, the fate of much of the $SO_4^=$ used by bacteria as an oxidant is to be buried in the sediment as a metal sulfide. Thus, if a major portion of the deep sea were to slip into anoxia, far too great a fraction of the carbon and sulfur passing through the ocean-atmosphere reservoir would be buried in reduced form. If such a slip to anoxia were to have taken place, then the O_2 content of the atmosphere would have experienced a climb which would have continued until newly formed deep waters were charged with sufficient oxygen to burn virtually all the organic residues falling into the deep sea. The episode of anoxia would be squelched.

Events which took place 250 million years ago at the beginning of the Triassic provide an interesting example of the interplay between the cycles of carbon and sulfur. The preceding Permian epoch was brought to an abrupt close by a major catastrophe which led to the extinction of 85 percent of the existing species. The consequences of this catastrophe are imprinted in both the isotopic records for marine calcium carbonate and calcium sulfate. The carbon isotope ratio ($^{13}C/^{12}C$) undergoes a sudden 3‰ drop and the sulfur isotope ratio ($^{34}S/^{32}S$) a more gradual 5‰ rise. If one assumes that both the oxidation states and isotopic composition of the carbon and sulfur added to the ocean

CONTRAST BETWEEN PERMIAN AND TRIASSIC CARBON AND SULFUR ISOTOPE BUDGETS



was the same during the early Triassic as during the late Permian, then these changes must herald a major change in the mode of output of carbon and sulfur to sediments. This should not be surprising as the terrestrial and marine ecosystems which had developed during the previous 200 or so million years must have unraveled as the result of the massive extinctions. The new food webs which replaced them likely operated quite differently. In order to produce a 3‰ drop in the $\delta^{13}C$ for marine $CaCO_3$, there must have been a 12 percent drop in the fraction of carbon removed in organic form. If, as is generally assumed, the $\delta^{13}C$ for the combined input of new carbon to the ocean-atmosphere reservoir is -5‰, then the fraction being removed as organic material would have to have dropped from 31 percent during the late Permian to 19 percent during the early Triassic. The imbalance between the oxidation state of the input and output created in this way would have had to be taken up by an increase in the fraction of the sulfur removed in reduced form. During the several million years required to reach a new steady state, part of the slack may have been taken up by a decrease in atmospheric O_2. But, as this gas governs the steady state, its content would have eventually stabilized at that level required to maintain an equality between the oxidation state of the output and that of the input. At steady state, a 15 percent increase in the fraction of the sulfur buried in reduced form would have to have taken place. Assuming that the $\delta^{34}S$ for incoming sulfur was +8‰, this would have required a shift from 10 percent removed in reduced form during the late Permian to 25 percent during the early Triassic.

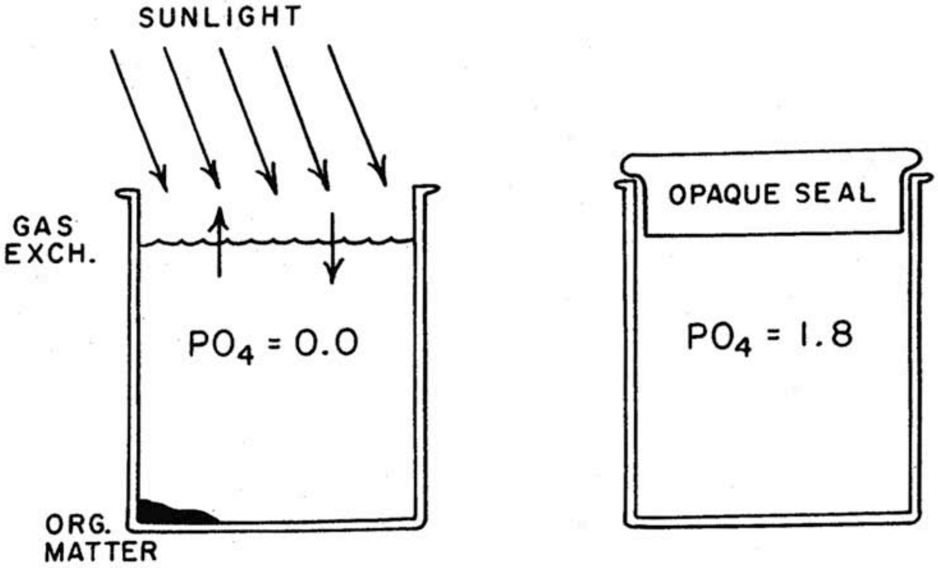
What might account for such a huge change? One possible scenario is as follows. Assume that during the Permian the burial of organic material in continental swamps was so great that it dominated the reduced component of the removal budget. As continental waters are low in $SO_4^=$ content even though the mud in swamps were anoxic, relatively little sulfur reduction would have accompanied the burial of reduced carbon. Then came the massive extinctions. Perhaps the terrestrial plants primarily responsible for the production of inedible carbon disappeared and with them the burial of large amounts of carbon on the continents. Simultaneously, an equally important change occurred in the marine environment. The efficient food web of late Paleozoic time then, as now, consumed most of the organic matter generated by marine plants before it reached the sediments. This is important because once in the sediment, the likelihood of adequate O_2 supply for their destruction drops substantially, for only by molecular diffusion can this gas be supplied to the pore waters. So the idea is that the food web void created by the great extinction event allowed a far greater fraction of the marine photosynthetic product to reach the sea floor. And, as documented by the geologic record, consequently anoxic conditions in sea floor sediments were widespread. It is well known that under such conditions both reduced carbon (as organic residues) and reduced sulfur (as iron sulfide) accumulate in the sediments. Together these two changes could account for the observed isotope shifts. During the Permian, the reduced fraction of the output to sediments was mainly terrestrial in origin and hence low in reduced sulfur. During the Triassic, the reduced fraction of the output to sediments was mainly marine in origin and hence rich in sulfides.

Controls on the Phosphate Inventory of the Sea

With this background in mind, it is easy to see that a tie must exist between the atmosphere's O_2 content and the ocean's PO_4 content. The amount of PO_4 dissolved in the sea determines how much organic matter is produced per oceanic mixing cycle and hence also the amount falling into the deep sea. The atmosphere's O_2 content sets the amount of O_2 dissolved in newly formed deep waters and hence how much is supplied to the deep sea. In order to maintain a balance between the oxidation state of materials entering and leaving the ocean-atmosphere reservoir, it is necessary that the amount of O_2 supplied to the deep sea exceed the amount required to consume the organic residues falling into the deep sea. For this to be the case, the concentration of O_2 in the polar surface waters must be comparable to the product of the PO_4 concentration of average ocean water times the ratio of O_2 utilization to PO_4 release during deep sea respiration

BUCKET EXPERIMENT

(CONCENTRATION UNITS μ mol/kg)



$\Sigma CO_2 = 2000$

$O_2 = 350$

EQIL. WITH ATMOS. AT 0°C

$$\Sigma CO_2 = 2000 + 1.8 \times 125$$
$$= 2225$$
$$O_2 = 350 - 1.8 \times 175$$
$$= 35$$

(175 moles per mole of phosphorus). In today's sea, the mean PO_4 concentration is about 2.2 micromoles per liter and the saturation O_2 concentration in polar surface water is about 330 micromoles per liter. Hence, the O_2 demand of 2.2 x 175 or 385 micromoles per liter would seemingly slightly exceed the supply. This is not the case because of the inefficient utilization of nutrients in polar surface waters from which deep waters form. The effective phosphorus content of sea water is more like 1.2 micromole per liter and hence the O_2 demand is only 210 micromoles per liter leaving one third of the O_2 entering the deep sea unused.

Another interesting aspect of the long term control of the atmosphere's O_2 is the so called O_2 compensation partial pressure. The key C-3 plant enzyme, rubisco, reacts with O_2 as well as with CO_2. As the O_2 partial pressure rises, the ratio of CO_2 uptake (which leads to O_2 production) to O_2 uptake (which leads to O_2 consumption) approaches unity. The partial pressure of O_2 at which this occurs is referred to as the compensation point. The point at which C-3 plants go from O_2 producers to O_2 consumers depends on atmospheric CO_2 content. For tobacco plants, the compensation point atmospheric composition is 23% O_2 at 220 ppm CO_2, 27% at 350 ppm CO_2, and 35% at 700 ppm CO_2. Were the O_2 content to approach this compensation limit, the ability of plants to grow and hence to produce O_2 would be seriously limited. Thus the O_2 level in the atmosphere appears to have an upper bound set by the level at which oxygen consumption by plants matches its production. We have already seen that 60 million years ago, the deep sea was about 10°C warmer. Hence, were the atmosphere's pO_2 the same as today's, the saturation O_2 concentration for the water descending into the deep sea would have been only 250 micromoles per liter. Under these conditions, too great a portion of the sea floor would have been anoxic and the O_2 content of the atmosphere would have been driven up as the result of the excess storage of reduced material until balance was restored.

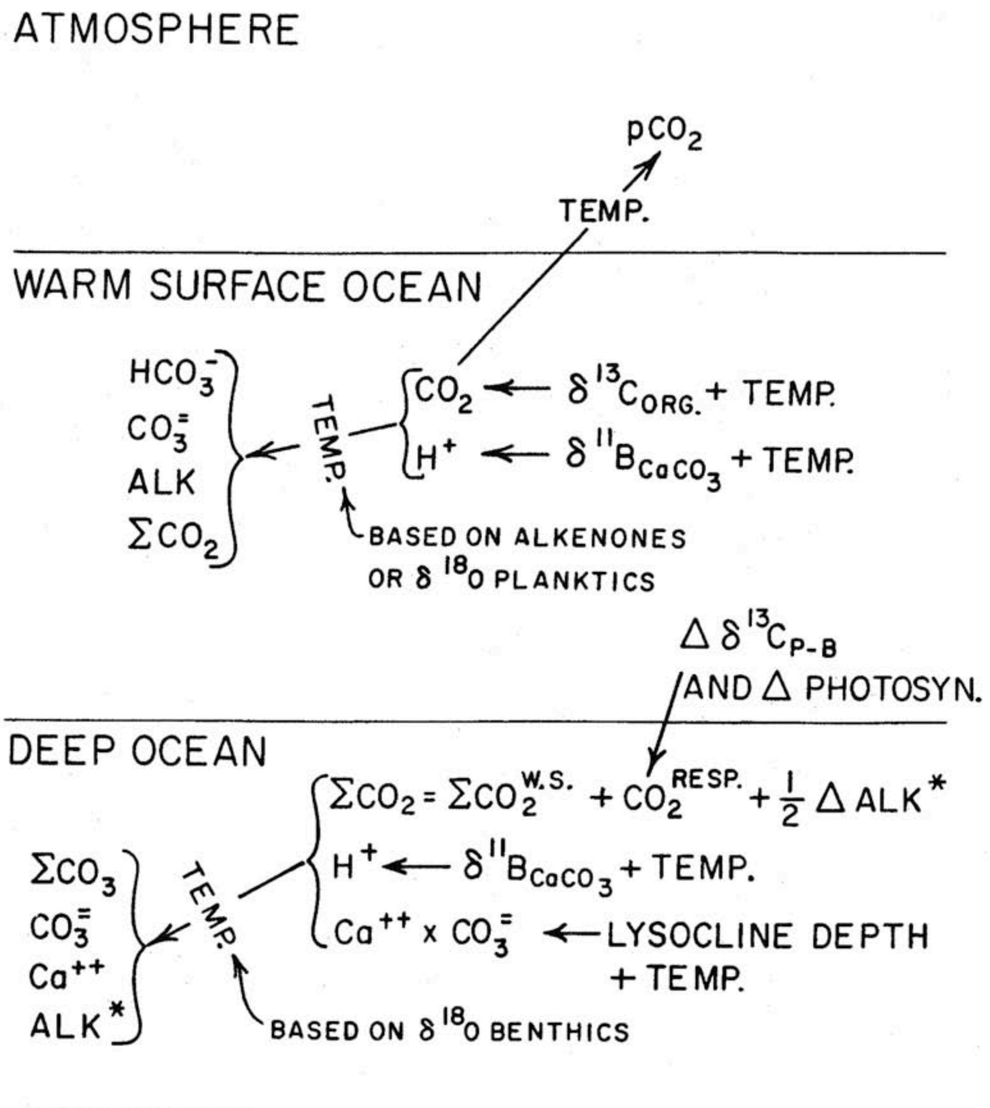
However, it is possible that the excess burial of organic carbon was accompanied by a reduction in the oceanic residence time of phosphate. The probability of loss during any given mixing cycle would have risen causing the steady state inventory of PO_4 in the ocean to fall. As the residence time for phosphorus in the sea (10^4 to 10^5 yr) is much less than the adjustment time for atmospheric O_2 content (10^6 to 10^7 yr), the job would be accomplished by a fall in the ocean's PO_4 content rather than a rise in the atmosphere's O_2 content.

Paleo pH Measurements

A complete description of the paleochemistry of both the warm surface ocean and the deep ocean requires that we have at least two additional pieces of information. The only candidates now in the offing are boron isotope-based paleo pHs. As we have seen, boron isotope ratios in foraminifera shells offer a potential pH recorder. While in theory this might be possible, two problems must be addressed. First, it will have to be shown that the boron contained in foraminifera shells remains firmly bound for periods of tens of millions of years. Were exchange with the boron dissolved in the pore water and that absorbed onto the clays surrounding the shell to occur, such measurements would prove misleading. In order to check this out, shells of the same geologic age from a wide range of burial environments will have to be analyzed to see if a self-consistent picture is obtained. One check will be to see if planktic-benthic boron isotope differences are consistent with carbon isotope differences. Second, it will have to be shown that the boron isotope composition of sea water did not change with time. While on the time scale of glacial cycles, no such change would be expected, on time scales approaching or exceeding the residence time of boron in the sea (i.e., 10 to 20 million years), it is possible that such changes did occur.

Art Spivack and his colleagues at Scripps took the first step toward evaluating the constancy of the boron isotope composition of sea water. Their strategy was to measure the boron content and boron isotope ratio in pore waters from a 700-meter-deep drill hole

A STRATEGY FOR DEFINING PALEOCEAN CHEMISTRY



ATMOSPHERE

pCO_2

TEMP.

WARM SURFACE OCEAN

HCO_3^-, $CO_3^=$, ALK, ΣCO_2 $\xleftarrow{\text{TEMP.}}$ $\begin{cases} CO_2 \leftarrow \delta^{13}C_{ORG.} + \text{TEMP.} \\ H^+ \leftarrow \delta^{11}B_{CaCO_3} + \text{TEMP.} \end{cases}$

TEMP. BASED ON ALKENONES OR $\delta^{18}O$ PLANKTICS

$\Delta \delta^{13}C_{P-B}$ AND Δ PHOTOSYN.

DEEP OCEAN

ΣCO_3, $CO_3^=$, Ca^{++}, ALK* $\xleftarrow{\text{TEMP.}}$ $\begin{cases} \Sigma CO_2 = \Sigma CO_2^{W.S.} + CO_2^{RESP.} + \frac{1}{2}\Delta ALK^* \\ H^+ \leftarrow \delta^{11}B_{CaCO_3} + \text{TEMP.} \\ Ca^{++} \times CO_3^= \leftarrow \text{LYSOCLINE DEPTH} + \text{TEMP.} \end{cases}$

TEMP. BASED ON $\delta^{18}O$ BENTHICS

* BY ITERATION

on the sea floor in the equatorial Pacific. Although the constituents of these pore waters are continuously exchanging with those in the overlying sea, the isolation time near the base of the sediment column is likely 10 or so million years. It is encouraging that these investigators found no evidence for either a shift in boron concentration or isotope ratio. Spivack and his coworkers also measured the boron isotope ratios in boron extracted from four foraminifera samples ranging in age back to 20 million years. They interpret these results to suggest that the pH of the surface ocean 20 million years ago was 7.4, or 0.8 pH units lower than today's. If so, then the hydrogen ion was likely about 6 times higher! If this were the case then, since the lysocline lay close to its present depth, the bicarbonate ion (and also the $\sum CO_2$) content of the sea must have been 6 times higher. Were this the case, then the $\Delta\delta^{13}C$ between surface and deep waters should have been much smaller than today's. It wasn't. Hence this boron-based result is difficult to accept. Many, many more boron isotope results will have to be obtained before the utility of this proxy will become apparent.

Summary

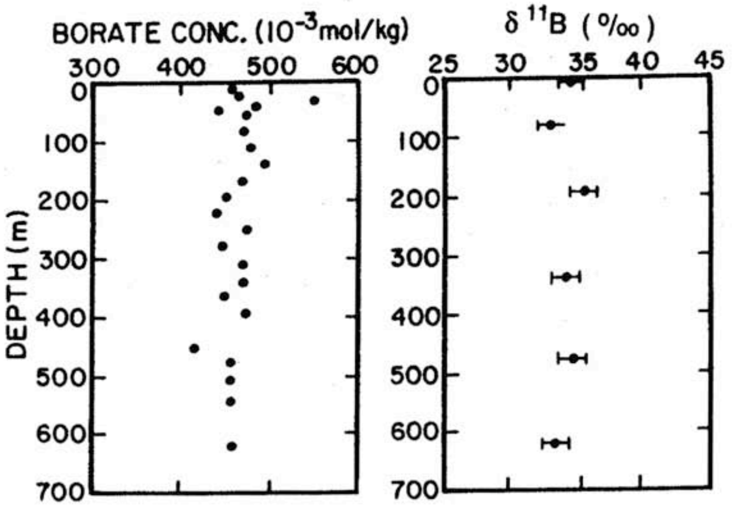
So where does this leave us as to the status of Walker's hypothesis that atmospheric CO_2 controls chemical traffic and hence that a tie must exist between Earth climate and tectonics? It is our view that the evidence is broadly consistent with this idea. Consider:

1) Although the rate of sea floor spreading has not slowed by the factor of two originally proposed by Pitman and Hays, a consensus exists among geophysicists that the rate was somewhat higher during Cretaceous time. Nor would many challenge that this post Cretaceous slow down in spreading rate was accompanied by a reduction in the rate of CO_2 outgassing. But the exact magnitude of this change remains uncertain.

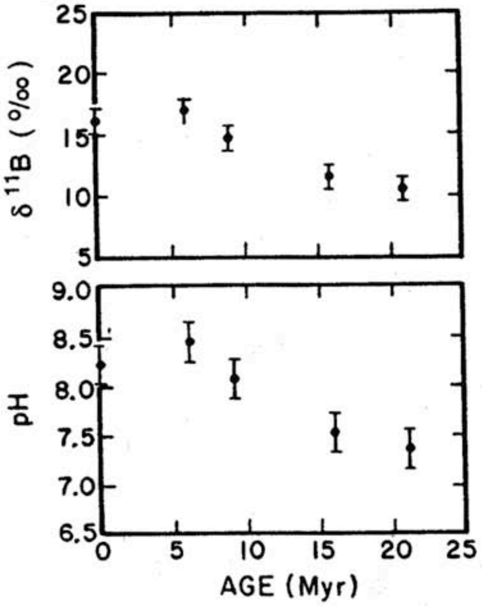
2) Based on oxygen isotope measurements on benthic foraminifera, it is clear that at least the polar regions have cooled dramatically since Cretaceous time. The absence of

PALEO pH ESTIMATES FROM BORON ISOTOPES

BORATE DISSOLVED IN PORE WATER
(ODP 803D 2°N 161° E)



BORATE FROM FORAMINIFERA SHELLS
(ODP 803D 2°N 161° E)



SPIVACK *ET AL.*

firm evidence for an equivalent tropical change, while complicating the situation, does not necessarily prove that the cooling was not CO_2 induced.

3) Based on carbon isotope measurements on marine organic residues, it appears that the CO_2 content of temperate surface waters has dropped since Cretaceous time. Taken together with the oxygen isotope-based cooling of these regions, these measurements suggest that the atmosphere's CO_2 content has dropped by several fold since that time.

4) The record of the planktonic-benthic carbon isotope difference is consistent with the carbon isotope-based estimate of the atmospheric CO_2 content decrease.

5) Unfortunately, no evidence in support of a drop in chemical weathering rates has been found. The strontium isotope record is inconclusive in this regard. BLAG would dictate that both the supply of strontium from ridge crests and the supply from continents would change in unison. Hence in the absence of changes in the isotope composition of the strontium end members, no change in the isotopic composition of ocean strontium would be expected. It is likely that the observed increase in the ^{87}Sr to ^{86}Sr ratio is related to the exposure to weathering of Himalayan rocks unusually rich in radiogenic strontium.

Critics of BLAG will scream "But the evidence is all circumstantial - it doesn't prove a thing." True, but keeping in mind that as some mechanism must exist by which chemical traffic is controlled, these critics are obligated to do more than throw stones. Rather, they must come up with an alternative set of controls and a scenario for post-Cretaceous time which is consistent with the above mentioned observations. It seems to us that the only feasible alternative scenario is to transfer traffic control to the ocean. This being the case, it is important to firm up our ability to define ocean chemistry at times in the past. This is no easy chore. It will require that each of our paleoindicators be pushed to its very limit.

Commentary of Walker's World Plates

pg. 3

Astrophysical models clearly indicate that the energy output from the Sun has steadily increased. Four and one half billion years ago, when the Earth formed, the Sun's output was about 30 percent lower than it is now. Were the Earth's reflectivity and greenhouse shielding no different from today's, then its surface would have been ice bound. But we know from the geological record that water-deposited sediments representing all ages are present. An obvious solution exists for this seeming enigma. Early in its history, the Earth's CO_2 greenhouse blanket was much thicker than today's. As explained in the text, a steady release of CO_2 from the Earth's interior guarantees that the Earth can never have become a permanently frosty ball.

pg. 8

Hypothetical Planet X has a very simple geochemical cycle. CaO dissolved from its soils combines with CO_2 outgassed from its interior forming $CaCO_3$. This material settles to the sea floor forming a blanket of sediment. As on Earth, the sea floor on Planet X is subducted beneath its continental crust. Some of the mantling sediment is dragged down into the hot interior where it is decomposed to CO_2 and CaO completing the cycle. While the Earth's geochemical cycle is more complex, the formation of calcite by organisms living in the sea and the thermal decomposition of carbonate minerals within the Earth's interior play dominant roles.

pgs. 10-11

Berner, Lasaga and Garrels (BLAG) reasoned that if, as geophysicists claim, over the last 100 million years the rate of sea floor spreading has slowed, then as a result, the Earth must have cooled. Their logic is as follows. A slowing of spreading would have led to a corresponding decrease in CO_2 outgassing. Further, as the rate of generation of sea floor dropped, more time would be available for the oceanic crust to cool. The shrinkage related to this extra cooling would lower the elevation of the sea bottom and hence also sea level. As sea level dropped more, land would be exposed to the atmosphere and hence be subject to chemical erosion. With less CO_2 to match and more land from which to derive CaO, the chemical weathering demand per unit of land area would lessen. As outlined in the text, this situation would have led to a drop in the atmosphere's CO_2 content and hence the Earth's surface temperature. If, as Pitman and Hays proposed, sea floor spreading rates were twice as high as today's 100 million years ago, then in order to deliver the amount of CaO to match the then higher CO_2 outgassing rate, the planet must have been about 10°C warmer. Other climatic factors being equal, this would have required an 8 fold higher atmospheric CO_2 content.

pg. 13

As explained in the text, BLAG assumes that the supply of CaO goes entirely into matching that of CO_2. If so, the system must be regulated by the CO_2 content of the atmosphere. By negative feedback, it is driven to that level where soil temperatures permit a chemical weathering rate just large enough to supply the needed calcium. By contrast, in the case of GALB, the supply of CaO is always in excess of that needed to balance the supply of CO_2. In this case, an oceanic feedback loop must operate which brings about a removal of the excess CaO into silicate minerals at just the rate this excess is added to the sea.

pg. 16

By measuring the volume flow and the concentration of dissolved chemical species in the world's major rivers, it is possible to estimate today's flux of cations to the sea. It turns out that about two times more Ca^{++} than Mg^{++} and about six times more Ca^{++} than K^{+} enters the sea. The dominance of calcium reflects both the recycling of ancient limestone ($CaCO_3$) and the ease with which calcium-bearing feldspars dissolve. Although weakly constrained, it is thought that the supply of calcium from limestone is about three times that from silicates. The circulation of sea water through the newly formed ridge-crest basalts modifies the sea's chemistry. The magnesium carried into the ridge crest is quantitatively removed as demonstrated by its absence in the high temperature effluents. While the total flux of hydrothermal water remains uncertain, the loss of Mg^{++} is thought to roughly match the input from rivers. In contrast, vent waters have higher Ca^{++} and K^{+} contents than do sea water. Thus high-temperature hydrothermal circulation enhances the supply of these cations to the sea. BLAG assumes that the amount of calcium reaching the sea is just equal to the amount needed to match the CO_2 added by planetary outgassing and limestone dissolution (minus that going into organic residues). In other words, all the calcium added to the sea leaves as $CaCO_3$. Thus if 14×10^{12} moles of calcium reach the sea each year, 14×10^{12} moles must also be buried in marine sediments as calcite. If as suggested by the global carbon isotope budget about 18% of the carbon reaching the sea is removed as organic residues, then a total of 17×10^{12} moles of carbon must reach the ocean-atmosphere reservoir each year. If only 9×10^{12} come from the weathering of limestone, the other 8×10^{12} must come from a combination of outgassing and the oxidation of recycled sedimentary organic matter.

pg. 18

Based on the analyses of carbonatites, diamonds and CO_2 contained in ridge crest glasses (i.e., of materials which have their origin in the mantle), the mean $\delta^{13}C$ for Earth carbon is estimated to be about -5‰. Carbon isotope analyses of organic matter and calcite from sediments covering the last 500 million years' record show that the former has hovered around -25‰ and the latter around 0‰. This suggests that on the average about 20% of the carbon entering the oceanic system is removed as organic matter and about 80% as calcite.

pg. 20

While a first order consideration of the carbon isotope geochemistry suggests that the $\delta^{13}C$ for the ΣCO_2 in rivers might provide a means of estimating the relative contributions of limestone and silicate weathering, in practice this approach cannot work. The reason is that excess organic-derived CO_2 pushes the isotopic composition toward the ^{13}C deficient value characteristic of organic matter (i.e., -26‰) while exchange with atmospheric CO_2 drives the value toward the ^{13}C-rich value of limestone (i.e., 0‰). As it is not possible to quantify these opposing influences, the $\delta^{13}C$ of ΣCO_2 in rivers is not a useful index of the source of the rivers cations.

pgs. 22-23

That over the past 40 million years the ^{87}Sr content of oceanic strontium has steadily risen is well documented by the analysis of strontium contained in marine carbonates. The fact that the onset of this rise just postdates to the time of the collision between the Indian and Asian continental blocks suggests that erosion of the great Himalayan mountain chain was responsible for this rise. This rise could reflect either an increase in the ratio of continental-derived strontium to ridge crest-derived strontium delivered to the sea, or an increase in the radiogenic ^{87}Sr content of continental strontium. The evidence appears to favor the latter explanation, for rivers draining the Himalayas carry unusually radiogenic strontium.

pg. 26

Oxygen isotope ratios in benthic foraminifera shells from marine sediments have undergone a 3‰ increase since early Eocene time (i.e., about 55 million years ago). While a small amount of this change is the result of the growth of the Antarctic and Greenland ice sheets, the remainder must reflect a major cooling (~10°C) of the high latitude oceans (and hence of the polar regions). The I and G on the left hand scale represent the swings in the $\delta^{18}O$ of benthic foraminifera associated with the glacial cycles of the last 800,000 years. In this case, the ice volume contribution is the larger (~1.2‰) and the polar temperature contribution the smaller (~0.6‰). The left end of the heavy black curve represents the average value for benthic ^{18}O during this period of repeated glaciation. For each meter of sea level lowering (resulting from glacial growth) the $\delta^{18}O$ of the sea increases by about 0.010‰. For each degree of ocean cooling, the $\delta^{18}O$ in $CaCO_3$ formed rises by about 0.23‰.

pg. 28

The igneous minerals formed when magmas cool are not chemically stable under the Earth surface conditions. The oxides of silica, potassium, sodium, calcium and magnesium tend to dissolve producing $H_4SiO_4^0$, K^+, Na^+, Ca^{++} and Mg^{++} ions which are carried by rivers to the sea. By contrast, the oxides of aluminum and iron are quite insoluble and remain behind in solid residues. But the weathering process is more complicated than a quick and complete separation of the five soluble oxides from the two insoluble oxides. In many cases, only part of the soluble oxides are delivered to solution. The rest remain behind bound into clay minerals. At some later time, these first generation clays may undergo a second round of weathering and will give up to solution some of their remaining silica and cations. The second generation residues are then greatly eniched in the oxides iron and aluminum.

pg. 31

The carbon in marine plant material is always depleted in ^{13}C relative to the CO_2 gas in the surrounding air or water. However, the extent of this depletion depends on the magnitude of the resistance posed by the cell membrane. The reason is that the ^{13}C depletion associated with molecular diffusion is on order of magnitude smaller than that associated with the enzymatic reaction which converts CO_2 to organic matter. Hence in situations where the supply of CO_2 is limited relative to the biochemical demand within the cell, the fractionation will shift toward the smaller value associated with molecular diffusion. By contrast, in situations where the CO_2 supply is plentiful compared to the biochemical demand, the magnitude of the fractionation will shift toward the larger value associated with the enzymatic reaction. It is for this reason that the isotopic composition of marine organic matter might serve as a paleo CO_2 concentration proxy. The higher the atmospheric CO_2 partial pressure, the higher the surface ocean CO_2 concentration and hence the less important the resistance posed by the cell membrane. Thus the extent of isotope fractionation should vary in direct proportion to the amount of CO_2 dissolved in surface sea water.

pg. 33

Measurements carried out by a New Zealand graduate student were the first to clearly demonstrate the dependence of the extent of carbon isotope fractionation on the concentration of aqueous CO_2. For his Ph.D. thesis research, McCabe grew algae (at the same temperature) but at different CO_2 concentrations and found that the higher the CO_2 pressure, the greater the depletion of ^{13}C in the organic matter. A similar trend was found by Rau and his coworkers for plankton samples from various regions of the ocean. Although the CO_2 partial pressure in the atmosphere is very nearly globally uniform, the CO_2 is much less soluble in warm waters than in cold water. Hence, organic matter formed in cold water is more deficient in ^{13}C than that formed in warm water. Thus in order to obtain a paleoatmospheric CO_2 partial pressure estimate from carbon isotope measurements in marine organic matter, the temperature of the water in which the organic matter formed must also be known.

pg. 35

The analysis by Freeman and Hayes of carbon isotope measurements on porphyrins from marine organic material samples ranging in age back to 135 million years suggest that the atmospheric CO_2 content has steadily declined. It appears to have been about 1000 μatm 100 million years ago. In order to obtain these CO_2 partial pressure, they had to reconstruct the latitude at which the organic matter grew (based on plate motion reconstructions). Then they had to use oxygen isotope-based reconstructions of the surface water temperature to convert from CO_2 concentration to CO_2 partial pressure.

pg. 37

CO_2 in soils is somewhat richer in ^{13}C than that in the organic matter being oxidized for two reasons. First, because $^{12}CO_2$ diffuses more rapidly than $^{13}CO_2$, the ^{13}C to ^{12}C ratio in soil air is about 4.4‰ higher than that in the CO_2 produced by respiration. Second, the soil contains atmospheric CO_2 which has a higher ^{13}C content than organic matter. In today's soils the atmospheric contribution is quite small. The reason is that the partial pressure exerted by respiration CO_2 is between one and two orders of magnitude higher than the partial pressure of CO_2 in the atmosphere. However, if at some time in the past, the atmospheric CO_2 pressure was, as proposed by BLAG, an order of magnitude higher than now, then its larger contribution would lead to a significant shift in carbon isotope ratio in soil CO_2. Thure Cerling proposed to use this shift as a paleo CO_2 indicator. His recorder, soil caliche ($CaCO_3$), has a $^{13}C/^{12}C$ ratio about 10‰ higher than that in soil CO_2. His method requires 1) that the respiration contribution to the soil CO_2 partial pressure has remained nearly the same, 2) that caliche forms sufficiently at a depth in the soil profile where the CO_2 concentration gradient has become small, 3) that the $^{13}C/^{12}C$ in the soil organic matter be known and finally, 4) that the soil temperature be known (in order to correct for the temperature dependence of the soil CO_2 to soil $CaCO_3$ carbon isotope fractionation).

pg. 40

The ionic charge in sea water is dominated by Na^+ and Cl^-. The remainder of the cationic charge is contributed by Mg^{++}, Ca^{++} and K^+. The remaining anionic charge is supplied mainly by $SO_4^=$ with only a small contribution from HCO_3^-, $CO_3^=$ and $H_4BO_4^-$ (i.e., alkalinity) .

pg. 42

At ridge axes where molten basalt is being injected from the underlying mantle, the Earth's lithosphere is puffed up forming a topographic high. As the crust moves away form the ridge axis, it slowly cools causing it to shrink and hence the ocean floor to deepen. Eventually, this deepening carries the sediment water interface below the $CaCO_3$ saturation horizon into corrosive water. This crossing is marked by a transition from the deposition of carbonate ooze (calcite rich) to red clay (calcite poor). This transition is encountered in holes drilled through sediment column. Its age is obtained from the fossils contained in the uppermost carbonate ooze. The depth of the saturation horizon at the time of the transition can be obtained by correcting for the sea floor sinking which occurred between the time of the transition and the present. Such a correction is possible because the cooling (and hence crustal shrinkage) proceeds as a simple function of time. By drilling many such holes, it has been possible to reconstruct the transition zone depth over the last 100 million years in all three oceans.

pg. 44

All the constituents in sea water are being gradually replaced. For any given problem, only the concentrations of those constituents having a residence time far longer than the time interval of interest can be considered to have remained unchanged. The rest are subject to change. For example, calcium which has a residence time of about one million years can be considered to remain constant during the course of the single glacial cycles of interest to Archer, but not over the 100 million year period of interest to BLAG.

pgs. 46

Carbon isotope measurements on material formed in surface ocean water and in the deep ocean water suggest that the approximately 1.8‰ difference between the ^{13}C to ^{12}C ratio for surface water and deep water carbon seen in today's ocean has persisted for the last 20 million years. This isotope ratio difference depends on the ratio of PO_4 to $\sum CO_2$ in average ocean water, on the C to P ratio in marine organic matter and on the isotope fractionation during photosynthesis. Assuming that the latter two of these factors have remained more or less constant, this record suggests that the ratio of $\sum CO_2$ to PO_4 in the sea has also remained more or less the same.

pg. 48

Detailed data from a single core in the Pacific Ocean suggest that during Paleocene and Eocene time the $\Delta\delta^{13}C$ was only slightly smaller than that for the last 20 million years. However, when account is taken of the larger photosynthetic fractionation factor (resulting from the higher CO_2 content of surface waters), this data set suggests that the oceanic $PO_4/\Sigma CO_2$ ratio might have been only two thirds today's value.

pg. 51

Four elements, carbon, iron, sulfur, and oxygen are the main participants in the electron trades conducted on the Earth's surface. The number of electrons associated with a carbon atom ranges from a deficiency of four in CO_2 and in $CaCO_3$ to an excess of four in methane. Iron atoms can go from a deficiency of three electrons in ferric compounds to a deficiency of two electrons in ferrous compounds. Sulfur can go from a deficiency of six electrons in sulfates to an excess of two electrons in sulfides. Oxygen can go from a deficiency of two electrons in oxides to null in oxygen gas. As electrons must be conserved, if one or more of these elements undergoes a net oxidation (i.e., loss of electrons) in passing through the ocean-atmosphere system, the others must undergo a corresponding reduction (i.e., gain of electrons). For example, if together carbon, sulfur and iron undergo a net reduction in passing through the ocean-atmosphere reservoir, then this imbalance would be compensated by an increase in the atmosphere's O_2 content. As the extent to which reduced species become oxidized in passing through the ocean-atmosphere system depends on the O_2 content of the atmosphere, this gas serves as the policeman for electron flow.

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Three examples of possible oxidation reduction situations for the Earth system. In the first, a net oxidation of sulfur is exactly balanced by a net reduction of carbon, leaving the oxygen content of the atmosphere unchanged. In the second, the net reduction of carbon is not adequate to balance the net oxidation of sulfur. This requires that a net consumption of O_2 occurs decreasing the atmospheric inventory of this gas. In the third, a net reduction of sulfur is not matched by the net oxidation of carbon. This means that a net production of O_2 occurs increasing the atmospheric inventory of this gas.

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The carbon isotopic composition of Permian marine carbonates averaged about 3‰ heavier than that of Triassic marine carbonates. Assuming that the isotopic composition of the combined carbon inputs remained unchanged, this requires a shift in the ratio of carbonate to organic matter being buried from 69:31 during the Permian to 81:19 during the Triassic. If then, as now, the turnover time of ocean carbon was on the order of 10^5 years, this new split must have been maintained for many, many ocean residence times; i.e., it represented a steady state flow of carbon through the ocean-atmosphere system.

The sulfur isotope composition of Permian marine sulfate deposits average about 5‰ lighter than that for their Triassic equivalents. Assuming that the isotopic composition of the combined sulfur inputs remained unchanged, this requires a shift in the ratio of sulfate to sulfide being removed from 90:10 during the Permian to 75:25 during the Triassic.

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A simple experiment carried out in a bucket of sea water illustrates the tie between the O_2 content of the atmosphere and the PO_4 content of deep sea water. Sea water containing 1.8 μmol/kg of PO_4 and 2225 μmol/kg of $\sum CO_2$ and kept at 0°C is exposed to sunlight. Plants grow until all the PO_4 has been utilized. The excess O_2 gas produced in this way is lost to the overlying air. Then an opaque seal is inserted into the top of the bucket, blocking out sunshine, eliminating the air space, and preventing gas exchange. Bacteria consume the plant mattter (and then each other) returning the PO_4 to solution. In so doing, 90% of the O_2 is consumed. If the PO_4 content of the water had been 2.2 instead of 1.8 μmol/kg, the O_2 would have been entirely depleted before the organic matter had been eaten. The water would have gone anoxic.

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Through information stored in deep sea sediments, it is potentially possible to define the carbon chemistry of the ocean atmosphere system for past times. The situation for surface waters could be defined from boron isotope measurements on planktonic shells (yielding H^+) and carbon isotope measurements on organic compounds (yielding CO_2) coupled with a paleotemperature estimate based on oxygen isotope or alkenone measurements. This information would allow the HCO_3^- , $CO_3^=$, ΣCO_2 and alkalinity to be computed. From the temperature and CO_2 content, the atmosphere's pCO_2 could be estimated. For the deep sea, the product of the Ca^{++} and $CO_3^=$ ion concentrations could be obtained from the paleo-lysocline depth, the pH could be obtained from boron isotope measurements on benthic foraminifera. Finally, the difference between the ΣCO_2 concentration between warm surface and cold deep water could be obtained from the $\Delta\delta^{13}C$ between planktic and benthic forams:

$$\Delta CO_{2_{resp}} \equiv \frac{\Delta\delta^{13}C_{p\text{-}b}}{\Delta photo} \times [\Sigma CO_2]_{S.W.}$$

This leaves only the alkalinity difference between surface and deep water resulting from $CaCO_3$ dissolution unaccounted for. It could be obtained by iteration.

pg. 62

Measurements of the pore water profile of borate and its isotopes have been carried out in only one place in the ocean. Pore water squeezed from sediments obtained from a long boring in the equatorial Pacific show no depth trend in either the concentration of borate or in its isotope ratio. As the time required for replacement of the water deep in the sediment by molecular diffusion from the overlying sea is ten or so million years, this provides evidence that changes in the isotope ratio for boron contained in the shells of planktic forams are the result of changes in the pH of surface water. Assuming this to be the case, Spivack and his co-workers used measurements on ancient forams to obtain paleo pH estimates for the period 5 to 22 million years ago.

They suggest that the ocean was 6 times more acid 20 million years ago than it is today. As explained in the text, this result is inconsistent with the Freeman and Hayes estimate of the CO_2 content difference at this time.

Super Problem

In the year 2250, Abe Highjit Sanyal, a distant descendant of an early 21st century geochemist, is assigned to an expedition to explore our galaxy. The Earth's environment has deteriorated to the point where serious consideration is being given to transferring civilization to another planet. Several promising candidates, spotted from space probe telescopes, appear to match Earth in size, stellar illumination, and day length. But from the great distance at which the observations were made, it is not possible to determine the composition of each planet's atmosphere, its surface temperatures, or whether life is present.

Jit, as he is known, has been assigned to determine the history of the planet's climate. As the task of moving will be monumental, the Masters of Earth, as the ruling class is known, want to be sure that the climate the expedition team experiences during their brief three-year visit will be the climate they get if they move there. Jit is well prepared. He has mastered all that is known about Earth's paleoclimate and has brought with him the equipment and technicians necessary to repeat these studies on the candidate planets.

Jit is disappointed when the expedition's commander decides to abandon the first candidate planet because it turns out to be too warm (40°C at its equator). Jit returns to his state of suspended animation, for it will be 10 years until the next candidate planet is reached. When he is at last awakened, Jit is excited to see that they are orbiting a planet which much resembles Earth. He notes about half ocean and half land and about half cloudy sky and half clear sky. He is struck by the absence of polar ice caps and mountain-top glaciers. Numerous volcanoes, some active, spot the landscape. The commander briefs the the party saying that from orbit this planet looks extremely promising. Its radius is 15% smaller than Earth's. Its mean surface temperature is 20°C and ranges from 10°C at the poles to 30°C at the equator. The planet's spin axis is perpendicular to the plane of its circular orbit (so it has no seasons). The green of chlorophyll is apparent both on land and in the sea. The atmosphere's O_2 partial pressure is 0.17 atm. The N_2 pressure is 1.2 atm.

Upon landing, the explorers are pleased to find an ecosystem not unlike Earth's. Rooted plants cover the continents. The sea abounds with fish. But there is no sign of civilization.

Jit immediately gets to work. He measures the carbon isotope ratio in the following materials and relates them to the Urey's standard.

marine plants (tropical ocean)	-35‰
CO_2 from air	- 4‰
ΣCO_2 from the sea	+ 3‰

He does some chemistry:

pCO_2^{atm}	900 μatm
$[CO_2]_{\text{tropical surf water}}$	$24 \times 10^{-6} \frac{\text{moles}}{\text{kg}}$
$[\Sigma CO_2]_{\text{tropical surf water}}$	$2200 \times 10^{-6} \frac{\text{moles}}{\text{kg}}$
$[ALK]_{\text{tropical surf water}}$	$2400 \times 10^{-6} \frac{\text{equiv}}{\text{kg}}$

Jit then turns his attention to the boron isotopes. He finds the following:

sea water	$\delta^{11}B = +40‰$
living shells	$\delta^{11}B = +21‰$

He prays thanks to his distant forefather, Abhijit. All is well in the world of boron.

Continuing, Jit measures the $\delta^{18}O$ in living shells and finds a value of +1‰ in Urey's scale.

Finally, he measures the strontium isotope in sea water and living shells. Both give a $^{87}Sr/^{86}Sr$ ratio of 0.7070. He also measures the ratio in all the major rivers, and is puzzled to find the average is 0.7060. He notes the diffference is the result mainly of the low radiogenic values for rivers draining a large area covered by lava flows. He determines their age to be about one million years by ^{40}K-^{40}Ar dating. Strontium from these flows has an isotope ratio of 0.7000.

Having completed his survey of the modern world, he turns to the geologic record to see whether he can detect any evidence for changes in climate. Marine sediments are an obvious source of this information. Curiously enough, the expedition surveyors find no evidence for sea floor spreading (but plenty of volcanoes). The first sediment core he takes consists of red clay all the way from top to the bed rock. So he chooses a shallower site and finds it to consist entirely of calcite ooze.

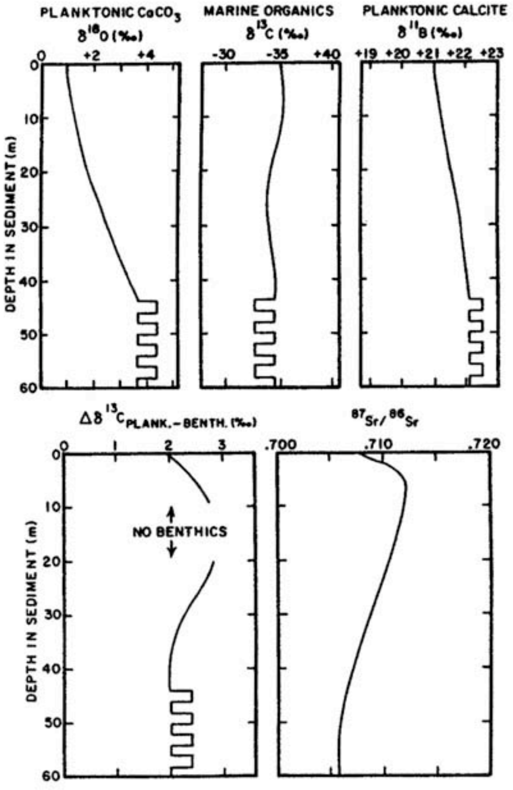
He measures the following properties as a function of depth in this second core:

1) $\delta^{18}O$ in planktonic $CaCO_3$
2) $\delta^{13}C$ in organic matter
3) $\delta^{11}B$ in planktonic $CaCO_3$
4) $\Delta\delta^{13}C$ planktonics - benthics
5) $^{87}Sr/^{86}Sr$ in planktonic $CaCO_3$

His results are shown in the graphs to the right.

Jit estimates the length of the sediment record to be 10 million years.

Based on this evidence, how should Jit's report to the Masters of Earth read? In other words, what is the sedimentary record from planet Q trying to tell Jit? Can Jit come up with a self-consistent explanation for all his observations?



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