

THE ROLE OF THE OCEAN IN CLIMATE YESTERDAY, TODAY, AND TOMORROW



Photo credit: Gary Comer

WALLACE S. BROECKER

ELDIGIO PRESS

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Cover picture: Taken by Gary Comer from his yacht “Turmoil” while anchored in Scoresby Sund, a fjord which extends 100 miles into the mountain belt to the east of Greenland’s ice cap.

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Preface

In 1975, I published a book entitled “Chemical Oceanography”. Then in 1982, I published a second book entitled “Tracers in the Sea”. The first was more of an idea book. The second immersed the reader in a host of new observations and a glut of first order quantification. Some readers felt that in the second book the big picture was obscured by too many details. I was asked over and over “Wally, why don’t you rewrite “Chemical Oceanography” so that our students can get a look at the forest instead of being lost among the trees?” My reply was that this was a task for some else for I no longer had my finger on the pulse of chemical oceanography.

Instead I concentrated my book-writing efforts on two subjects representing my current research interests. The first entitled “Greenhouse Puzzles” dealt with the Earth’s carbon cycle present and past. The second entitled “The Glacial World According to Wally” covered late Quaternary paleoproxies, chronometers and records. Both of these books are more in the vein of “Tracers in the Sea” in that they take in-depth looks at the subject rather than emphasizing the big picture.

Early this summer (2004) it occurred to me that it might be worthwhile to write a book which presented the big picture regarding two of the subjects which dominate thinking with regard to our planet’s climate during glacial times. One involves the role of the Atlantic Ocean’s conveyor circulation in the abrupt reorganizations of the Earth’s climate system. The other has to do with the cause for the large drop in atmospheric CO₂ content which accompanied each major glaciation.

The same two subjects lie at the core of attempts to come to grips with the man-induced global warming. Much has been written about the possibility that, if unabated, the ongoing atmospheric CO₂ buildup will lead to a conveyor shutdown. Some have predicted that such a shutdown would plunge northern Europe back into an ice age. Reacting to these fears, public opinion is gradually shifting toward the need to stem CO₂ emissions. It is my opinion that the one sure way to do this would be to recapture CO₂ from the atmosphere and store it either in liquid or mineral form.

The book is divided into two major sections. The first of these deals with the ocean's conveyor circulation. As this circulation is influenced by water vapor transport through the atmosphere, the operation of the ocean and atmosphere must be considered together. The first chapter deals with the factors influencing the present day operation of the conveyor. The second recounts what we have learned about changes in the conveyor circulation during the last glacial period and the third discusses the potential impact of rising atmospheric CO₂ on the conveyor.

The second section is devoted to the influence of the ocean on the atmosphere's CO₂ content. As the availability of the element phosphorus plays a big role in what is termed the ocean's biological pump, the cycles of phosphorus and carbon are considered together. Chapter four looks at the ocean's carbon cycles as they operated just prior to the Industrial Revolution. Chapter five is concerned with the scenarios which have been put forth to explain the 30 percent reduction in atmospheric CO₂ during the last glacial maximum. Finally, Chapter six deals with the ability of the ocean to suck up fossil fuel CO₂.

For each text page, there is a companion figure page. Each figure is designed to amplify the text material found on the facing page.

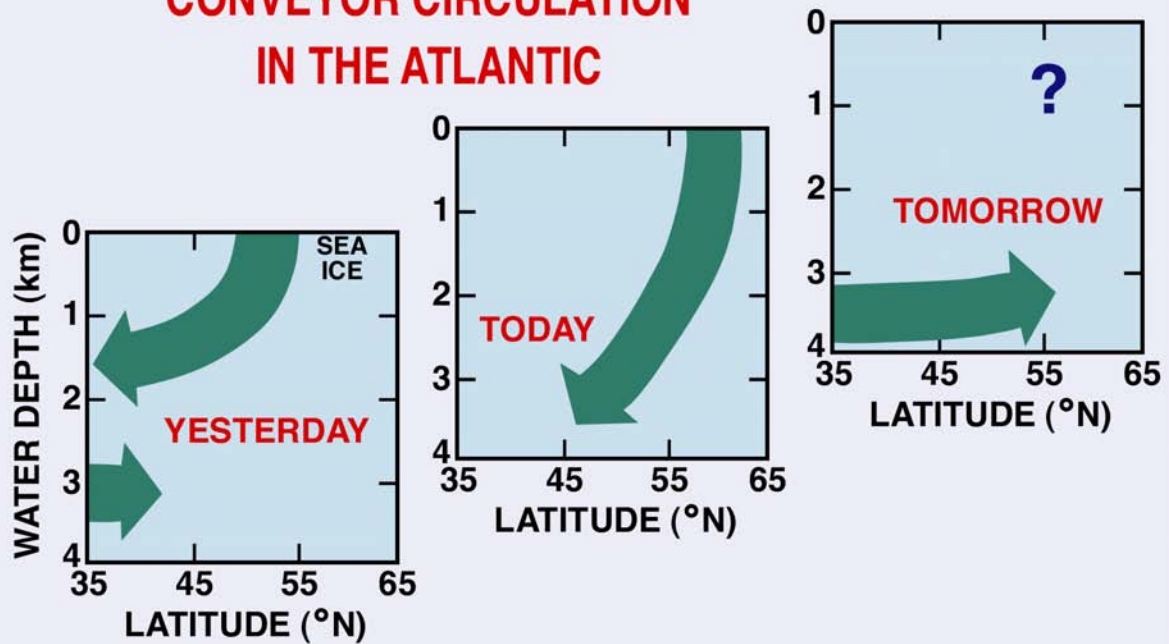
Key people involved in the measurements and ideas presented in this book are identified in the text along with their institution. Instead of using the standard scientific referencing system (authors and publication date), I have used small numbers to identify references listed at the end of the book. The references are chosen to provide an entre by the reader into each particular subject area.

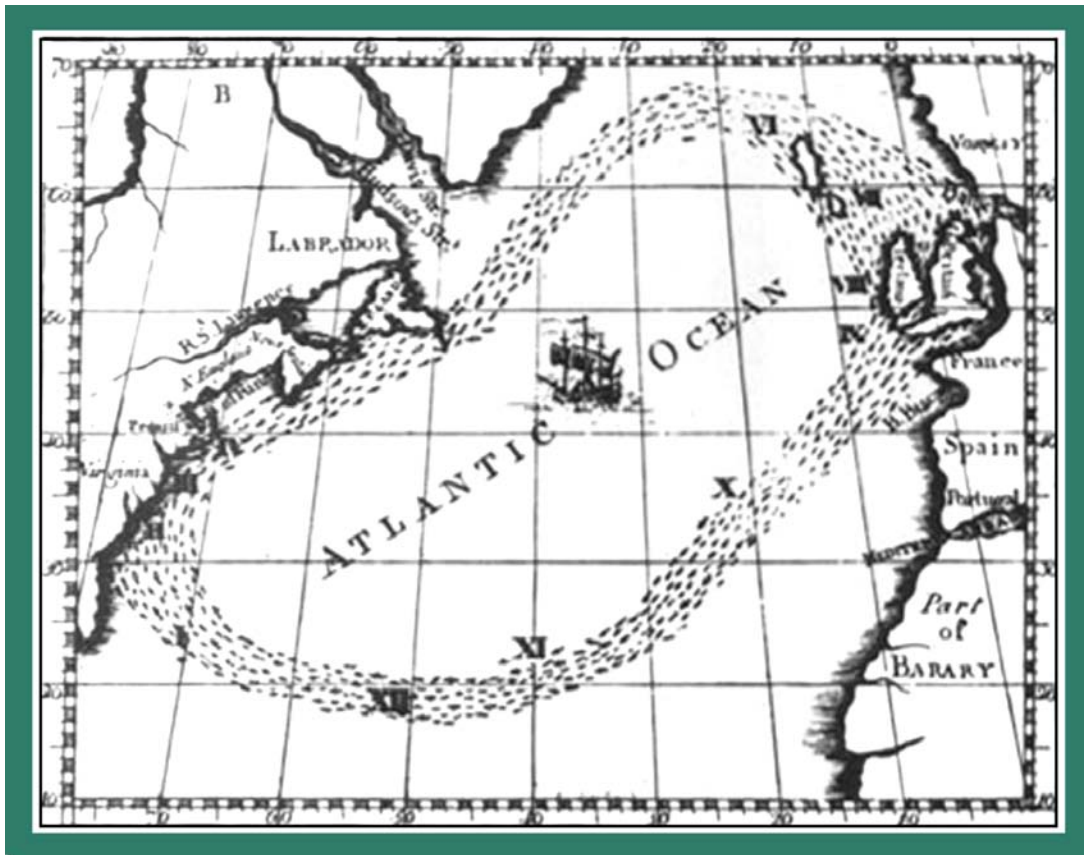
Acknowledgements

This book was inspired by Gary Comer (originator of Lands End Clothing Company) who late in life realized that the ongoing buildup of fossil fuel CO₂ in our atmosphere threatened the delicate Arctic ecosystems that he had come to love. This concern led him: 1) to encourage efforts to better understand our climate system and, in particular, its proclivity to undergo abrupt reorganizations, 2) to create a cadre of researchers equipped to expand these studies and 3) to communicate the results of these studies to the public in hopes of bringing about a demand for actions designed to halt the ongoing CO₂ buildup. Jeff Sachs, the head of Columbia University's Earth Institute, provided not only encouragement, but also the financial where-with-all to produce this book. LDEO's Taro Takahashi and Stew Sutherland generously helped by carrying out needed calculations. Klaus Lackner of our Earth and Environmental Engineering Department pumped me up with his ingenious ideas about CO₂ capture and burial. Robert Key of Princeton and Peter Brewer of MBARI kindly provided unpublished material for use in illustrations. Richard Alley (Penn State) and George Denton (University of Maine) helped to keep my aging brain alert by peppering me with neat ideas and observations. Patty Catanzaro produced the beautiful illustrations. Joan Totton turned my hand-written drafts into something readable.

SECTION 1

CONVEYOR CIRCULATION IN THE ATLANTIC





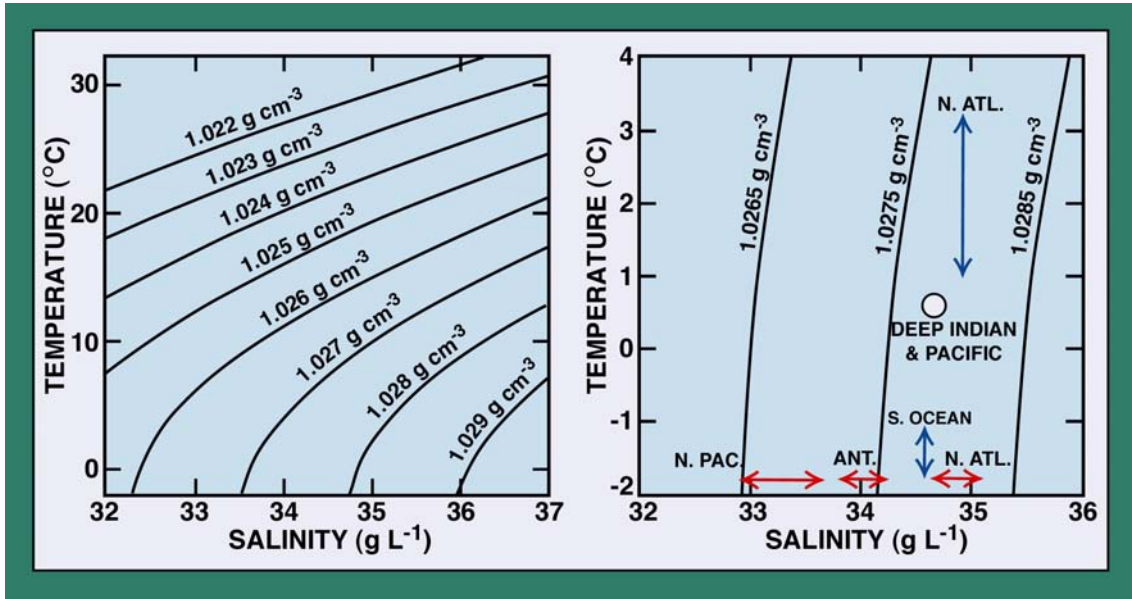
Benjamin Franklin's map of the Gulf Stream.

CHAPTER 1

TODAY'S CONVEYOR

It has long been realized that the Gulf Stream carries warm water into the Norwegian Sea. The release to the atmosphere of the heat delivered in this way takes much of the sting out of Scandinavian winters. Less obvious, but more important, is that this warmth inhibits the formation of sea ice. Were the Norwegian Sea to freeze over each winter, Scandinavia's climate would rival that in Siberia for the ice would prevent ocean heat from escaping to the atmosphere. As we shall see, during epochs of continental glaciation, winter sea ice appears at times to have covered the entire Norwegian Sea. Further, rather than being a product of the glacial world, expanded sea ice cover appears to have been a major player in bringing it about.

In order to understand this, we must first learn a bit about the forces which drive the oceans largest transport system, i.e., its thermohaline circulation. Key to this circulation is the difference between the density of surface waters in the polar regions and those in the tropics. Thermo refers to the temperature of the water; the colder it gets the more dense it is. Haline refers to the salt content of the water; the saltier it gets the more dense it is. In today's ocean, temperature dominates; thus, the densest surface waters are found at high latitudes. It is these polar surface waters that sink into and flood the abyssal ocean. Once in place, the downward mixing of heat from the overlying ocean and the upward mixing of heat escaping from the Earth's hot interior gradually warm and hence reduce the density of the resident deep water. This allows the slightly more dense surface waters to sink and under-ride the resident deep water lifting it to shallower depths. In this simplest of all conceptual oceans, one could imagine that this cycle is repeated over and over again until the original slug of deep water has been lifted all the way back to the surface. It would then flow poleward and be re-cooled to the point where it, once again, was densified to the point where it could sink into the abyss. While the circulation in

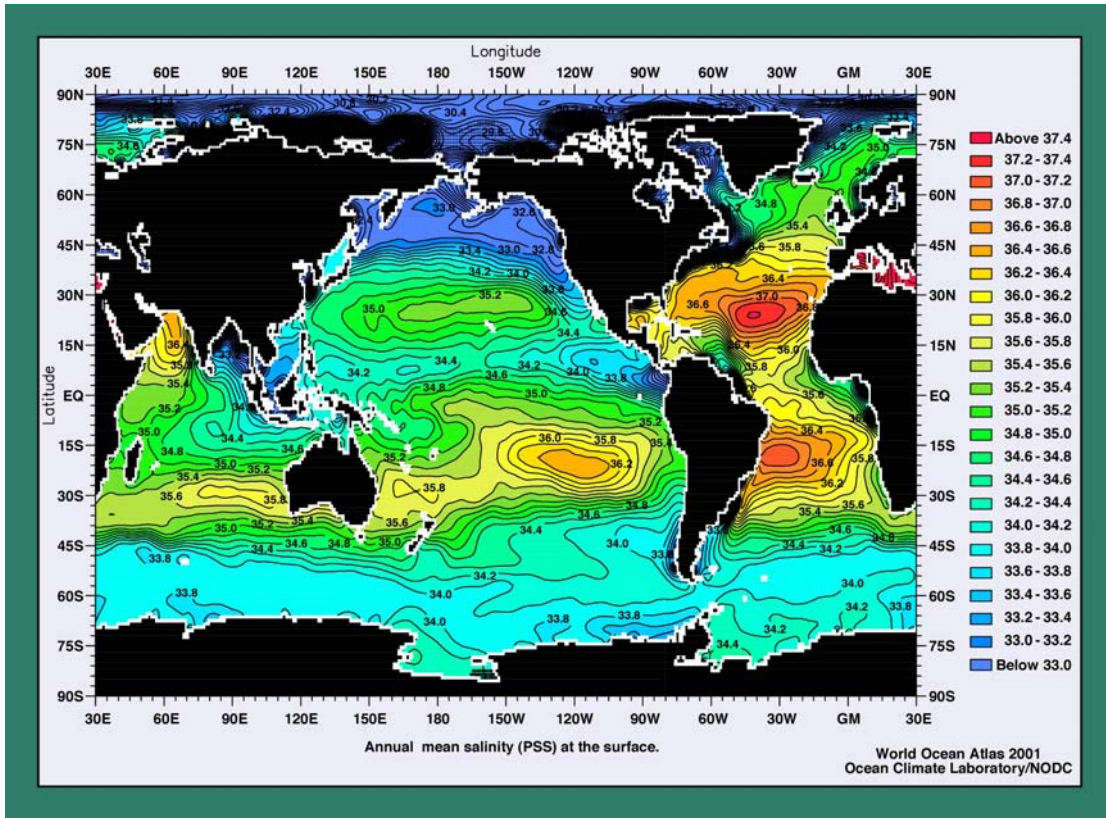


Density of surface sea water as a function of temperature and salt content. As the freezing point of sea water (-1.8°C) is approached, the dependence of density on temperature becomes ever smaller and hence it is the salt content that matters. The red arrows indicate the density range achieved if surface waters in the three high latitude regions of the ocean were cooled to the freezing point. The blue arrows represent the range of characteristics of deep waters formed in the northern Atlantic and of those formed in the Southern Ocean. The circle represents the characteristics of the water entering the deep Indian and Pacific Oceans from the circum Antarctic current.

the real ocean is more complicated, this hypothetical thermally-driven circulation provides a useful basis for our thinking.

It's the haline part which creates many of the complications. And, as we shall learn, provides the excitement. The important point is that to a large extent, the haline influence works to counter the thermal influence. To understand this we must consider the cycle of water vapor. The water which evaporates from the ocean eventually falls as rain or snow. However, during its residence in atmosphere, water vapor is transported by the winds from one place to another. Hence any given water molecule returns to the planet's surface at a different place than it originated. This gives rise to an important difference between those parts of the sea poleward of 40° latitude and those parts equatorward of 40° latitude. The difference is that at low latitudes evaporation exceeds precipitation while at high latitudes the opposite is true. In polar regions, precipitation and river inflow add more fresh water than is lost by evaporation. This excess dilutes the salt, and in this way the hydrologic cycle works to undo the density advantage provided by cold winter temperatures. The extent of the salinity reduction depends on the efficiency with which polar surface waters mix with their higher salinity counterparts elsewhere in the ocean. At steady state, the excess fresh water must be mixed away just as fast as it is supplied by precipitation and runoff.

As it turns out, the salinity reduction created in this way differs from place to place in the high latitude ocean. The largest reduction occurs in the northern Pacific where salt contents as low as 33 grams per liter are found. Next is the Southern Ocean where salinities of 34 grams per liter are common. The smallest reduction is found in the northern Atlantic where surface water salinities as high as 35 grams per liter occur. At the near freezing winter temperatures which prevail at high latitudes, the presence of one extra gram of salt per liter raises the water's density by the same extent as a 4 to 5°C cooling. Because of this, even if cooled all the way to the freezing point, surface waters in the northern Pacific are incapable of sinking more than a couple of hundred meters. In

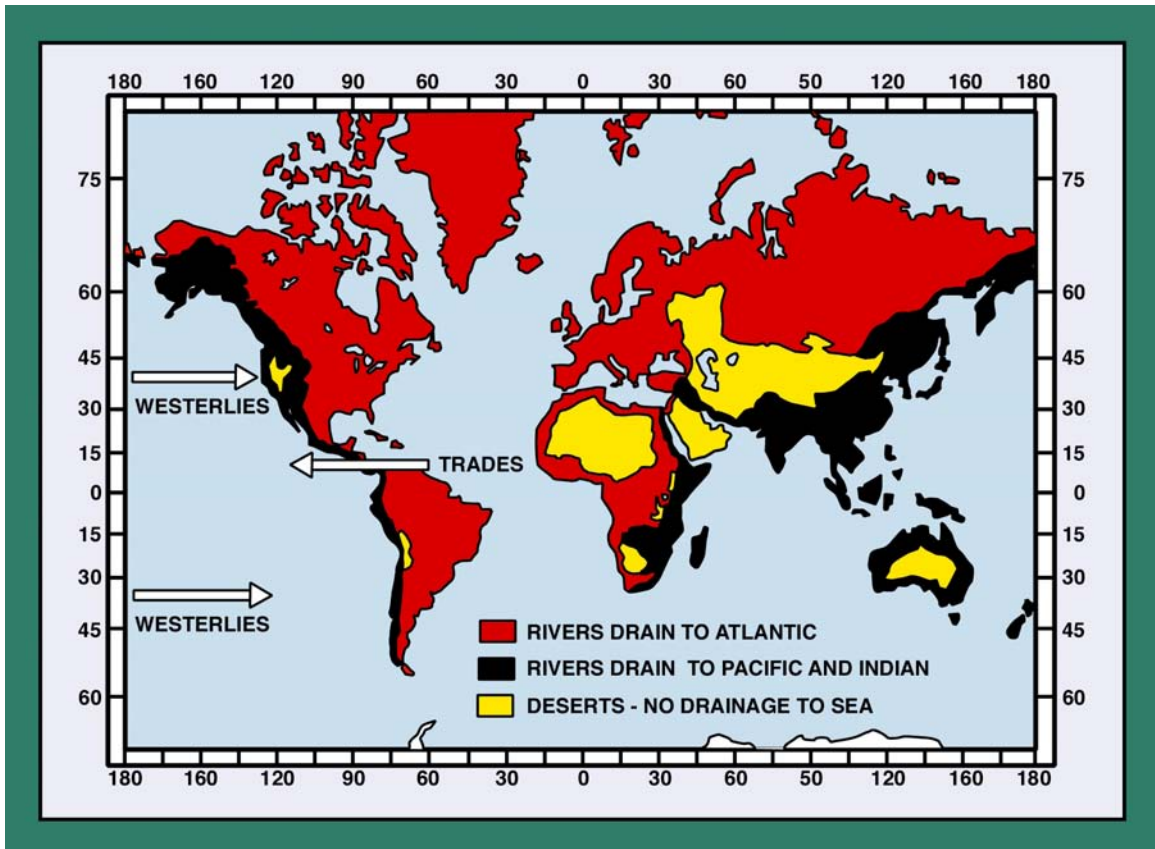


Map of the distribution of surface ocean salt content. The “warm” colors represent waters with higher than average salinities and the “cool” colors those with lower than average salinities. Note that in each ocean a salinity maxima exists in the latitude range 15° to 30° (i.e., from regions where evaporation exceeds rainfall). Also note that salinities in the northern Pacific are everywhere about two grams per liter lower than those at the same latitude in the northern Atlantic Ocean.

contrast, Atlantic waters cooled to 2°C (i.e., 4°C above the freezing point of sea water) are able to sink all the way to the bottom.

So why are the northern Atlantic and northern Pacific so different in this regard? There are two interrelated reasons. The first has to do with a more subtle aspect of the Earth's hydrologic cycle. Not only does this cycle create a net transport of water vapor from low to high latitudes, it also gives rise to a net transport from the Atlantic Ocean to the Pacific Ocean.^{1,2} This transport owes its existence to the interaction of planetary winds with major mountain ranges. The westerly winds which circulate around the planet at temperate latitudes encounter the high mountains which line the western edge of the Americas. These mountains act as water traps. The moisture contained in the air which enters the Americas from the Pacific Ocean can only reach the continental interior if it survives passage over these mountains. However, in order to get over, the air must rise. As a consequence, it cools causing much of its moisture load to condense and fall as rain or snow on the western slopes of the American Cordillera. Hence, rather than reaching the interior of the Americas, most of this water is carried back to the Pacific Ocean by rivers.

The situation for the Atlantic is quite different. The moist air carried by the westerlies to Europe and Africa need not pass over any high mountains and hence it can transport its burden of water vapor well inland. Of course, the vapor does not get too far before it falls as rain or snow and, of course, some of this precipitation runs back into the Atlantic via rivers which flow into the Baltic, the Arctic and the Mediterranean. As all three of these seas are linked to the Atlantic, the water is thereby returned to its source. There is, however, a difference; roughly half of the water which falls as rain and snow evaporates and continues its eastward journey. Despite repeated precipitation-evaporation cycles along the way, some of the Atlantic-derived water vapor is carried all the way across to the Pacific. Hence, the temperate latitude westerlies serve to transport water



Map of the global drainage system. The boundary between the black and red regions corresponds to the divide separating drainage to the Atlantic from that to the Indian and Pacific Oceans. The yellow areas are deserts from which no river outflow occurs. Also shown are the directions of the major wind systems.

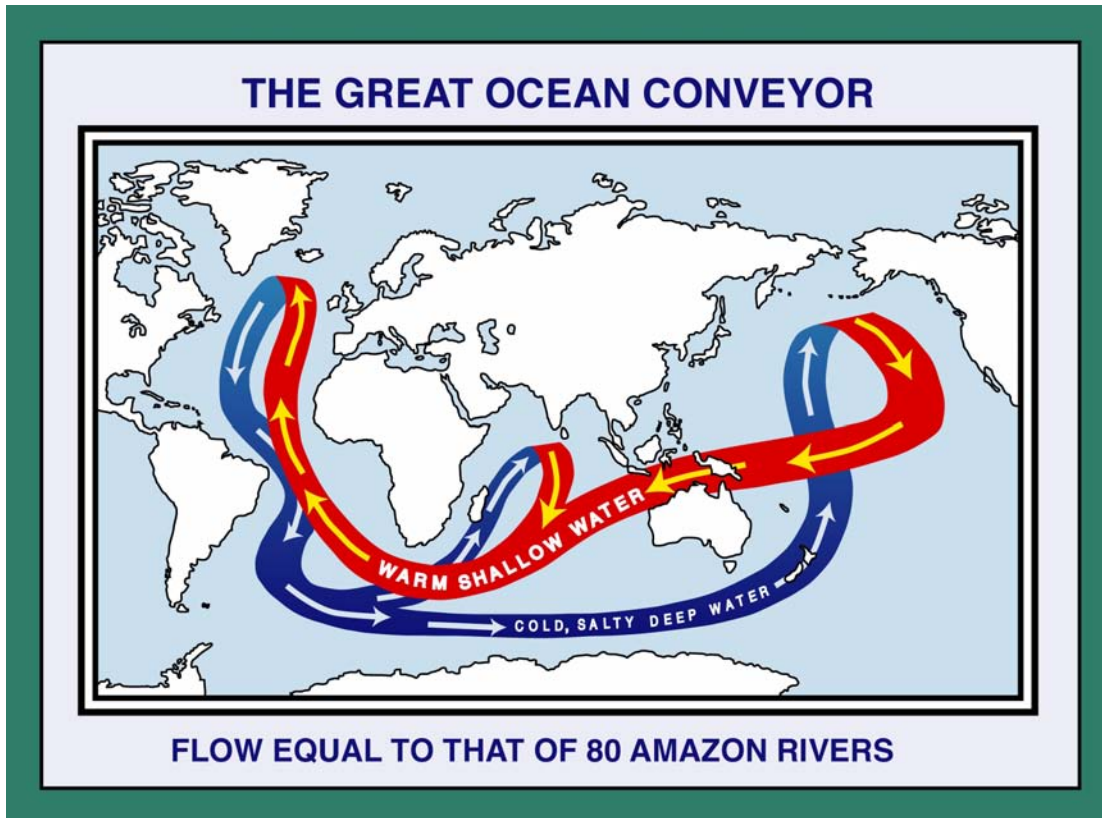
from the Atlantic Ocean to the Pacific Ocean and, in so doing, drive up the Atlantic's salinity and drive down the Pacific's salinity.

The trade-winds compensate for the eastward transport of air at temperate latitudes by carrying air back to the west. While these winds are blocked by the mountains in Africa, they take advantage of the break in the American Cordillera which occurs in Panama and transport water vapor picked up in the Caribbean Sea across to the Pacific. So, as do the westerlies, the trades serve to transport fresh water from the Atlantic Ocean to the Pacific Ocean.

Taken together, westerlies and trades export from the Atlantic an amount of water comparable to the flow of the Amazon River. The amount of water transported averages a staggering 0.27 ± 0.10 million cubic meters per second (i.e., 9 ± 3 trillion tons per year). The large uncertainty in this flux stems from the difficulties associated with documenting it. These difficulties relate to the fact that the export flux is only a small fraction (6 ± 2 percent) of the total evaporation from the Atlantic Ocean.

Were the Atlantic to be dammed off from the rest of the world ocean, this loss of water vapor would lower sea level in the Atlantic by about 8 cm per year. If continued for 1000 years, the lowering would be 80 meters. As salt remains behind, the salinity of the Atlantic water would rise by about three quarters of a gram per liter each millennium of isolation (a densification equivalent to that created by a 3°C cooling of winter surface waters in polar regions).

Of course, the Atlantic is not dammed off from the rest of the ocean. Hence an amount of water equal to that lost by vapor export flows back into the Atlantic. But, as the salt content of the returning water is only slightly different from that in the Atlantic, it does little to balance the Atlantic's salt budget. Hence, the enrichment of salt in the absence of the dam is about the same as that with the dam. As salt enrichment has likely gone on much as now for the entire Holocene (i.e., $\sim 11,000$ years), were the excess salt



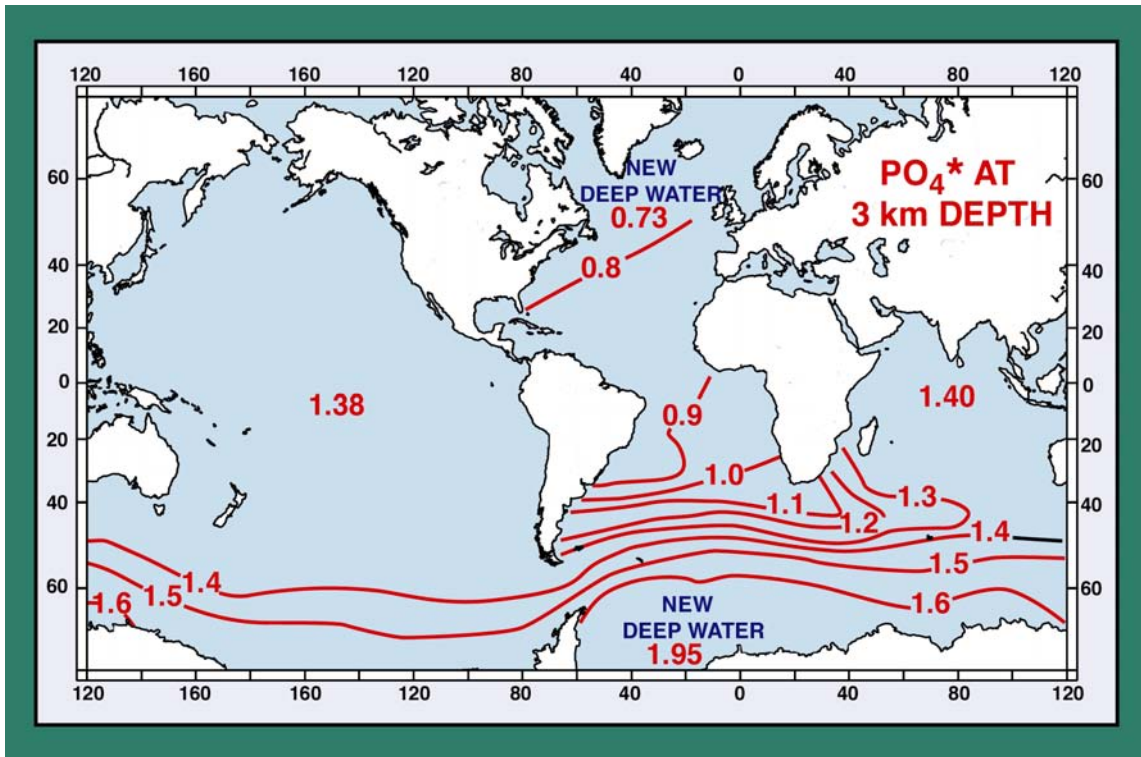
Cartoon of the global conveyor circulation. I say cartoon because the actual flow pattern is somewhat different and, of course, considerably more complex. For example, the northward transport of the Atlantic's upper limb water is confined almost entirely to the Gulf Stream and the lower limb water leaving the Atlantic hugs the tip of Africa. Also, much of the water entering the abyssal Pacific doubles back and upwells in the Southern Ocean.

not exported, the salt content of Atlantic waters would have increased by many grams per liter. Clearly this has not happened. The reason is that the densification of Atlantic waters caused by the buildup of salt must eventually create a circulation system capable of carrying away the excess salt as fast as it is being left behind by water vapor export.

This export of salt is accomplished by the Atlantic's conveyor circulation.³ The Gulf Stream brings salty water to the region around Iceland. Winter cooling makes this water sufficiently dense to sink to the abyss. This newly formed deep water flows southward the entire length of the Atlantic and passes around the tip of Africa. It carries with it the excess salt. The export of deep water is compensated by a return flow of lower salt content upper ocean water into the southern end of the Atlantic and also by the flow of low salinity northern Pacific water northward through the Bering Straits into the Arctic and from there into the Atlantic. While the input from the Bering Straits is only about one sixteenth that from the southern end of the Atlantic, as its salt content is ten percent lower than that in ambient Atlantic water, its impact on the salt budget is important. The Bering Straits inflow balances about one third of the fresh water lost by vapor transport.

The term conveyor is apt in that the north-flowing upper limb water supplies heat to the cold air moving across the Norwegian Sea and the south-flowing lower limb water carries away excess salt to the Southern Ocean. The transport by the conveyor is immense, averaging about 16 million cubic meters of water per second, a flow which equals that of 80 Amazon Rivers. This flow also matches global rainfall.

It is the sweeping action of the conveyor circulation which limits the extent of the reduction of salt content resulting from the precipitation and river water delivered to the northern Atlantic. The amount of excess fresh water delivered to the northern Atlantic is about 0.32 million cubic meters per second. When combined with the 16 million cubic meters of upper ocean water delivered by the conveyor's upper limb, the resulting



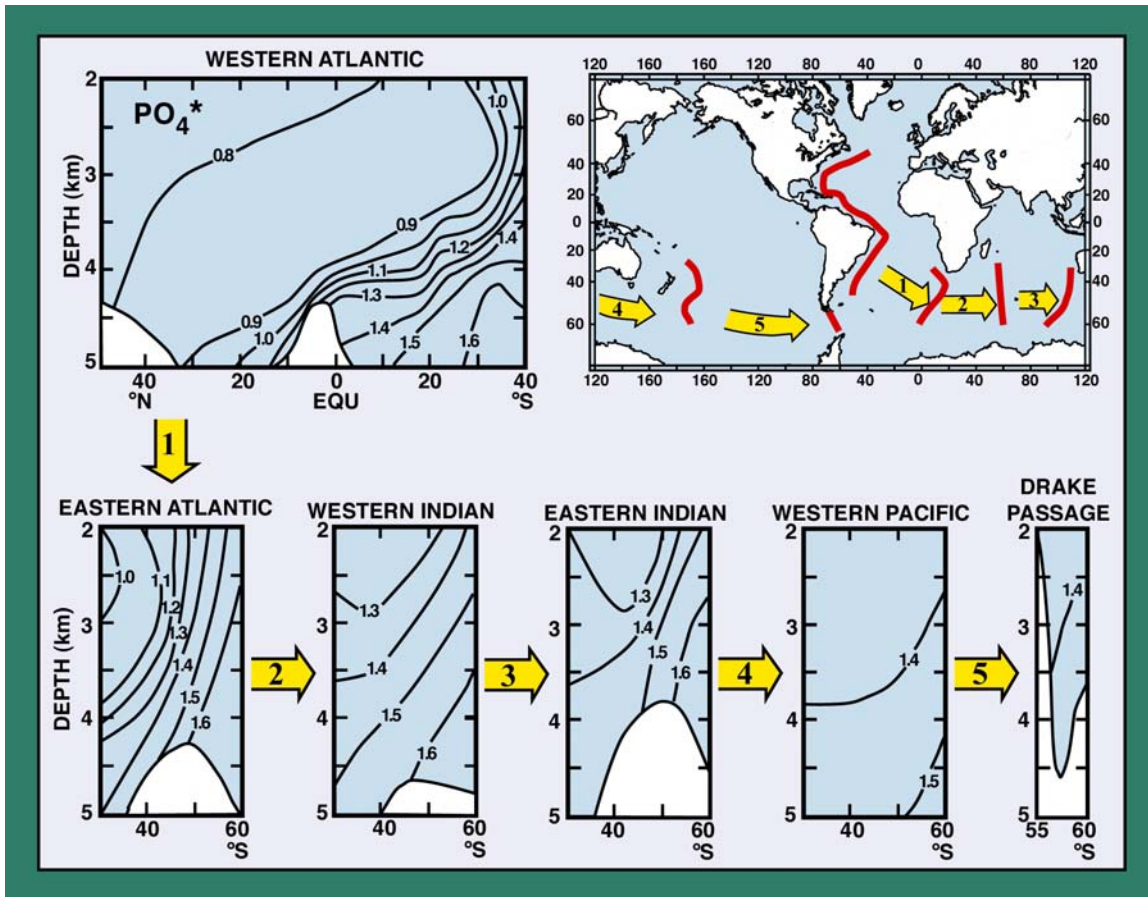
The distribution of PO_4^* (i.e., $PO_4 + O_2/175 - 1.95$) at 3 kilometers depth in the world ocean. Deep waters formed in the northern Atlantic have PO_4^* values in the range 0.73 ± 0.03 and those formed in the Southern Ocean values in the range 1.95 ± 0.05 . The two end members are homogenized in the circum Antarctic ring current creating the mixture ($\sim 45\%$ northern component and $\sim 55\%$ southern component) which floods the deep Pacific and Indian Oceans.

dilution in salt content is only 0.5 gram per liter. In the absence of the conveyor, the reduction in salt content would be much larger.

So, we see that northern Atlantic surface waters owe their high salinity in part to the export of water vapor from the Atlantic to the Pacific and in part to the efficiency with which the fresh water added to the northern Atlantic is swept away by the conveyor.

Only about half of the water replenishing that in the abyssal ocean is generated in the northern Atlantic. The other half sinks from sites along the margin of the Antarctic continent. As do the deep waters exiting the Atlantic, those produced in the Southern Ocean join the rapidly moving circum polar current. During a single pass around Antarctica, these injections of new deep water become thoroughly mixed. Part of this mixture peels off and heads northward into the deep Indian Ocean and part peels off and heads northward into the deep Pacific Ocean. One might ask how we know that the two types of deep water are produced in nearly equal amounts. The obvious approach would be to take advantage of the fact that the deep water formed in the northern Atlantic is several degrees warmer and a bit saltier than that produced in the Southern Ocean. However, as the northern source generates a package of waters with a range of temperatures and salinities, any estimate based on temperature or salt content has an unacceptably large uncertainty.

Fortunately, a much better way to make this assessment exists. It involves a property referred to as phosphate star (PO_4^*). It is based on a combination of the dissolved phosphate and dissolved oxygen gas concentrations in abyssal waters. One might ask how these biologically influenced properties could possibly be useful in determining the relative strengths of the two deep water sources for organisms living in the deep sea consume oxygen gas and in the process release to solution the phosphate contained in their food. Hence, as the deep water ages, its O_2 content steadily drops and its PO_4 content steadily rises. The secret lies in the fact that the ratio of the amount of



Sections showing how PO_4^* (i.e., $PO_4 + O_2/175 - 1.95$) changes down the western Atlantic and around the circum Antarctic ring. Deep waters formed in the northern Atlantic have PO_4^* values in the range 0.73 ± 0.03 and those formed around the perimeter of the Antarctic continent have values in the range 1.95 ± 0.05 . The entire deep Indian and deep Pacific are filled with water with a PO_4^* value of 1.38 ± 0.05 , i.e., about halfway between those for these two source waters. As can be seen, the contrast between waters rich in the northern component and those rich in the southern component seen to the south of Africa is largely mixed out during a single pass around the Antarctic continent.

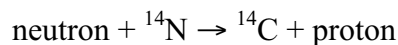
PO₄ released to the amount of O₂ consumed is very nearly constant throughout the ocean's interior. For each molecule of phosphate released close to 175 molecules of O₂ are consumed. Thus, the sum of PO₄+O₂/175 remains unchanged. The definition of phosphate star is as follows:

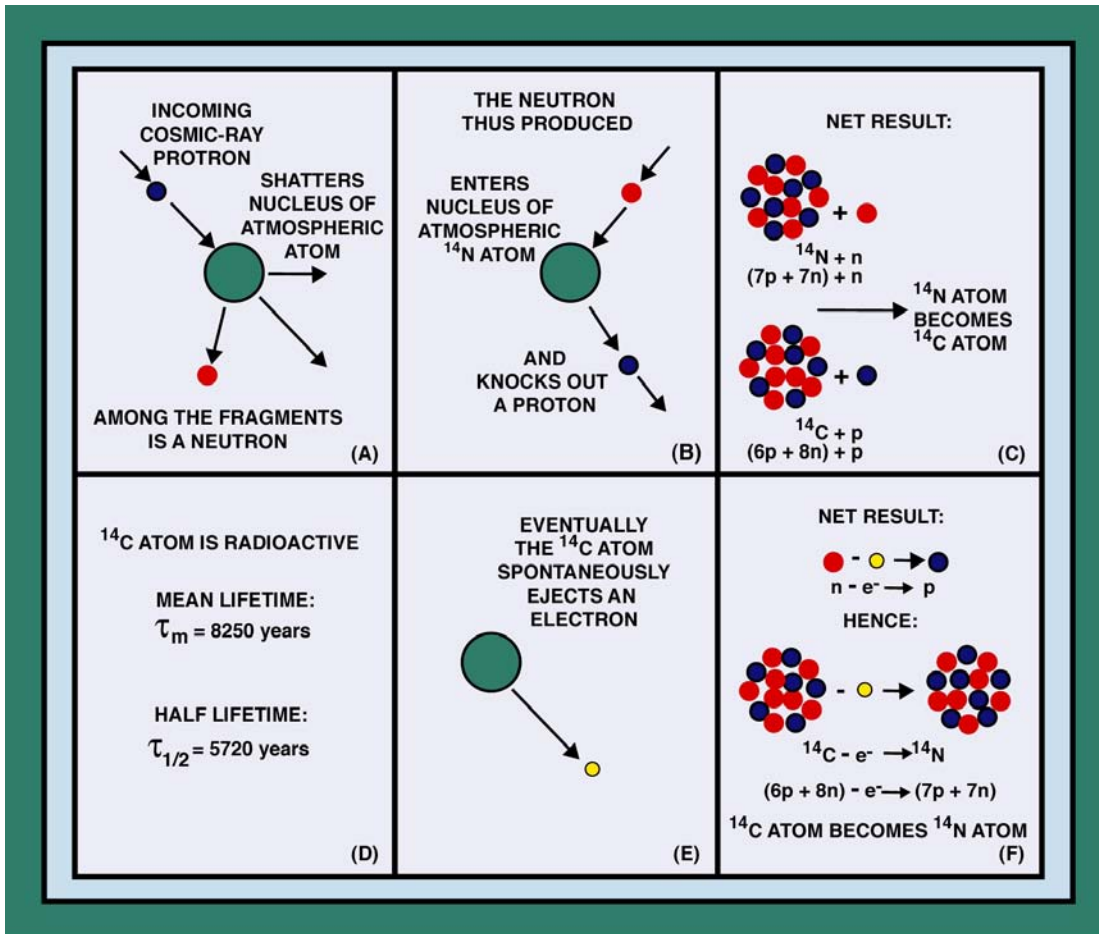
$$PO_4^* = PO_4 + \frac{O_2}{175} - 1.95$$

The constant, 1.95, is of no importance. Its value was arbitrarily chosen and could have just as well been set at 0.00.

Phosphate star proves to be superior to either temperature or salinity as a blend indicator because the range in deep waters produced both in the northern and in the southern source regions is small compared to the difference between the PO₄^{*} values for these two deep water suppliers. All the northern source waters have PO₄^{*} values which lie in the narrow range 0.73±0.03 and all the southern source waters values which lie in the narrow range 1.95±0.05 micromoles per liter. A 50-50 mixture of these two source waters would have a PO₄^{*} value of 1.34. Deep waters in the Indian and Pacific have nearly uniform PO₄^{*} values averaging 1.38 micromoles per liter. Hence, we can state with confidence that deep Pacific and Indian waters must consist of nearly equal parts northern and southern source water.

Although PO₄^{*} values define the blend of the deep waters formed in the northern Atlantic with those formed around the Antarctic continent, they do not constrain the rate at which these sources generate new deep water. Information regarding the rate of formation comes from the ratio of radiocarbon to carbon in the dissolved inorganic carbon (i.e., CO₂, HCO₃⁻, CO₃⁼) in sea water. A radiocarbon atom is produced in atmosphere when a neutron generated by the bombardment of galactic cosmic rays slips into the nucleus of a nitrogen atom and knocks out a proton:





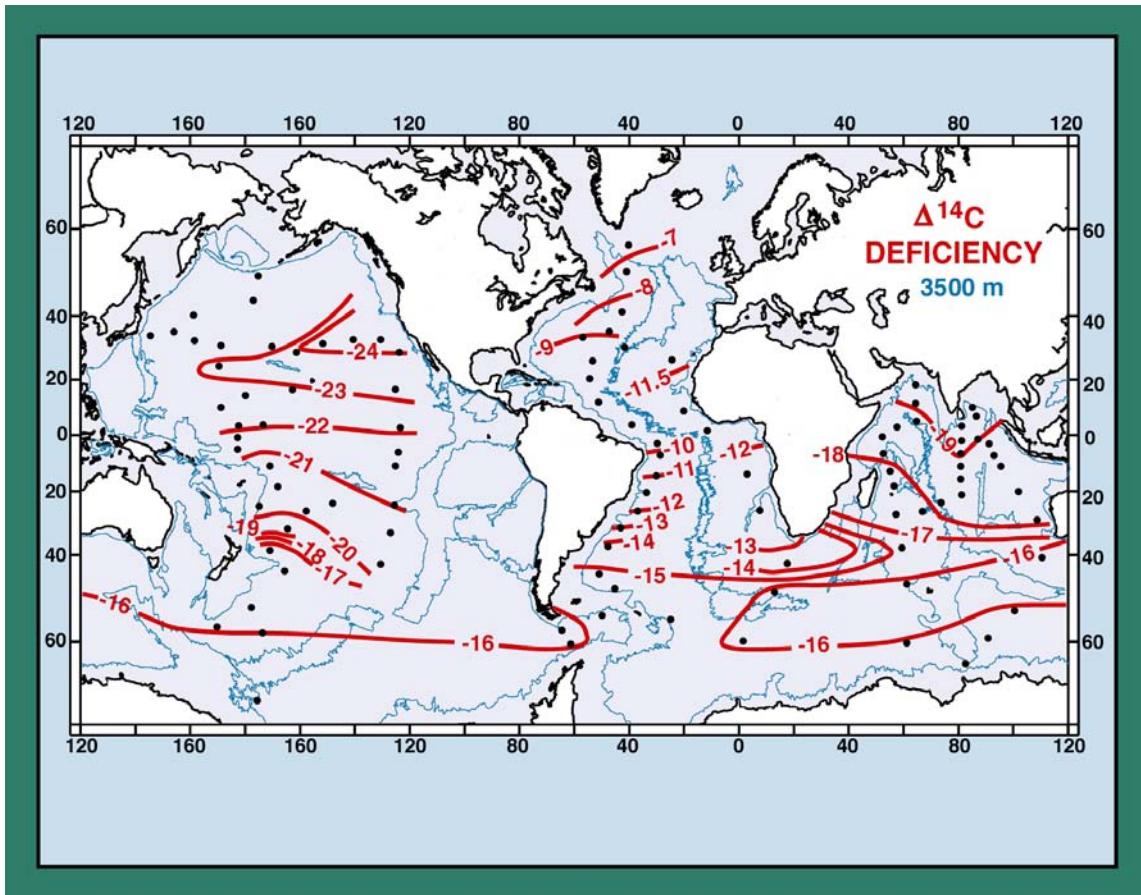
The “life cycle” of a carbon-14 atom. Created in the atmosphere by the collision of a neutron with the nucleus of a nitrogen atom, the average ^{14}C atom “lives” for 8250 years. Its existence is terminated by the ejection of an electron which returns the atom to its original form, ^{14}N .

The radiocarbon atoms formed in this way quickly latch onto oxygen atoms to become CO₂ molecules. These molecules exchange with inorganic carbon dissolved in the ocean.

¹⁴C is radioactive with a half-life of 5720 years. Its radiodecay depletes the radiocarbon at the rate of one percent each 80 years. In any given sample of sea water the extent of this depletion is a measure of the duration of its isolation from the atmosphere. The inorganic carbon in the deep equatorial Atlantic is depleted by 10 percent. That in the deep water in the equatorial Pacific and Indian Oceans is depleted by 20 percent.⁴ If referenced to atmospheric CO₂ these depletions would convert to isolation times of respectively 870 and 1840 years.

However, these ages do not provide meaningful measures of the rate of production of deep water. The key is to reference the ¹⁴C to C ratio in deep waters to that in their surface water sources. Despite the fact that these source waters are in contact with the atmosphere, they are deficient in ¹⁴C. This deficiency is maintained by mixing with radiocarbon-deficient subsurface water which counterbalances the increase resulting from the exchange with atmospheric CO₂. As a result, the inorganic carbon in newly formed deep waters in the northern Atlantic has 7 percent less ¹⁴C and the inorganic carbon in newly formed deep waters in the Southern Ocean has 15 percent less ¹⁴C than atmospheric CO₂. The large difference is related to the fact that while the northern Atlantic source region is fed by upper ocean water moving the length of the Atlantic, the Southern Oceans source regions are fed by the upwelling old deep water. This gives the waters feeding the northern source much more time to take up ¹⁴CO₂ from the atmosphere than those feeding the southern source.

Hence, a more appropriate way to compute the age of deep water is to reference its ¹⁴C to C ratio to that in the appropriate blend. So, for example, the source for deep waters in the equatorial Indian and Pacific Oceans are characterized by a ¹⁴C to C ratio half way between that for the northern source (i.e., -7%) and that for the southern source (i.e., -15%), namely -11%. The time required for ¹⁴C to decrease from minus 11 to minus



The distribution of natural radiocarbon at a depth of 3500 meters in the world ocean. The blue contours represent the margins of the ocean at this depth. The red contours represent the percentage difference in ^{14}C to C ratio from that in a hypothetical surface water which had achieved isotopic equilibrium with the CO_2 in the pre-industrial atmosphere. The black dots show the locations of the stations occupied as part of the GEOSECS survey.

20 percent is 880 years. Hence the average time elapsed since deep waters in the equatorial Pacific and Indian Oceans left the surface is close to 900 years. Based on its PO_4^* value, deep water in the equatorial Atlantic consists of 85 percent northern source and 15 percent southern source water. So the initial ^{14}C to C ratio in this blend is close to -8 percent. The time required for the ^{14}C to C ratio to decrease from -8 percent to -10 percent is 180 years.

Rather than bore the reader with the arithmetic, when account is taken of the volume of deep waters in the Atlantic and in the Indian - Pacific Oceans, it turns out that the amount of new deep water produced in each source region must average close to 16 million cubic meters per second.⁵ At this rate the waters in the deep Atlantic are replaced roughly once each 200 years and the waters in the deep Indian and Pacific roughly once each 800 years.

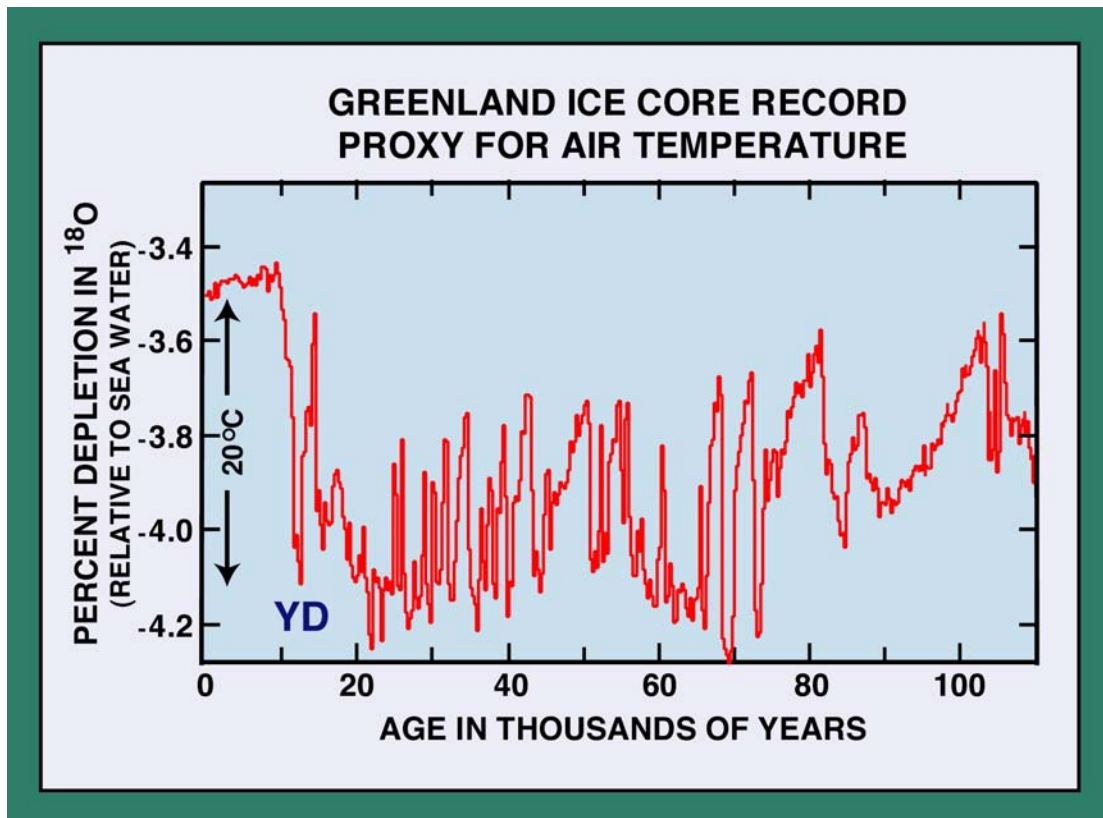
Now all the above calculations implicitly assume that the ocean's circulation system has been operating at steady state. In other words, none of the elements influencing its circulation have changed with time. Had a survey of O_2 , PO_4 and ^{14}C been carried out 1000 years ago, their distributions would have been the same as today's. It is not difficult to imagine that changes have occurred. For example, what is to prevent one of the two deep water sources from temporarily gaining the upper hand? Ocean theorists tell us that the total amount of deep water produced each year is set by the rate at which heat from the warm overlying water is mixed down into the deep sea. They also tell us that this mixing is generated by winds and by tides. But, what fixes the ratio of the amount of this water which descends into the northern Atlantic to that which descends into the Southern Ocean? Is there some feature of the system which locks in the one to one proportion?

As we shall see, compelling evidence exists that during glacial time the ocean's thermohaline circulation underwent a number of first order reorganizations. In addition, I suspect that during the last 10 or so thousand years the strength of the conveyor has

RADIOCARBON BALANCE SHEET FOR THE DEEP SEA	
GAIN	
VIA NORTHERN COMPONENT WATER	
WATER FLUX	$\sim 6 \times 10^{14} \text{ m}^3 / \text{yr}$
ΣCO_2 CONCENTRATION	$2.1 \text{ mol} / \text{m}^3$
$(^{14}\text{C} / \text{C})_{\text{no. comp.}} / (^{14}\text{C} / \text{C})_{\text{atm}}$	0.933
$(^{14}\text{C} / \text{C})_{\text{no. comp.}} - (^{14}\text{C} / \text{C})_{\text{mean deep sea}}$	0.13×10^{-12}
FLUX OF ^{14}C	165 mol / yr
VIA SOUTHERN COMPONENT WATER	
WATER FLUX	$\sim 6 \times 10^{14} \text{ m}^3 / \text{yr}$
ΣCO_2 CONCENTRATION	$2.2 \text{ mol} / \text{m}^3$
$(^{14}\text{C} / \text{C})_{\text{so. comp.}} / (^{14}\text{C} / \text{C})_{\text{atm}}$	0.846
$(^{14}\text{C} / \text{C})_{\text{so. comp.}} - (^{14}\text{C} / \text{C})_{\text{mean deep sea}}$	0.025×10^{-12}
FLUX OF ^{14}C	35 mol / yr
VIA PARTICULATE RAIN	
CARBON FLUX	$0.5 \text{ mol} / \text{m}^2\text{yr}$
$(^{14}\text{C} / \text{C})_{\text{part.}} / (^{14}\text{C} / \text{C})_{\text{atm}}$	0.930
$(^{14}\text{C} / \text{C})_{\text{part.}} - (^{14}\text{C} / \text{C})_{\text{mean deep sea}}$	0.126×10^{-12}
FLUX OF ^{14}C	20 mol / yr
AMOUNT OF ^{14}C ADDED TO THE DEEP SEA	220 mol / yr
LOSS	
VIA RADIOACTIVE DECAY	
VOLUME OF DEEP SEA	$\sim 8 \times 10^{17} \text{ m}^3$
MEAN ΣCO_2 CONCENTRATION	$2.3 \text{ mol} / \text{m}^3$
$(^{14}\text{C} / \text{C})_{\text{d.s.}} / (^{14}\text{C} / \text{C})_{\text{atm}}$	0.825
MEAN $^{14}\text{C} / \text{C}$ DEEP SEA	1.00×10^{-12}
AMOUNT OF ^{14}C IN DEEP SEA	$1.8 \times 10^6 \text{ mol}$
AMOUNT OF ^{14}C DECAYING IN THE DEEP SEA	220 mol / yr

Approximate radiocarbon budget for the global deep ocean (>1500 meters). Radiocarbon is added to the deep sea by waters descending from the surface of the northern Atlantic and from the surface of the Southern Ocean. Although the amount of deep water formed in these two source regions is about the same, radiocarbon delivery from the northern source exceeds that from the southern source by roughly a factor of five. The reason is that during their passage up the Atlantic the ΣCO_2 in the conveyor's upper limb waters have time to approach isotopic equilibrium with the atmosphere. By contrast, the deep waters upwelling in the Southern Ocean experience such a rapid turnaround that their ΣCO_2 has little chance to equilibrate. About ten percent of the radiocarbon reaching the deep sea is carried down either as organic matter which is eaten in the deep sea or as CaCO_3 which dissolves in the deep sea. Assuming that the ocean has been operating at steady state for the last several thousand years, these additions must be matched by radiocarbon decay in the deep sea (about one percent is lost each 800 years).

undergone millennial time-scale oscillations. It is not difficult to see why such changes might occur for seeds of instability lie in the fact that two sources feed the deep sea. An important point is that, as the replacement time of waters in the deep sea is many hundreds of years. Hence, the distributions of properties we map represent an average over that period of time. Although physical oceanographers would like to believe that the distribution of properties in the deep sea represents a steady state, is this the case? While no one has as yet put a finger on any aspect of the present day distribution of properties which suggests that this is not the case, paleoclimatic observations exist which could be explained were the relative strength of the two deep water sources changing back and forth on a millennial time scale. Were this the case, the Little Ice Age (~1350 to ~1850 A.D.) may have been a time when deep water formation in the northern Atlantic was stronger than today's and the Medieval Warm Period (~850 to 1350 A.D.) a time during which deep water formation in the northern Atlantic was somewhat weaker than today's. Before exploring this speculative point of view, let us turn our attention to the repeated reorganizations of thermohaline circulation which certainly occurred during glacial time.



Unlike the record in Antarctic ice which is dominated by stately 100,000- and 20,000-year cycles, that in Greenland ice is dominated by large and abrupt millennial-duration fluctuations known as Dansgaard-Oeschger events. Another difference between these records is that while ice as old as 900,000 years has now been recovered in Antarctica, despite repeated attempts the Greenland records all terminate during the last interglacial period giving rise to the hypothesis that Greenland's ice cap largely melted during the early phase of interglacial warmth. The temperature scale on this diagram is based on a deconvolution of downhole thermal profile rather than on the ^{18}O measurements themselves which suggest only half as large a temperature change as shown here. The reason appears to be that, during glacial time winter snowfall was largely absent, strongly biasing the ^{18}O toward the less negative summer values.

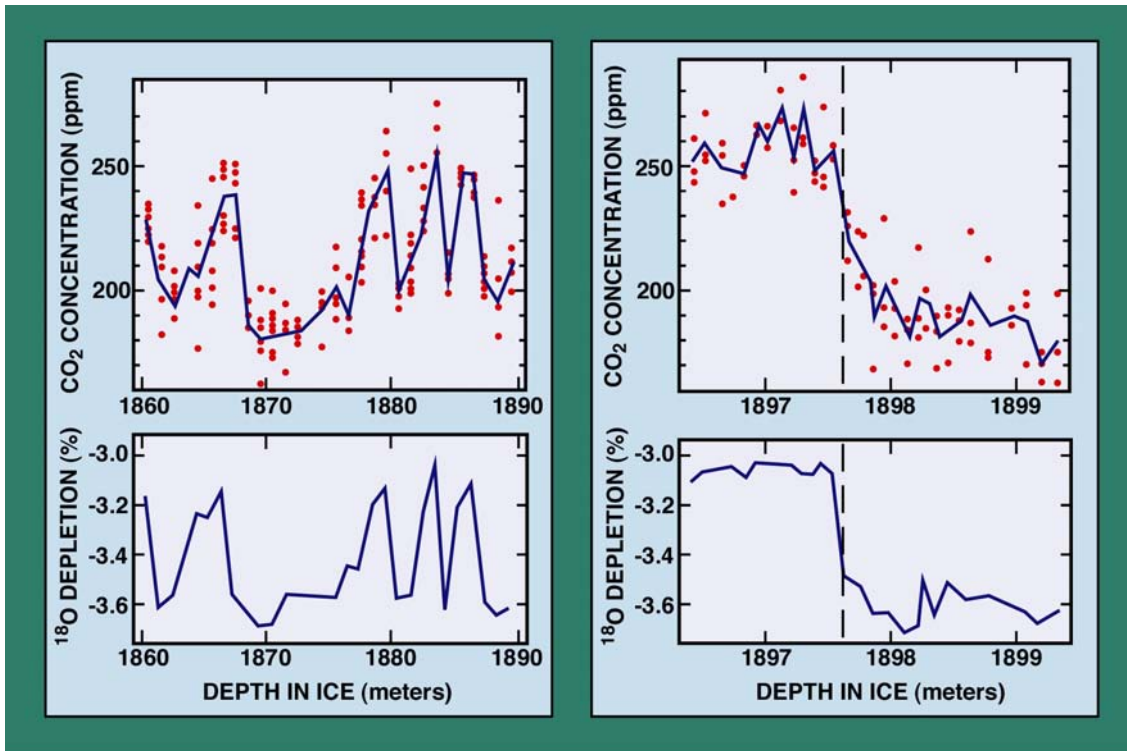
CHAPTER 2

YESTERDAY'S CONVEYOR

It was the record kept in Greenland ice that tipped me off to the likelihood that during glacial time frequent interruptions of the ocean's conveyor circulation occurred. In 1984, as I listened to Hans Oeschger, professor of physics at the University of Bern, lecture on the results of measurements made on a new ice core from southern Greenland, my mind began to churn. He pointed out that the series of back and forth jumps in air temperature (recorded by the ^{18}O to ^{16}O ratio in the ice) suggested to him that the Earth's climate system had at least two modes of operation and that it could abruptly jump back and forth between them. He went on to suggest that these states might somehow be related to conditions in the northern Atlantic Ocean. In addition, Oeschger showed new measurements, made in his laboratory, of the CO_2 content of air bubbles trapped in the ice. These results suggested that each time the climate system jumped into its intense cold mode the atmosphere's CO_2 content dropped to about 195 parts per million and each time it jumped back into its warm mode the CO_2 content rose to about 250 parts per million.⁶

As, for a number of years I had been pondering what might have caused the atmosphere's CO_2 content to drop to about 70 percent its pre-industrial value during glacial time, I was aware that only changes in the ocean's carbon cycle could produce such large changes in the atmosphere's CO_2 content. Hence, I picked up on Oeschger's suggestion regarding the involvement of the northern Atlantic and quickly realized that his two states very likely involved conveyor-on and conveyor-off episodes.

Although this scenario remains the top contender, it turns out that the hot clue which led me to propose it proved to be invalid. When detailed CO_2 analyses were performed on air samples from Antarctic ice cores, no jumps from 195 to 250 parts per million were found.⁷ During the same time intervals when values of 250 were encountered in Greenland, the Antarctic values remained close to 195. It was later



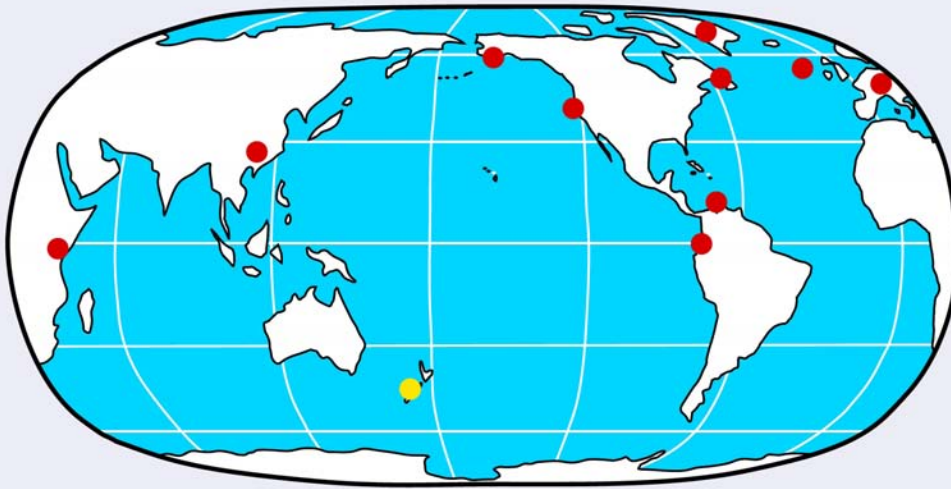
In the left-hand panel are plotted the CO₂ content of trapped air and the extent of ¹⁸O depletion in the ice itself for a several thousand-year period centered at about 30 thousand years ago. During this time interval, four Dansgaard-Oeschger (D-O) events occurred. As can be seen, during the warm phase (lower ¹⁸O depletion) of each D-O event, the CO₂ content of the bubbles rises from about 190 ppm to about 250 ppm. These increases were brought into question when CO₂ results from Antarctica ice cores became available. During this time period, all the measurements on air from Antarctic ice were in the range 190 to 200 ppm. The explanation appears to be that the high CO₂ values in the Greenland record were the result of the release within the ice of CO₂ generated as a result of interaction between CaCO₃ and acids contained in the ice. This explanation received strong support when it was shown by the Swiss group that the expected offset between the record kept in ice and that kept in air-bubbles did not exist (see right-hand diagram).

demonstrated that the high values in Greenland ice were very likely the result of in situ CO₂ additions caused by the interaction of acid aerosols with CaCO₃ dust (we'll return to this subject later in the book). So in a sense I was a lucky man. A false clue led me to the correct answer.

In 1984 only the Younger Dryas (i.e., the last of the back and forth jumps in temperature seen in the Greenland record) had been documented elsewhere on the planet. Evidence for the cold snap was first noted more than a century ago in records of plant remains from Scandinavia. Leaves of the dryas plant, which lives today only in the mountains, were present in sediments deposited near sea level during Younger Dryas time. The existence of this 1200-year duration cold snap was subsequently confirmed in pollen records from across northern Europe. In addition, evidence for the return of glacial conditions was recorded in sediment cores from the northern Atlantic by the renewed dominance of the cold-loving planktic foraminifera species, *N. pachyderma* (left coiling). This evidence nicely meshed with the idea that during the Younger Dryas the Atlantic's conveyor circulation was shut down. When deprived of the heat carried into the northern Atlantic by the conveyor, computer simulations produced a pronounced cooling in northern Europe but little change elsewhere on the planet.

The initial euphoria generated by this match between the pollen records and the model simulations was short lived, for evidence for Younger Dryas impacts outside the areas predicted by the simulations began to pop up. First of all, large and abrupt changes in the dust content of Greenland ice^{8,9} and in the methane content of the air trapped in bubbles in Greenland ice^{10,11,12} suggested widespread impacts. Dust implicated storminess in the Asian deserts¹³ and methane implicated the extent of tropical wetlands. Then, in rapid succession, Dorothy Peteet, a pollen specialist working at Columbia University, found evidence for a pronounced Younger Dryas cooling in Alaska;¹⁴ Jim Kennett, a paleoceanographer at the University of California, demonstrated that during

LOCATIONS OF WELL-DOCUMENTED YOUNGER DRYAS IMPACTS

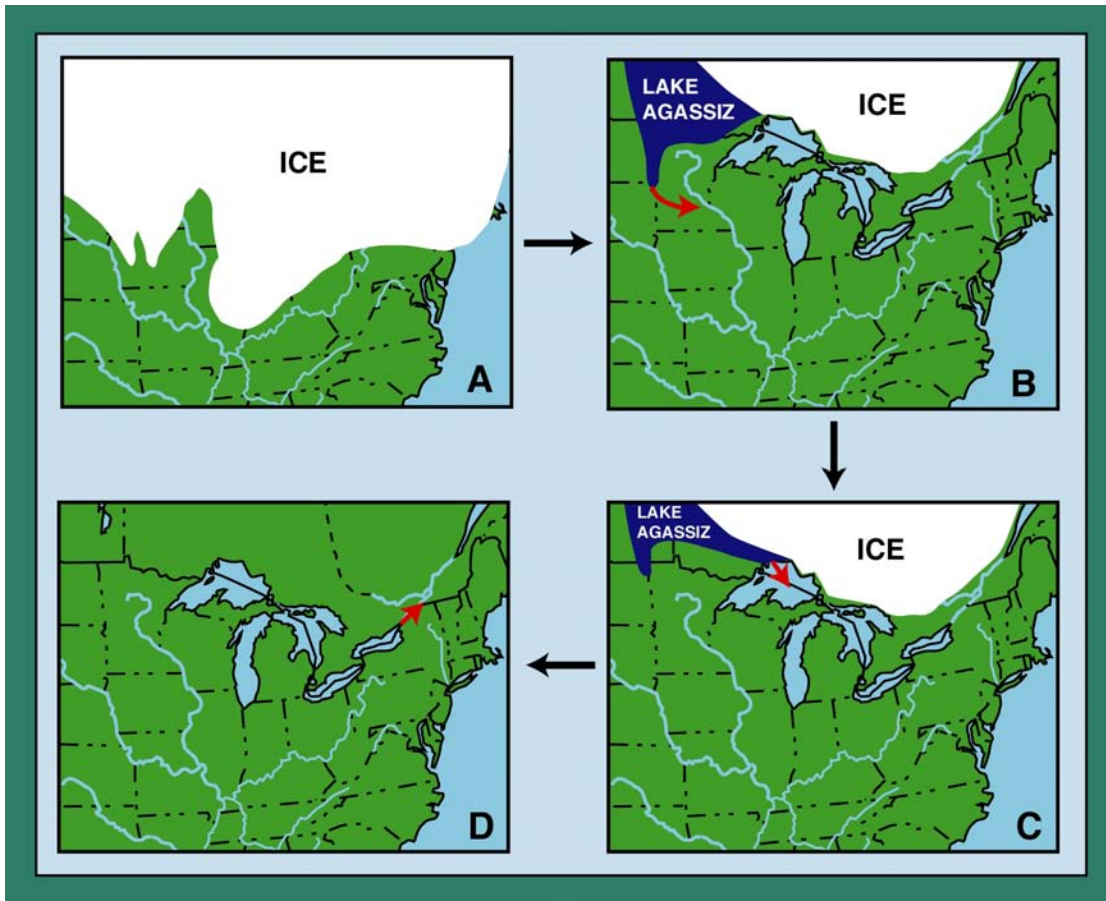


The red dots show the locations of well documented Younger Dryas impacts. These include records in ice (Greenland), in marine sediments (Venezuela's Cariaco Basin, California's Santa Barbara Basin, northern Atlantic), in moraines (equatorial Andes, Swiss Alps), in stalagmites (China's Hulu Cave), and in lake and bog sediment (Alaska, East Africa, and Newfoundland). The yellow dot represents a moraine in New Zealand's Alps whose radiocarbon age suggests that it represents a glacial advance which reached its maximum extent just prior to the onset of the Northern Hemisphere's Younger Dryas cooling.

the Younger Dryas a pronounced change in the upper ocean circulation occurred along the California margin;¹⁵ Konrad Hughen, as part of his PhD thesis at the University of Colorado, showed that pronounced changes occurred in sediments in the Cariaco Basin off Venezuela;¹⁶ Larry Edwards of the University of Minnesota showed that the Younger Dryas time interval stuck out like a sore thumb in the record from a stalagmite from China's Hulu Cave;¹⁷ Mark Atlabet of the University of Massachusetts used nitrogen isotope ratios organic matter from an Arabian Sea sediment core to show that the upwelling induced by monsoons weakened during the Younger Dryas;¹⁸ Lonnie Thompson of Ohio State University showed that this cold snap was recorded in ice from high in the tropical Andes.^{19,20} These results made clear that the impacts of the Younger Drays extended throughout the Northern Hemisphere and into the tropics. It must be stressed that in all these records the onset and ending of the Younger Dryas are abrupt. In the Greenland ice cores, where annual layers are readily counted, it was shown that both transitions were completed in a period of three decades. During this short period climate appears to have flickered back and forth between its medium cold and its extreme cold states.^{21,22}

These findings encouraged detractors of the conveyor hypothesis to propose an alternative scenario. Led by Columbia's Mark Cane, they postulated that, as the tropics rule the Earth climate, it was more likely that the Younger Dryas was triggered from the tropical Pacific than from northern Atlantic. Only in this way could its wide spread impacts be explained.

One problem these revisionists faced involved a smoking gun which points to the northern Atlantic. The Younger Dryas followed on the heels of a several-thousand-year-duration interval of warmth rivaling that we now enjoy. At the peak of glacial time, the margin of the great North American ice sheet reached as far south as Cincinnati. Then during the Bölling-Allerød warm interval which preceded the Younger Dryas, the ice front rapidly retreated to a position corresponding to the northern limit of the present day

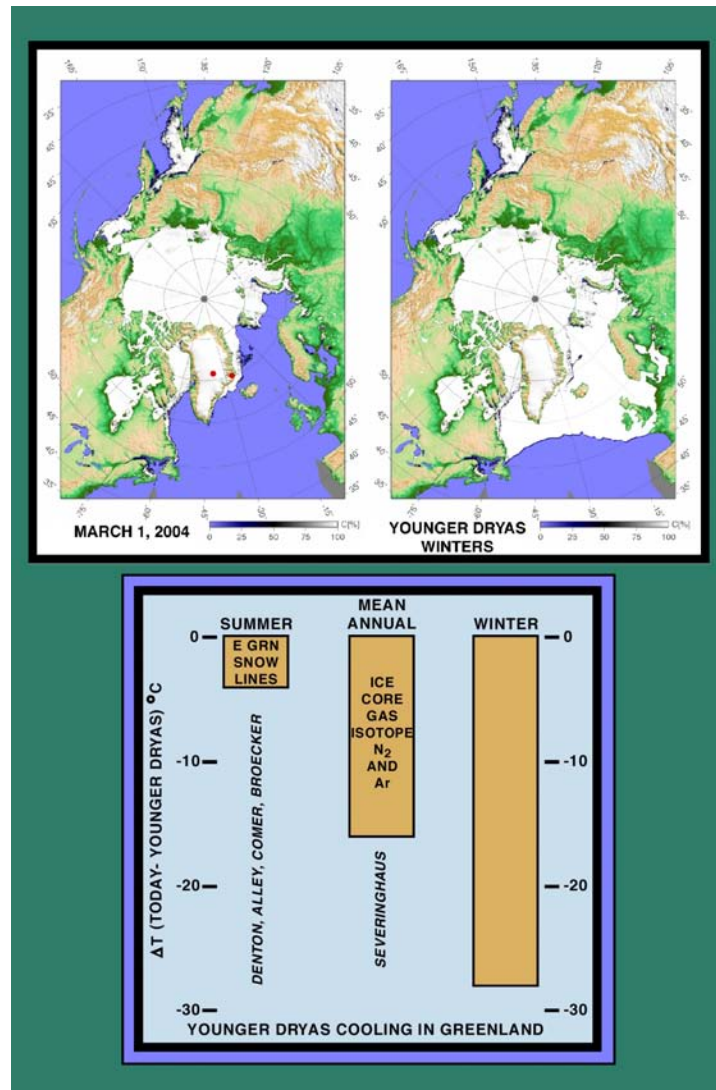


Maps showing the situation in the Great Lakes area (A) at the time of the last glacial maximum (~19,000 ^{14}C years ago), (B) just prior to the onset of the Younger Dryas (~11,000 ^{14}C years ago), (C) just after the onset of the Younger Dryas (~10,800 ^{14}C years ago), and (D) today. It is well documented that at close to 10,900 ^{14}C years ago, an ice dam which confined the waters of proglacial Lake Agassiz was breached allowing about 10,000 cubic kilometers of stored water to escape to the northern Atlantic. It is postulated that this deluge shut down the conveyor and thereby ushered in the Younger Dryas cold episode.

Great Lakes. Unlike what occurred during the demises of the ice sheets of each of the earlier climate cycles, this retreat was interrupted by a catastrophic release of 10 thousand cubic kilometers of water stored in the lake which filled in the depression in front of the retreating ice. Prior to the Younger Dryas, the lake waters had spilled over a rock sill into the Mississippi drainage and flowed to the Gulf of Mexico. Then one day part of the ice which formed the northern shoreline of the lake gave way opening a new and lower outlet.^{23,24} Ten thousand cubic kilometers of stored water was suddenly released and flooded into the northern Atlantic. The conveyor scenario holds that this deluge diluted the salt content of surface waters in the northern Atlantic to the extent where surface waters were no longer sufficiently dense to sink to the abyss. This brought the conveyor to a halt and thereby triggered the Younger Dryas cold epoch.

While nicely explaining the abrupt onset of the Younger Dryas, this scenario fails to explain its equally abrupt ending. It also fails to explain why the impacts were felt throughout the Northern Hemisphere and in the tropics as well. Using simulations of the ocean, modelers provided an answer to the first of these deficiencies. If the model ocean preferred the conveyor-on mode, then, at some point, its circulation would spontaneously (and abruptly) revert to that mode of operation.

The second deficiency proved to be a tougher nut to crack. The answer came only after a new realization had sunk in. Several lines of evidence suggested that the extent of cooling during Younger Dryas winters was several times larger than the extent of cooling during Younger Dryas summers. The most convincing being the finding by University of Maine's George Denton and Penn State's Richard Alley, that while the Greenland ice core gas measurements required a 16 degree centigrade mean annual cooling, the extent of Younger Dryas age glaciers in the mountains of eastern Greenland pointed to only a 4° to 6°C summer cooling.²⁵ Taken together, these two observations suggested a whopping ~30°C winter cooling. The only way to produce such a large winter cooling would be to freeze over much of the northern Atlantic. What better way to trigger such a freeze-over



Measurements by Jeff Severinghaus of the isotopic composition of the nitrogen and argon trapped in Summit Greenland ice provide a firm estimate that the mean annual air temperature was 16°C colder than today during the Younger Dryas. In contrast, the lowering of the snowlines in the mountains surrounding Scoresby Sund suggests only a 5°C cooling. The explanation for this large difference appears to be that winters during the Younger Dryas were so cold that little snow fell in the mountains of eastern Greenland. Therefore the snowline lowering records only summer conditions. Together, this 5°C summer cooling and a hypothesized 27°C winter cooling would yield the mean annual cooling documented by Severinghaus.

The ultra cold winter conditions require a climate akin to that in Siberia. This could only have been possible if the northern Atlantic was totally ice bound during winter months. During glacial time, a shutdown of the Atlantic's conveyor circulation would have starved the northern Atlantic of ocean-borne heat and permitted sea ice to form. In the presence of sea ice, no heat could escape from the ocean to the atmosphere.

Not shown on the Younger Dryas map are either the glacial ice which covered much of Canada and Scandinavia, or the expansion of sea ice in the northern Pacific. The purpose of this omission is to focus the readers' attention on the northern Atlantic.

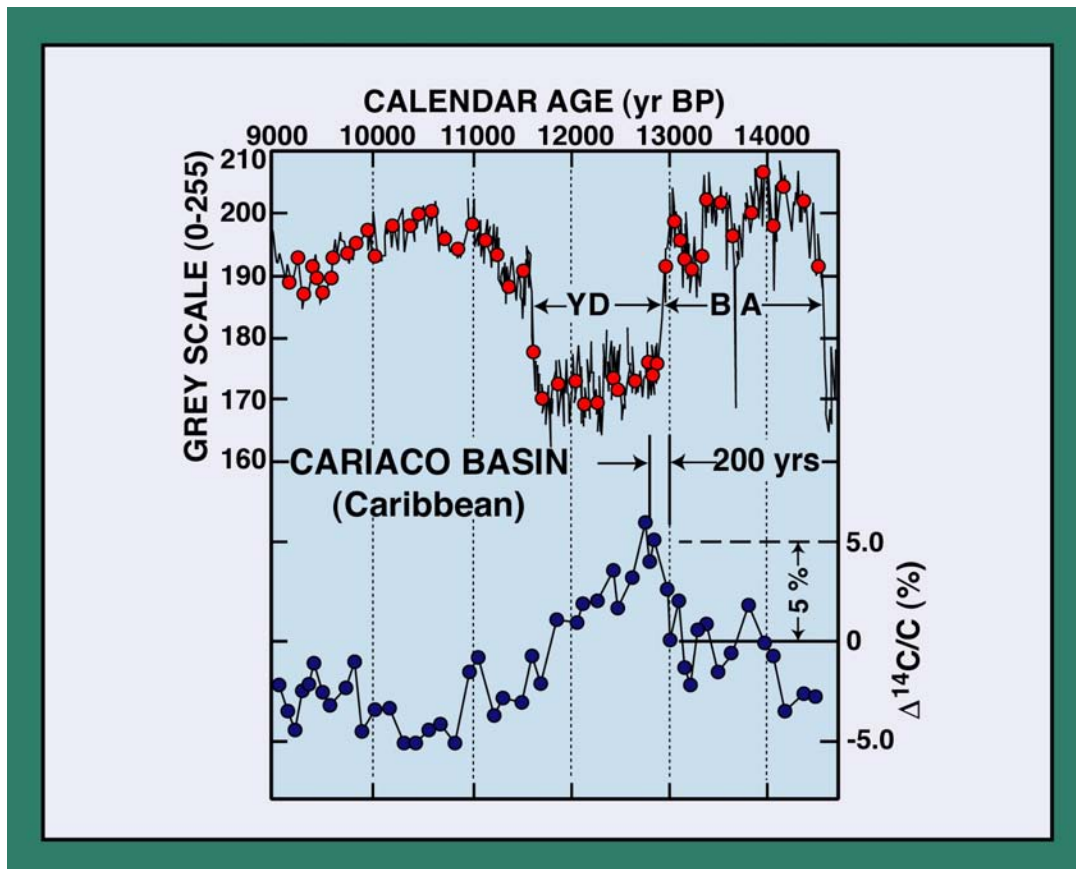
than to shut down the supply of ocean heat. The presence of sea ice would greatly amplify the cooling of northern Europe for not only would the heat delivered by the conveyor be cut off, but also any heat transported by alternate routes to the northern Atlantic. Winters in northern Europe would have become akin to those experienced today in Siberia.

But this scenario left the far-field impacts unexplained. As the onset of these impacts was also abrupt, some means was needed to transmit the message from the northern Atlantic quickly as well as efficiently. Of course, the proponents of a tropical trigger are quick to point out that this challenge would be more easily met by a tropical trigger.

John Chiang, a modeler at the University of California, supplied a tantalizing explanation. He showed that when winter sea ice covering a major portion of the northern Atlantic was introduced into his simulation, the model's Inter-Tropical Convergence Zone was pushed to the south.²⁶ Locales like Venezuela's Cariaco Basin which now lie within the bounds of the convergence zone's seasonally shifting rain belt found themselves to the north of the belt. This perturbation affected not only the Atlantic sector of the tropics but the rest of the tropics as well.

George Denton proposed a second link to the tropics. As model results obtained by Scripps Oceanographics' Tim Barnett²⁷ showed that widespread snow cover in Eurasia weakened the monsoons, Denton envisioned that during the Younger Dryas sea ice cover in the northern Atlantic would have led to more persistent snow cover in Eurasia and hence to weaker monsoons. Such a weakening would account for Larry Edward's record in the Hulu Cave stalagmite and Mark Altabet's record in Arabian Gulf sediments. In any case, the scenarios by Chiang and by Denton provide a means of rapidly transmitting a strong message from the northern Atlantic to the tropics.

One might ask what exactly is meant by a conveyor shutdown. Does it imply that the conveyor circulation ceased? If so, how was the salt left behind by water vapor

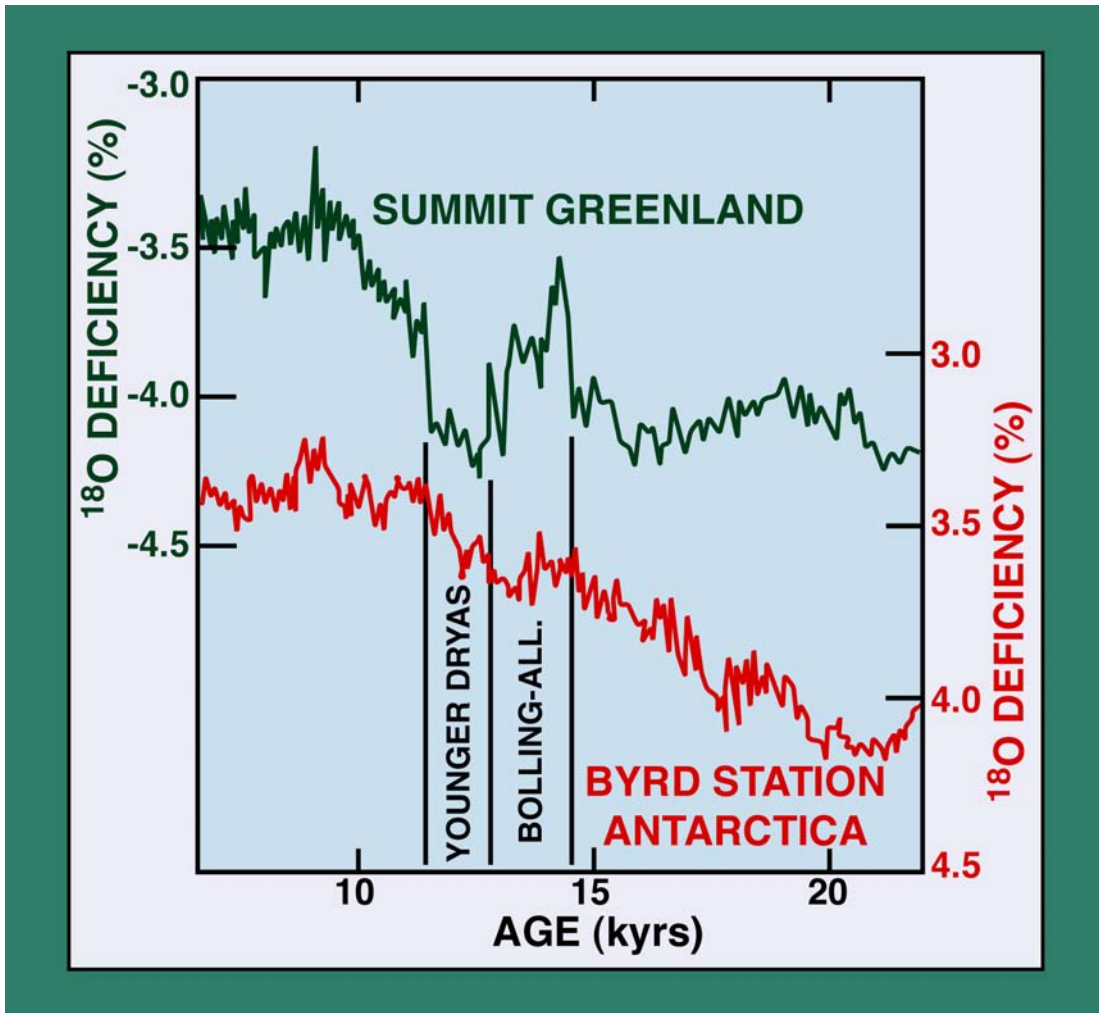


Based on counts of annual layers, Konrad Hughen was able to construct an absolute chronology for a sediment core from the Cariaco Basin off Venezuela. Based on this chronology, he converted radiocarbon measurements on planktic foraminifera to ^{14}C to C ratios at the time the shells formed. As the sediment deposited during the Younger Dryas is lighter in color than that deposited during the preceding Bölling-Allerød or the subsequent Holocene, the boundaries of this episode during which glacial conditions returned are well marked. As can be seen, during the first 200 years of the 1200-year duration YD, the ^{14}C to C ratio in Cariaco Basin surface waters (and presumably also in the atmosphere) rose by 5 percent. This rise is thought to be the result of the shutdown in the delivery of ^{14}C to the deep sea. As a result the newly produced ^{14}C atoms were backlogged in the atmosphere and upper ocean. After 200 years had passed, somewhere in the polar regions, renewed deep-water production must have commenced which caused the backlogged ^{14}C to be drained back down. The circles represent the ^{14}C measurements.

transport exported from the Atlantic? Did deep water formation in the Southern Ocean take up the slack? While these questions remain largely unanswered, we do have some hot clues as to what went on. First of all, as shown by Konrad Hughen at the onset of the Younger Dryas, the radiocarbon concentration in upper ocean inorganic carbon and atmospheric CO₂ began an astounding rise.²⁸ In 200 years, it climbed by 5 percent. The obvious explanation is that a shutdown of the conveyor would have starved the deep sea of up to three quarters of its radiocarbon supply. This radiocarbon would instead have been backlogged in the upper ocean and atmosphere.

But why did the rise in radiocarbon stall after 200 years and slowly subside during the remaining 1000 years of the Younger Dryas? Jochem Marotzke, a German physical oceanographer, provided the answer. He explained to me that if one of the major deep water sources were to be shut down, some other source would have to take up the slack. The dedensification of the deep water reservoir resulting from earth heat (from below) and from downward upper ocean heat (from above) would eventually create an opportunity for some alternative mode of deep water formation to spring into existence. Marotzke concludes that the mismatch between dedensification and resupply could not persist for more than a couple of hundred years. So it appears that this is exactly what happened 200 years into the Younger Dryas. A reorganization occurred in the ocean's thermohaline circulation system which led to the production of more deep water. This allowed the radiocarbon which had been backlogged in the upper ocean during the first 200 years of the Younger Dryas to be transferred to the deep sea.

While the identity of this new mode remains obscure, we do know that it did not involve a rejuvenation of the Atlantic's conveyor, for had this happened, the winter sea ice cover in the northern Atlantic would have been largely eliminated. But, as the air temperature in Greenland, the inflow of Asian dust, the reduced atmospheric methane inventory and the weakening of the monsoons remained largely unchanged for the entire duration of the Younger Dryas, a conveyor restart can not be the answer.

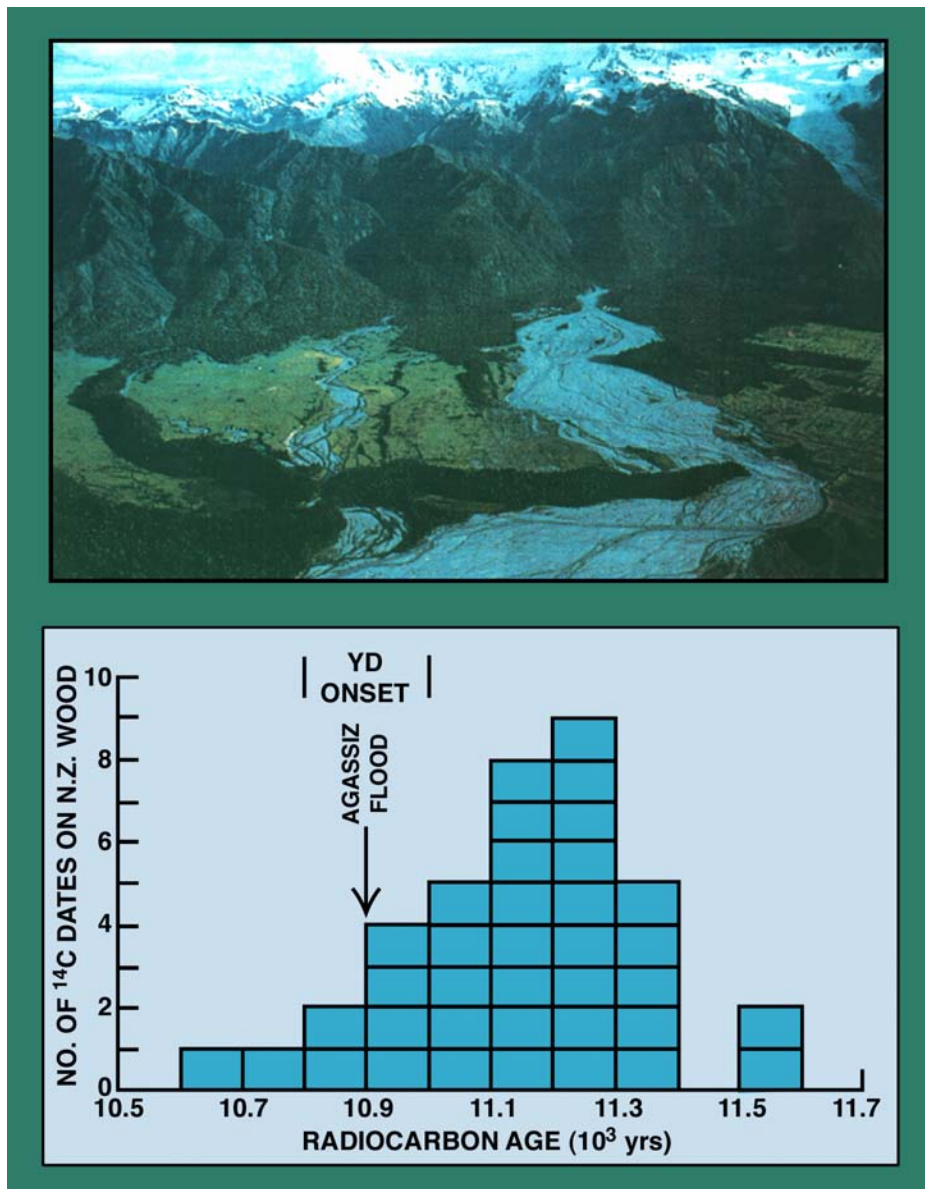


Comparison of the ice core ^{18}O records for Greenland's Summit locale and Antarctica's Byrd Station locale for the transition from the last glacial maximum to the Holocene. As can be seen, the records are antiphased. Prior to the time of the Bölling-Allerod, Antarctica warmed while Greenland appeared to have cooled a bit. Then when Greenland underwent its pronounced Bölling-Allerod warming, the warming in Antarctica came to a halt. Finally, when Greenland lapsed in its Younger Dryas cold, warming in Antarctica resumed. The chronology for the Greenland record is based on the counting of annual layers. The Antarctic record is correlated with that for Greenland based on the methane content of air trapped in the ice.

The contrast in the records kept in Greenland and Antarctic ice during the transition from full glacial to full interglacial conditions offers a further clue. At both ends of the planet, full glacial conditions prevailed as late as 20 thousand years ago. Then about 19 thousand years ago, the first signs of a “thaw” became apparent in Antarctica.²⁹ The air temperature there commenced a steady rise which continued to about 14 thousand years ago. Then a pause referred to as the “Antarctic cold reversal” occurred and for the next two thousand years there was no further warming. This pause continued until the time of the onset of the Younger Dryas at which point air temperatures resumed their warming reaching close to their present day level by the end of the Younger Dryas. The record in Greenland is quite different. Between 19 thousand and 14 thousand years ago, air temperatures remained at their glacial level. Then, just at the time the warming in Antarctica stalled, temperatures in Greenland underwent a dramatic increase ushering in interglacial conditions. Then just at the time the plateau in Antarctic temperatures came to its end and the temperature resumed its rise, Greenland underwent its dramatic Younger Dryas cooling.

A possible explanation for what happened in Greenland is provided by the conveyor scenario. During glacial time, the conveyor as we know it was shut down. Then about 14 thousand years ago, it snapped back into action, eliminating winter sea ice cover in the northern Atlantic and ushering in the warm climate of the Bölling-Allerød time interval. Then the collapse of the ice front which allowed a huge amount of stored melt water to deluge into the Atlantic, once again shut down the conveyor returning northern Europe to its glacial state.

The fact that events in Antarctica during this period were antiphased with respect to those in Greenland points a finger at the balance between deep water production in the Southern Ocean and deep water production in the northern Atlantic.^{30,31} In simplest terms, it suggests that when the conveyor is operative, the role of the Southern Ocean is diminished and vice versa. Unfortunately, at this point, the details elude us.

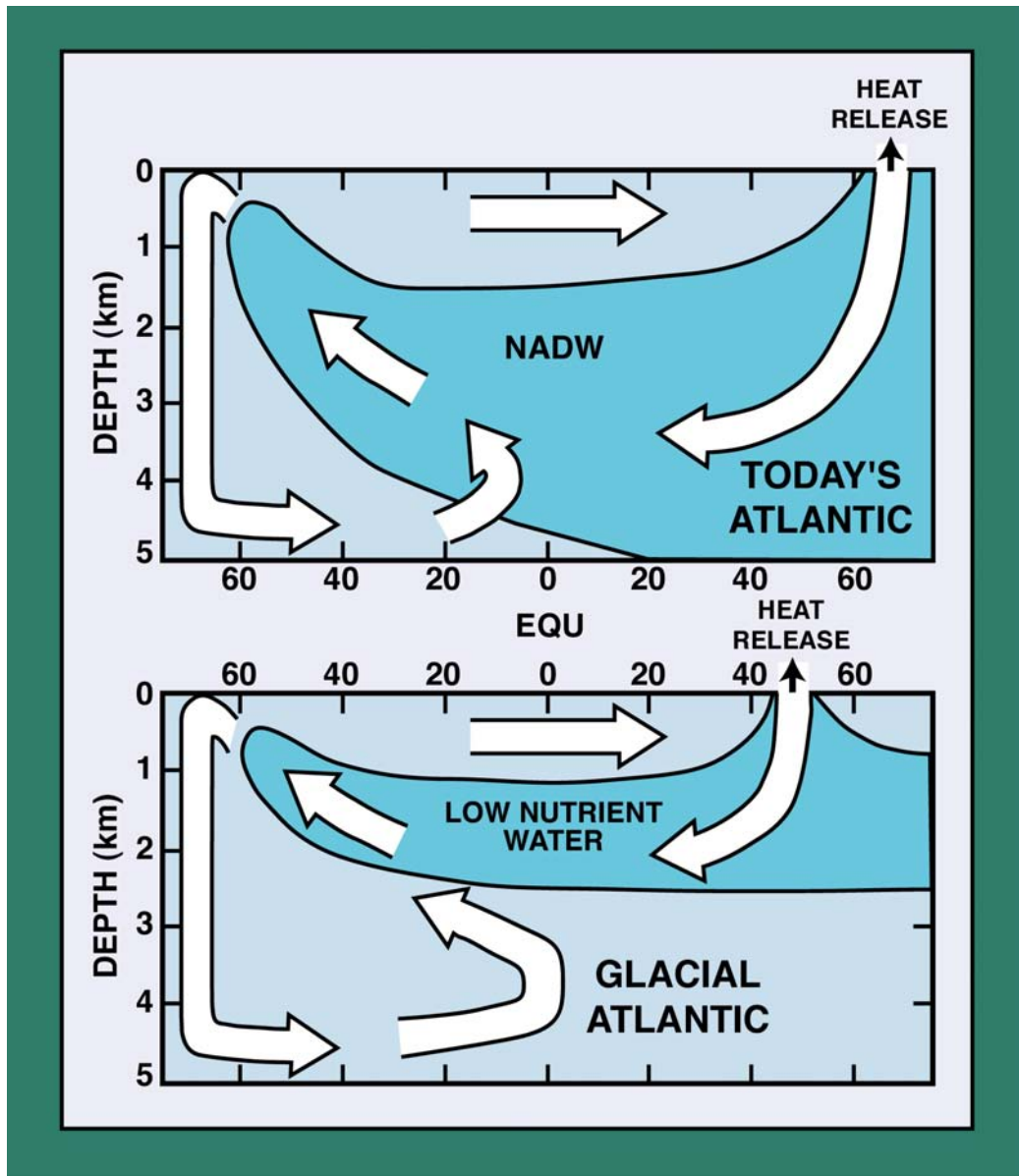


The moraine shown in this picture was produced by an advance of the Franz Josef Glacier down the steep western flank of the New Zealand Alps. Initial dating of wood samples from the Canavan Knob (located just behind the moraine itself at the river's edge) yielded radiocarbon ages which span from late Bölling-Allerød time into the Younger Dryas, raising the question as to whether this glacial advance was a Younger Dryas correlative or an event correlating with the Antarctic cold reversal. Recently, George Denton has obtained radiocarbon ages on newly collected samples of Canavan Knob wood. These ages (obtained on bark) suggest that the culmination of this advance occurred prior to the onset of the Younger Dryas. The importance of the bark is that its preservation eliminates the possibility that the wood was exhumed from avalanche deposits (i.e., that the wood was "pre-aged").

The question naturally arises as to which parts of the planet followed Greenland's pacing and which Antarctica's pacing. For a number of years, I was convinced that instead of lying at the equator, this boundary lay at the northern fringe of the Southern Ocean. This conclusion was based on the radiocarbon dating of wood buried by an advance of a glacier descending from New Zealand's Mount Cook. George Denton and New Zealand's Chris Hendy obtained radiocarbon ages which averaged 11,200 years.³² While a couple of hundred radiocarbon years older than radiocarbon dates for the onset of the Northern Hemisphere's Younger Dryas, the difference was deemed small enough to be disregarded. So the Waiho Loop glaciation was declared to be a southern hemisphere expression of the Younger Dryas. If so, as Mount Cook is 40° south of the equator, the boundary between Greenland and Antarctic impacts must have lain to the south of 40°S.

A recent reexamination of the Waiho radiocarbon dates focused attention on several that dated 11,500 to 11,200 years. These woods must have grown during the Bölling-Allerød time period. A return visit to this site by Denton in January 2004 seemed to eliminate the explanation that the older woods had been exhumed from avalanche deposits by the advancing Younger Dryas ice tongue. The reason is that many of the pieces of wood had retained their bark. Were the wood buried by an avalanche and subsequently exhumed by the advancing glacier, the bark would surely have been lost. At this writing, bark from 15 of Denton's samples had been radiocarbon dated. The results favor the interpretation that the culmination of the Waiho advance predated Younger Dryas. Combined with new evidence from deep sea cores, it now appears that the boundary between impacts following the Greenland pattern and those following the Antarctic pattern lies within the tropics rather than to the south of New Zealand.

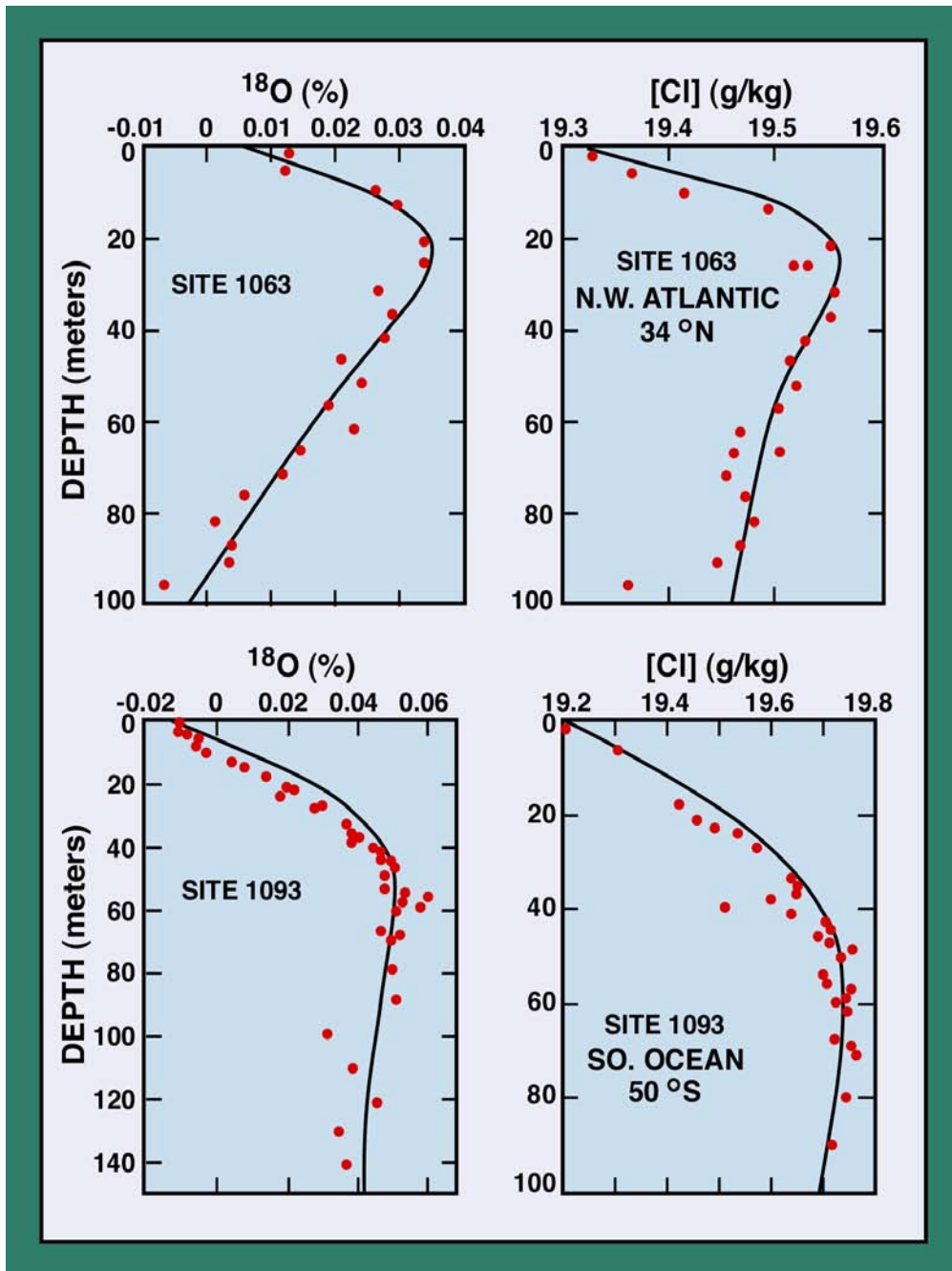
If ocean circulation differed during the Younger Dryas, it must also have differed during peak glacial time. It turns out that we have learned much more about the glacial ocean than about the Younger Dryas ocean. One reason is that in most of the ocean



Contrast between the distribution of phosphate in today's ocean with that reconstructed for glacial time. The major difference is that the high phosphate content waters entering the abyssal Atlantic from the Southern Ocean occupied much more space during glacial time. Deep water generated in the northern Atlantic penetrated to a depth of only 2.5 kilometers. Also, the formation zone was shifted southward. This reconstruction is based on measurements of ^{13}C to ^{12}C ratios and cadmium to calcium ratios in the shells of benthic foraminifera.

sediment cores that have been studied, benthic worms have obscured the Younger Dryas by mixing the sediment deposited during this cold snap with that deposited during the preceding Bölling-Allerod and that deposited during the subsequent early Holocene. As the peak glacial conditions prevailed for a much longer period of time, its record is well preserved almost everywhere on the sea floor. Key evidence regarding the nature of ocean circulation during peak glacial time comes from measurements of the $^{13}\text{C}/^{12}\text{C}$ ratio³³ and cadmium concentrations³⁴ in the shells of bottom dwelling (i.e., benthic) foraminifera. Both of these properties have quite different values in deep waters in today's Pacific than in today's Atlantic Ocean. The ^{13}C to ^{12}C ratio is lower in deep Pacific waters and the cadmium content higher than in the Atlantic. A discussion of the reasons for this difference will be given later in the book. Throughout the deep sea, both of these properties co-vary with the amount of dissolved phosphorus. Hence, the tiny shells of benthic foraminifera carry a record of the distribution of phosphorus in the deep sea. What this record tells us is that waters deeper than 2500 meters in the glacial Atlantic had higher than present phosphorus content whereas waters shallower than 2500 meters had a lower phosphorus content. The interpretation is that, while during glacial time a conveyor-like circulation was active in the Atlantic, its lower limb extended to a depth of only 2500 meters and likely its formation area was displaced equatorward. Under-riding this shallow conveyor was deep water which entered the South Atlantic from the Southern Ocean. This suggests that deep water formation in the Southern Ocean dominated during peak glacial time. While conveyor circulation was not absent, it played a less important role than it does now.

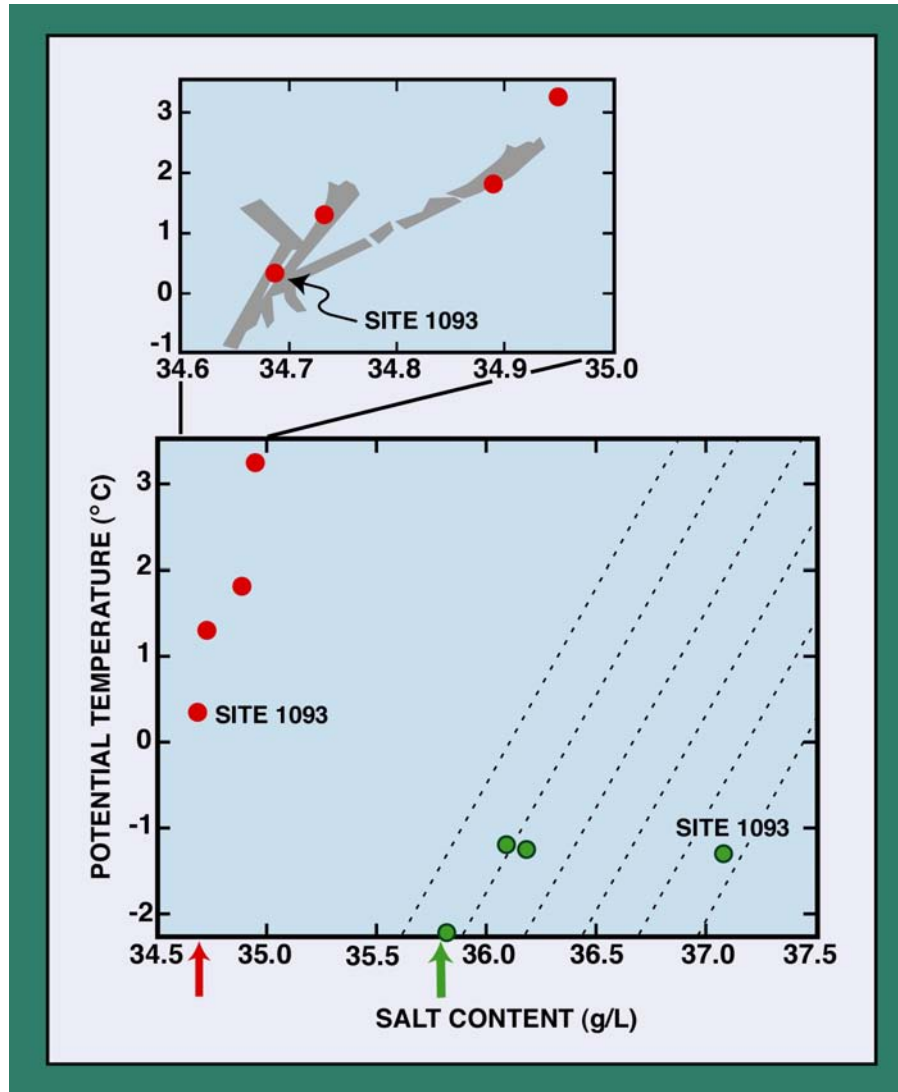
Jess Adkins³⁵ of Caltech made an extremely important discovery regarding the operation of the glacial ocean by measuring the salt content of water squeezed from deep sea sediment cores. The removal of a layer of ocean water about 120 meters thick to create the expanded ice sheets of peak glacial time would have left enough salt behind to have raised the ocean's average salinity by about one gram per liter (i.e. from about 35 to



Profiles of the composition of pore waters extracted from deep sea sediments at two sites in the world ocean. The maximum in ^{18}O to ^{16}O ratio and that in the chloride ion concentration reflect the higher ^{18}O and higher Cl of glacial age deep waters. Although diffusion of post glacial bottom water into the sediment is gradually erasing the memory of glacial time, Schrag and Adkins were able to make models (solid lines) which fit the data and thereby reconstruct the ^{18}O to ^{16}O and salinity of bottom water at these sites during peak of the last glacial period.

about 36 grams per liter). Although diffusion of post glacial water down into the sediment pores is gradually erasing the memory of this high salinity episode, Adkins reasoned that enough should remain to allow him to make a direct assessment of the salt excess which existed during glacial time. As the sediments recovered using the standard piston device widely deployed by paleoceanographers did not reach deep enough to capture the record he sought, Adkins had to turn to piston cores recovered by an ocean drilling ship. Instead of obtaining only a single core 10 or so meters in length, through a combination of piston coring and drilling, a series of such cores, each a core length deeper than the previous one could be obtained. The first four such records Adkins analyzed yielded results consistent with expectation, but a fifth from the Southern Ocean yielded a big surprise. Instead of the expected one gram per liter salt excess, it came out two grams per liter. The increase in density created by this extra gram of salt would have been equivalent to that produced by a 5°C cooling.

On the same pore water samples analyzed by Adkins, Harvard's Dan Schrag³⁵ measured the ratio of heavy oxygen (^{18}O) to light oxygen (^{16}O). The growth of ice sheets which enriched the ocean in salt, also enriched it in ^{18}O . The reason is that the water vapor reaching the ice sheets is depleted in the heavy isotope. Today snow falling in the interior of Antarctica is five percent deficient in ^{18}O relative to average sea water and that falling in Greenland is three percent deficient. But, as no way exists to pin down the exact deficiency in the now-gone excess ice of glacial time, Schrag could not use the ^{18}O to ^{16}O ratio in pore waters as a cross check on Adkins paleosalinity estimates. But he put them to an even better use. The ^{18}O to ^{16}O ratio increase in glacial-age benthic foraminifera shells taken at the same site as the pore water profile was caused by a combination of a change in the ^{18}O to ^{16}O ratio in deep water and a change in deep water temperature. Using his pore water-based reconstruction of the bottom water ^{18}O to ^{16}O ratio, Schrag was able to tease out the glacial bottom water cooling contribution. He found something that was not unexpected. At all five sites, the bottom water temperature during peak



In the upper diagram is shown the potential temperature - salt-content trends in today's deep ocean. Shown by the red dots are the present-day coordinates for the bottom waters at the four sites where Adkins and Schrag did their pore water measurements. These same red dots are repeated in the lower diagram which also includes the LGM coordinates (green dots) reconstructed from the pore water measurements. As can be seen, the potential temperatures at these sites all lie close to the freezing point of sea water (i.e., -1.8°C). For three of the sites, the reconstructed salt content is close to that expected for an ocean which had given up a 125-meter-thick layer of water to the ice sheets of peak glacial time. The red arrow represents the average salinity of today's deep ocean, and the green, that expected for the ocean during peak glacial time. However, the fourth (Southern Ocean pore water profile, site 1093) yields a salt content one gram per liter greater than that for the other three.

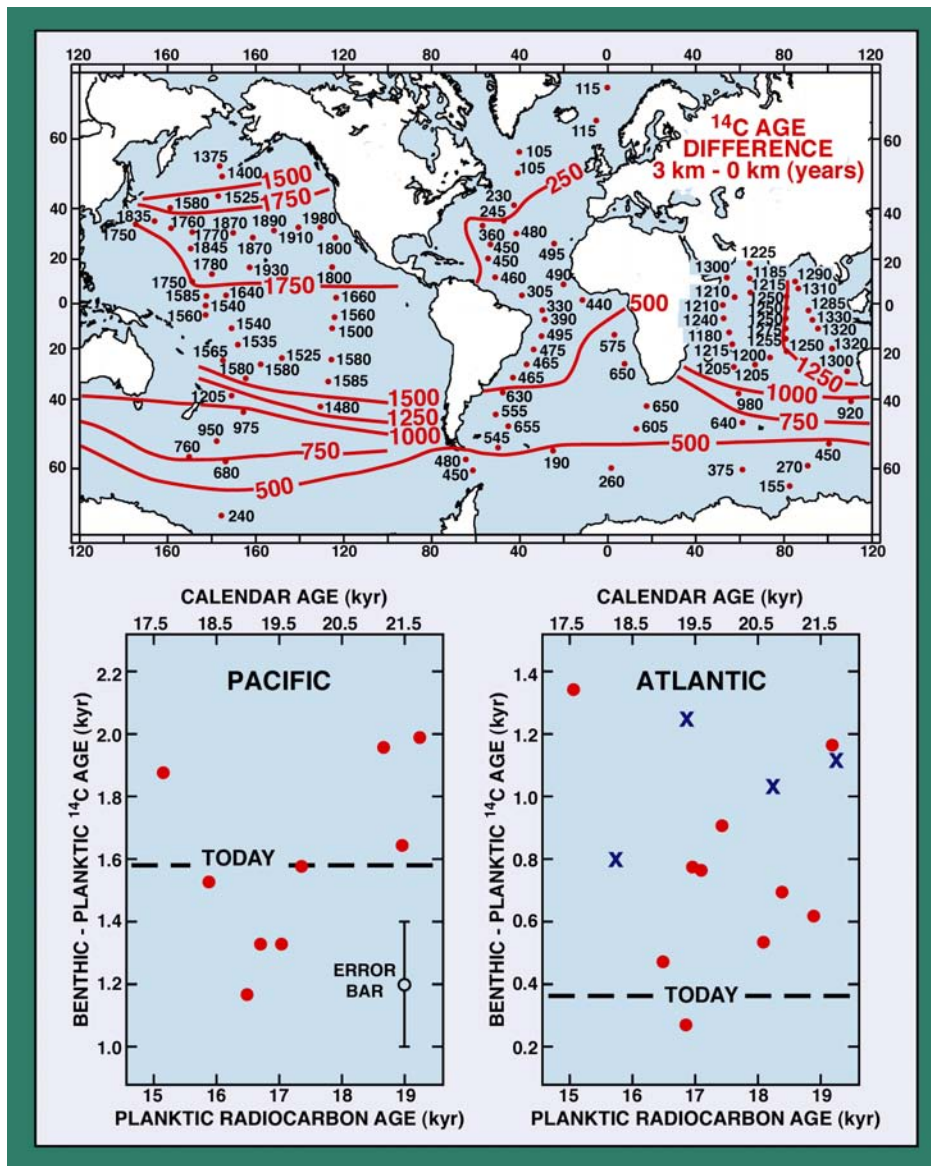
The diagonals are lines of constant density. Potential temperature is the temperature the water would have if decompressed to sea surface pressure. Compression of sea water raises its temperature by about 0.1°C per kilometer depth.

glacial time was within the uncertainty of the freezing point of sea water (i.e., -1.8°C). I say “not unexpected” because during glacial time, no matter where new deep water were to have formed, it must have done so in association with sea ice. Hence there would have been little chance for waters with temperature of $+2^{\circ}\text{C}$ to sink to the abyss as occurs today in the northern Atlantic.

Taken together, Adkins’ paleosalinities and Schrag’s paleotemperatures tell us that there was a fundamental difference between the glacial deep ocean and today’s deep ocean, namely, while the density differences in today’s deep sea are primarily the result of differences in temperature, those in the glacial deep sea were primarily the result of differences in salt content.

What could be the explanation for the two gram per liter excess of salt in the deep glacial Southern Ocean? Once again, sea ice steps to the fore. This time, it is sea ice in the Southern Ocean rather than that in the northern Atlantic. We know from studies of the diatoms in Southern Ocean sediments that during peak glacial time sea ice extended 8 or so degrees latitude further away from the Antarctic continent than it does today. Presumably, like today, this sea ice cover was more extensive during southern hemisphere winters than during southern hemisphere summers. The growth of sea ice cover each winter is accompanied by the formation of pockets of sea water highly enriched in the salt excluded by the ice crystals as they form. Some of this dense brine escapes the ice and falls through the underlying water column. Apparently during glacial time, a portion of these brine dollops were able to accumulate in the abyss and create a water mass with one gram per liter higher salt content than the rest of the deep ocean. So, we see that the glacial deep ocean had a very different layout than today’s. This makes it more difficult to make a meaningful reconstruction of the circulation in the glacial ocean.

Theory suggests that the overall rate of deep water formation was not much different during glacial time. Winds and tides mixed warm upper ocean waters down into the cold deep ocean as they do today. Geothermal heat leaked through the sea floor then

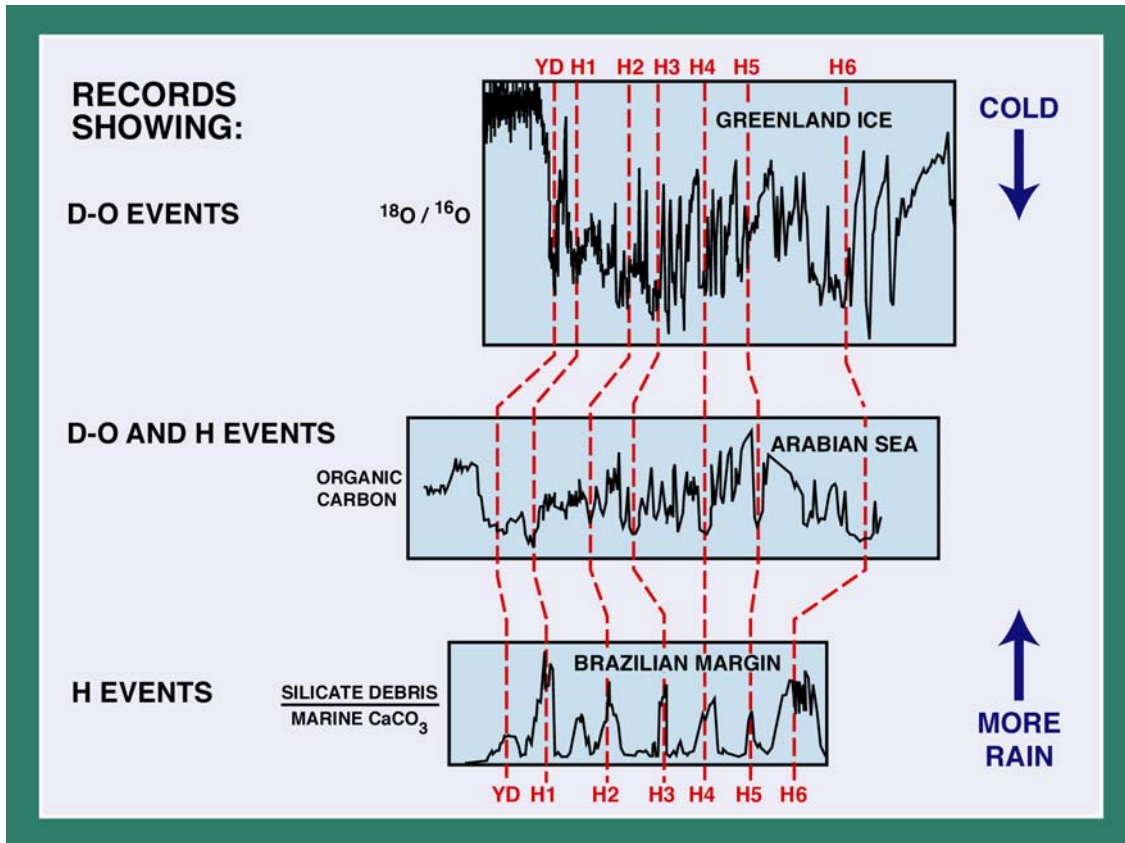


The map in the upper panel depicts today's apparent radiocarbon age difference (in years) between water at 3 km depth and surface water for each of the stations occupied as part of the GEOSECS survey. The small age differences in the Southern Ocean reflect the low ^{14}C to C ratio in surface waters rather than young bottom water.

In the lower panel is a summary of benthic-planktic age differences for coexisting benthic and planktic foraminifera in late glacial-age samples. On the left are those obtained for samples representing a water depth of about 2 kilometers in the western equatorial Pacific. On the right are samples from deeper than 2.5 kilometers water depth in the western Atlantic. Some of the scatter reflects the measurement error which averages about ± 200 years. Note that as is the case for today's ocean, the late glacial-age differences for Atlantic samples (850 ± 300 years) are, on the average, smaller than those for the Pacific (1600 ± 300 years). However, although the Pacific age difference is not significantly different from today's, the Atlantic differences average more than double today's. The red dots represent results published by Broecker and his co-workers and the blue x's those published by Lloyd Keigwin of Woods Hole Oceanographic.

as now. However, as today's tidal friction occurs mainly in shallow portions of the ocean, the 125 or so meter drop in sea level during peak glacial time would have led to a reduction in this friction for most of the ocean's shallows were eliminated. Also, the presence of ice sheets altered wind patterns. Hence, theory alone is not adequate. Rather, we need some means to directly assess the rate of ventilation of the deep ocean during glacial time. Fortunately, there is a way to obtain such information. It involves radiocarbon measurements on coexisting benthic and planktic foraminifera from glacial-age sediment samples. The difference between these two ages can be compared with that calculated from the difference between the ^{14}C to C ratio in today's deep water and that reconstructed for pre-industrial surface ocean water. Sounds simple but in practice there are a number of biases which must be circumvented. To date, relatively few such measurements can be declared reliable. These few results suggest that the waters below 2500 meters in the Atlantic were replaced more slowly than now.^{36,37} In contrast, waters down to a depth of 2000 meters in the Pacific appear to have been ventilated at about the same rate as they are today.³⁸ Unfortunately, no reliable glacial-age benthic-planktic pairs have yet been measured from Adkins' high salinity water mass. Because of their large density contrast with other deep waters, this high salinity water mass might be expected to have been more depleted in radiocarbon.

The Younger Dryas is not the only millennial-duration event recorded in Greenland ice. Depending on how one counts, a dozen or so others occurred during the interval from 25,000 to 50,000 years ago. The difference is that they appear to be warm excursions from a cold state instead of cold excursions from a warm state as is the case for the Younger Dryas. In honor of Denmark's Willy Dansgaard and Switzerland's Hans Oeschger who pioneered geochemical research on polar ice, they are referred to as D-O events. Each involves an abrupt warming followed in 700 or so years later by an abrupt cooling. Jeff Severinghaus at the University of California, San Diego has shown that at Summit locale in Greenland the amplitude of these changes was about 9 degrees

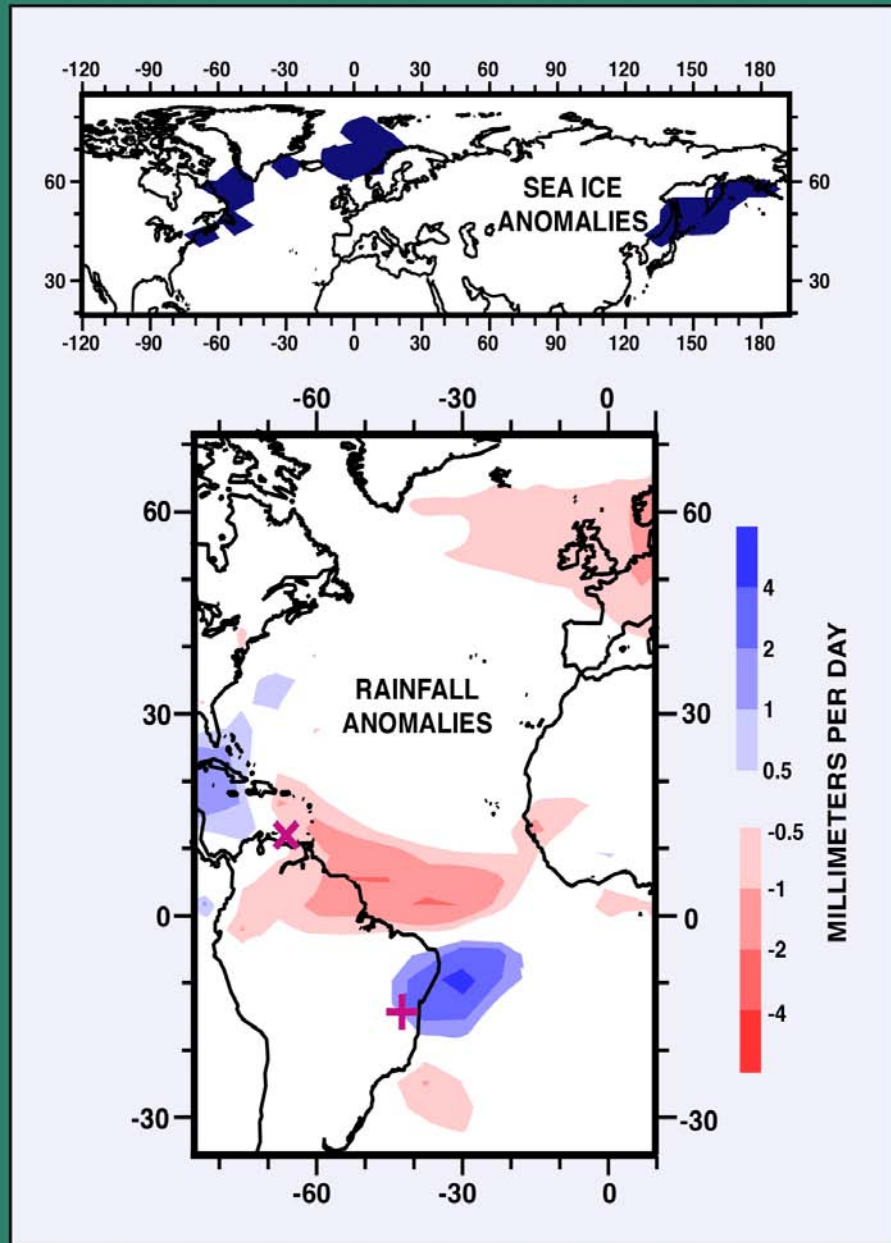


Records for the last ~70,000 years from three locales. The point of this figure is to show that some records (like that contained in Greenland ice) are dominated by the millennial-duration Dansgaard-Oeschger (D-O) events while others (like that from the Brazil margin) are dominated by Heinrich (H) event impacts. Still others (like that for Arabian Sea sediments) show both. Why the difference? The likely explanation is that the low latitude locales respond to rainfall changes related to shifts in the position of the ITCZ (Inter Tropical Convergence Zone) and in the strength of the monsoons while at high northern latitudes, temperature changes are more important. H events led to larger shifts than D-O events.

centigrade.³⁹ During the warm phase of these events, the methane content of the air trapped in the ice was 15 or so percent higher⁴⁰ and the dust content three times lower than during the cold phases.⁴¹ The sediment core and stalagmite records in which the Younger Dryas event is present are also punctuated by these D-O events documenting that their impacts also spread across the Northern Hemisphere. It is not clear what paced these multiple events. Peter Clark of Oregon State University proposed that each was triggered by a melt water flood similar to that which predated the Younger Dryas.⁴² His hypothesis involves an oscillatory interaction between ice extent and conveyor strength. On the other hand, Germany's Stefan Rahmstorf has constructed an ocean model which undergoes self-sustained oscillations involving jumps back and forth between two different states of ocean operation.^{43,44}

Making the situation more complicated but more interesting is the existence of Heinrich events. Six times during the last glacial period huge armadas of ice were launched from Canada's Hudson Straits into the northern Atlantic.^{45,46} These catastrophic inputs were likely caused by sudden disintegrations of the ice dome over Hudson Bay. Carried by the prevailing currents, these bergs drifted across the Atlantic melting as they went. In the sediments underlying this track, easily identifiable layers of debris released from the melting of the ice are found. These layers are tens of centimeters thick at the track's western end and thin to a few centimeters thickness at its eastern end. Judging by the amount of material dropped to the sea floor, the melting of these icebergs must have added amounts of fresh water to the northern Atlantic even larger than that associated with the flood which initiated the Younger Dryas.

Compared to the large imprint D-O events, those associated with the Heinrich armadas are barely detectable in the record kept in Greenland ice. Why this is remains somewhat of a mystery. At first it was thought that perhaps the climate impacts of Heinrich events were very modest. But when the evidence started to roll in from sediment and stalagmite records, it became clear that the far-field impacts of Heinrich events were

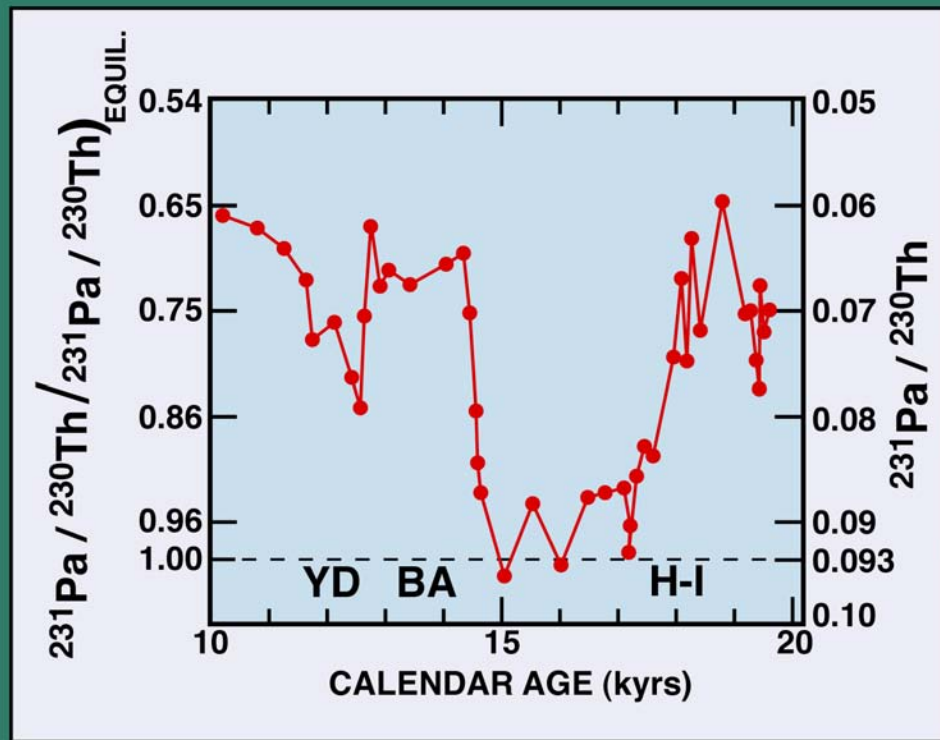


The impact of excess sea ice on rainfall in the tropics. In his computer simulation, John Chiang added extended January sea ice cover to the areas shown in blue in the upper map. The resulting May to July rainfall anomalies produced by this extension are shown in the lower map. The blue areas receive more rainfall than today and the orange areas less. The x shows the location of the Cariaco Trench sediment record and the $+$ the location of Larry Edwards stalagmite record. These records portray the shifts predicted by Chiang.

larger than those associated with D-O colds. Off Portugal in Atlantic⁴⁷ and in the western Mediterranean,⁴⁸ Heinrich-correlated temperature drops recorded in marine sediments are larger than those associated with the D-O cold episodes. The sediment record in the Arabian Sea⁴⁹ and the stalagmite record in China's Hulu Cave¹⁷ suggest that a greater weakening of the monsoons accompanied Heinrich events than those associated with D-O cold episodes. In Florida, a pollen record reveals a series of pine (ie., wet) events and oak (i.e. dry) events which follow the Heinrich pacing.⁵⁰ No evidence for D-O events is found in this record. In the currently dry areas of eastern Brazil, the Heinrich events appear to have triggered large increases in rainfall which are recorded by deluges of soil material sluiced from the continent out onto the adjacent continental margin⁵¹ and by a rejuvenation of calcite deposition in otherwise dry caves.⁵² As in Florida, no evidence for D-O events is to be seen.

These results suggest that Heinrich events led to an even greater sea ice cover in the northern Atlantic than that present during the cold phases of D-O events. Following Chiang's²⁶ line of reasoning, they pushed the Inter-Tropical Convergence Zone even further to the south bringing rain to currently dry eastern Brazil. Of course, the expanded ice cover would also have caused even larger coolings in Europe.

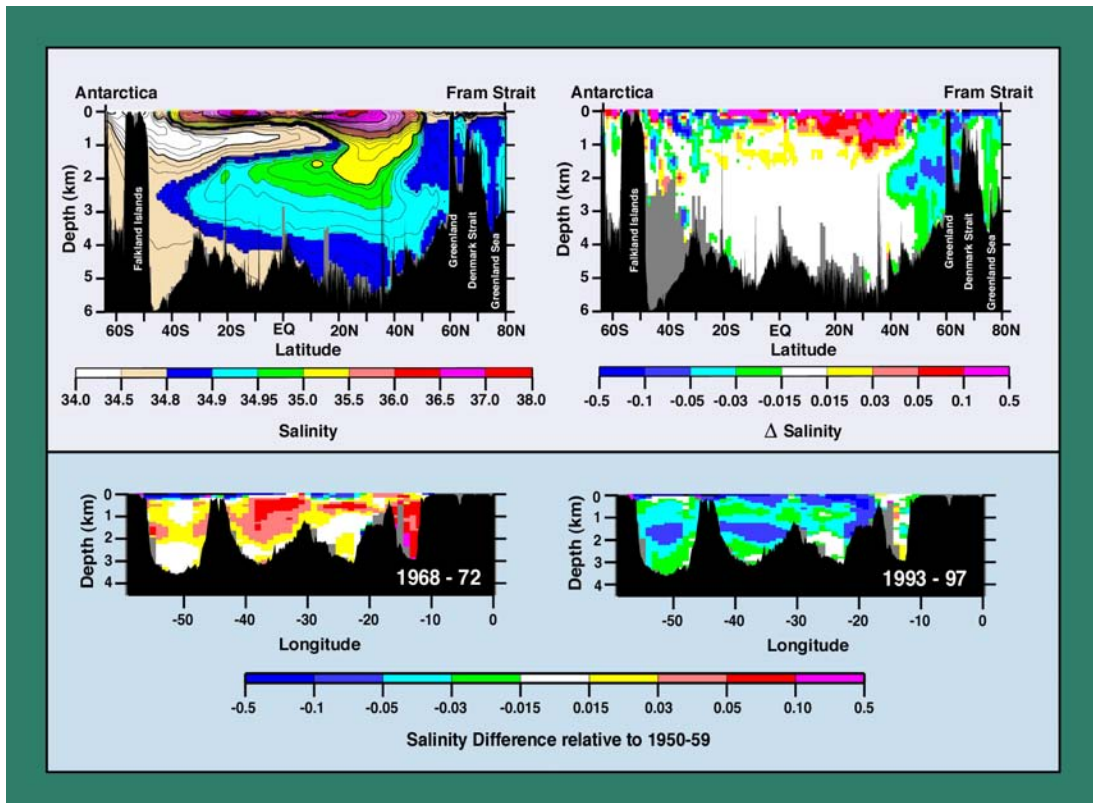
Jerry McManus at Woods Hole Oceanographic came up with a novel way to gauge the strength of conveyor circulation.⁵³ He did this by comparing the amount of a radioisotope of the element protactinium (²³¹Pa) with the amount of a radioisotope of the element thorium (²³⁰Th) in an Atlantic sediment core. Both of these isotopes are produced in the sea by the radiodecay of parent uranium isotopes. Unlike uranium which is quite soluble in sea water, both protactinium and thorium have strong tendencies to attach themselves to particulate matter as it rains down through the water column. As a result, both isotopes are efficiently carried to the sea floor. But it turns out that, as thorium has a greater affinity for particles than does protactinium, ²³⁰Th atoms born in the sea remain in the water column for only a very short time (less than 10 years). In contrast, the



Ratio of two particle-reactive nuclei produced by the decay of uranium dissolved in the sea as a function of depth in a core from the northern Atlantic Ocean. The residence time of ^{230}Th with respect to removal to the sediments is measured in decades. That for ^{231}Pa is measured in centuries and is thus comparable to the present-day residence time of water in the Atlantic Ocean. Because of this, about 40 percent of the ^{231}Pa produced in the Atlantic is currently carried by the lower limb of the conveyor into the Southern Ocean. Analyses by Woods Hole's Jerry McManus reveal that during the time interval between Heinrich event #1 and the onset of the Bölling-Allerod, the ratio of these two isotopes was close to that expected had no loss to the Southern Ocean occurred. This suggests that during this time period conveyor circulation was greatly reduced. During the Bölling-Allerod, conveyor export rose to a value almost as great as that during the Holocene. Then, with the onset of the Younger Dryas, the rate of export was once again cut back, but not nearly to the extent as it was during the time interval postdating H-1.

somewhat less particle-reactive ^{231}Pa atoms remain in the water column on the average of a century or so. As we have already seen, the deep water in the Atlantic is currently replaced roughly once each two centuries. Thus, while few of the highly-reactive ^{230}Th atoms produced in the Atlantic manage to escape to the Southern Ocean, a fair fraction of the ^{231}Pa atoms produced in the Atlantic are exported by the conveyor's lower limb.

Measurements of the ratio of ^{231}Pa to ^{230}Th in core-top sediments confirm expectation. The ratio in the sediment is only a fraction of the ratio in which the two isotopes are produced in the overlying water column by the radiodecay of uranium. The missing ^{231}Pa atoms have presumably been exported to the Southern Ocean. McManus measured this ratio at several depths in a sediment core from the northern Atlantic. He found the expected ^{231}Pa deficiency in sections representing the Holocene and the Bölling-Allerod. This made sense because the conveyor is thought to have been at full strength during both of these time intervals. As might be expected, the deficiency in ^{231}Pa was smaller during the Younger Dryas when the conveyor is thought to have been largely shut down. The surprise came when in the sediments deposited during the time interval between the last of the series of Heinrich events (~17,000 years ago) and the abrupt onset of the Bölling-Allerod (~14,500 years ago) showed no measurable deficiency in ^{231}Pa relative to ^{230}Th . This suggests that the onslaught of melt water produced by the melting of the Heinrich icebergs pretty much brought to a halt export of Atlantic deep water to the Southern Ocean.



In the left-hand upper panel is shown the salinity distribution along a section in the western basin of the Atlantic Ocean. In the upper right-hand panel is shown the salinity change which occurred along this section between the periods 1955-1969 and 1985-1999. Note that at high latitudes, the salinity decreased and that at low latitudes it increased.

In the lower panels are shown the salinity changes (from the mean for the period 1950 to 1959) along a west to east section in the sub polar northern Atlantic. A salinity maximum achieved during the 1968 to 1972 period was followed by a period during which the salinity steadily declined reaching a minimum during the period 1993 to 1997.

These summaries were provided by Ruth Curry of Woods Hole Oceanographic.

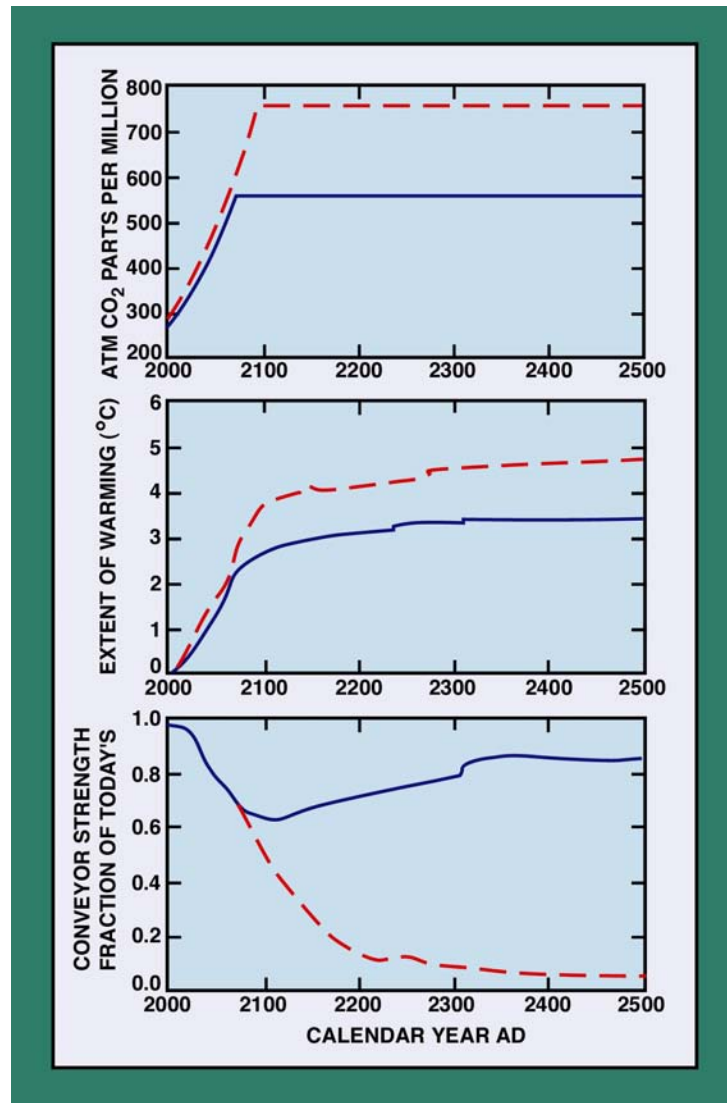
CHAPTER 3

TOMORROW'S CONVEYOR

A number of television documentaries have touted the scenario that the ongoing global warming might bring conveyor circulation to a halt and that the consequence of such a shutdown would be the return of glacial conditions in northern Europe. Ruth Curry^{54,55} of Woods Hole Oceanographic has compiled measurements of salinity made over the last 50 years in the Atlantic Ocean and found that during this time period a steady decrease in salinity has occurred at high northern latitudes. Low latitude Atlantic waters gained in salt content during this period. These observations suggest that the fresh water balance is changing. If continued, this freshening will eventually weaken the conveyor. Based on this observation scientists funded by the Pentagon put together a worst case scenario which called for a conveyor shutdown sometime during the next twenty years. Not only was a major cooling in Europe called for but also the drying out of desert regions. The movie entitled "The Day after Tomorrow" trumped these dire predictions by portraying an instantaneous catastrophic freeze over of much of North America and Europe provoked by a sudden conveyor shutdown.

Does this scenario make sense? The answer to this question requires that two of its aspects be examined. The first has to do with the likelihood that global warming will bring about a conveyor shutdown. The second has to do with the consequences of such a shutdown.

As discussed in the last chapter, the conveyor shutdowns associated with the Younger Dryas cold snap and with the Heinrich events were caused by sudden injections of large amounts of fresh water into the northern Atlantic. Today only the Greenland ice cap holds the quantity of fresh water necessary to produce a comparable deluge. But not even the most ardent eco-doomsayers have proposed that this ice cap is on the verge of breaking up and sliding into the sea. Granted that on a several century time scale under



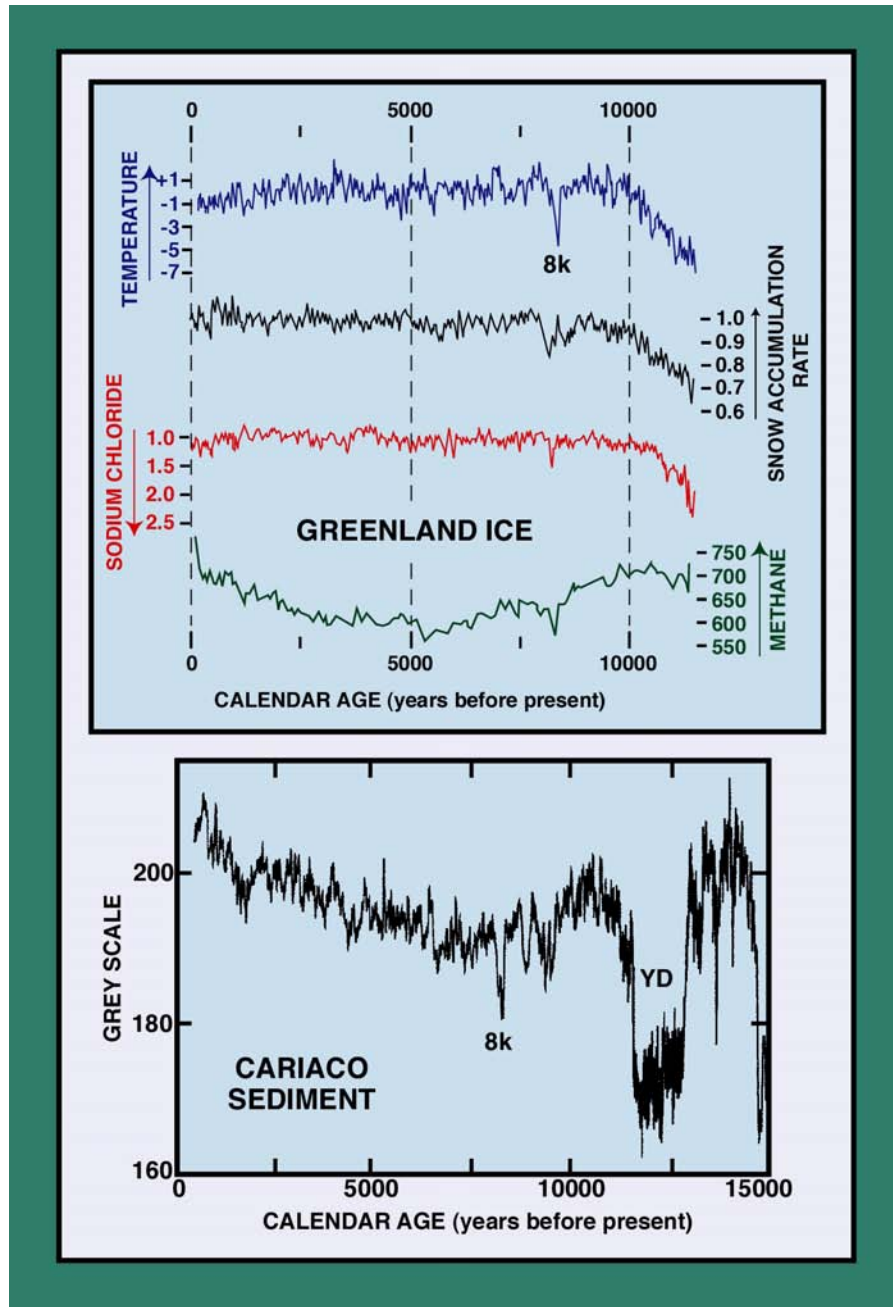
Simulations carried out by Thomas Stocker of the Bern University in a simplified ocean-atmosphere model designed to gauge the responses of global temperature and conveyor strength to long-term increases in atmospheric CO₂ content. In one (shown by the blue curves), the CO₂ content rises is increased at the rate of one percent per year until it reaches 560 parts per million where it is maintained for the next 400 years. The result is a warming of a bit more than 3°C. This warming causes the Atlantic's conveyor circulation to sag to 65 percent of its original strength. However, it then rebounds to about 85 percent of its original strength. In the second scenario (red curves), the CO₂ rise continues to 760 ppm before leveling off. The result is a warming of between 4 and 5°C which leads to a steady drop in conveyor strength. In this case, no recovery occurs. Note that, unlike the abrupt responses of glacial time, in this simulation, the shutdown is spread over the better part of two centuries.

the influence of a long-lasting global warming, the Greenland cap will likely disappear. But this melt back would in all likelihood be gradual rather than catastrophic.

In the absence of any possibility of a massive injection of fresh water, the only way to shut down the conveyor would be to enhance the input of fresh water via precipitation and river runoff. No one disputes that as the planet warms both of these modes of delivery will increase in strength. By increasing the vapor pressure of water, the warming will strengthen the hydrologic cycle. More rain and snow will fall onto the northern Atlantic and more water will be supplied to rivers draining into the Arctic and northern Atlantic. A warming will also accelerate the rate at which the Greenland ice cap releases water to the sea. The ongoing decrease in the Arctic's inventory of sea ice will, of course, contribute. But, even if this floating ice were to completely disappear during the next few decades, the amount of fresh water released would not be enough to disrupt the conveyor.

How great an increase in these fluxes would be required in order to shut down the conveyor? The only way to answer this question is through the use of computer simulations involving both the atmosphere and the ocean. Many such simulations have been conducted.^{56,57,58,59} Most show that as the planet warms, the model's conveyor circulation weakens. In the extreme, some of the models produce a shutdown. But none of the models produce a shutdown in the absence of a large warming, i.e., 4 to 6 degrees centigrade. Further, in order to produce a warming of this magnitude, business-as-usual dependence on fossil-fuel energy would have to continue for on the order of a century. The bottom line is that a conveyor shutdown on the time scale of decades is extremely unlikely and, even on a century time scale, it will not occur unless the Earth experiences a substantial warming. Finally, the shutdown is more likely to be gradual rather than abrupt.

The second question regards the consequence of such a shutdown. In particular, would it plunge Europe into an ice age? As we have seen, the key to the pronounced

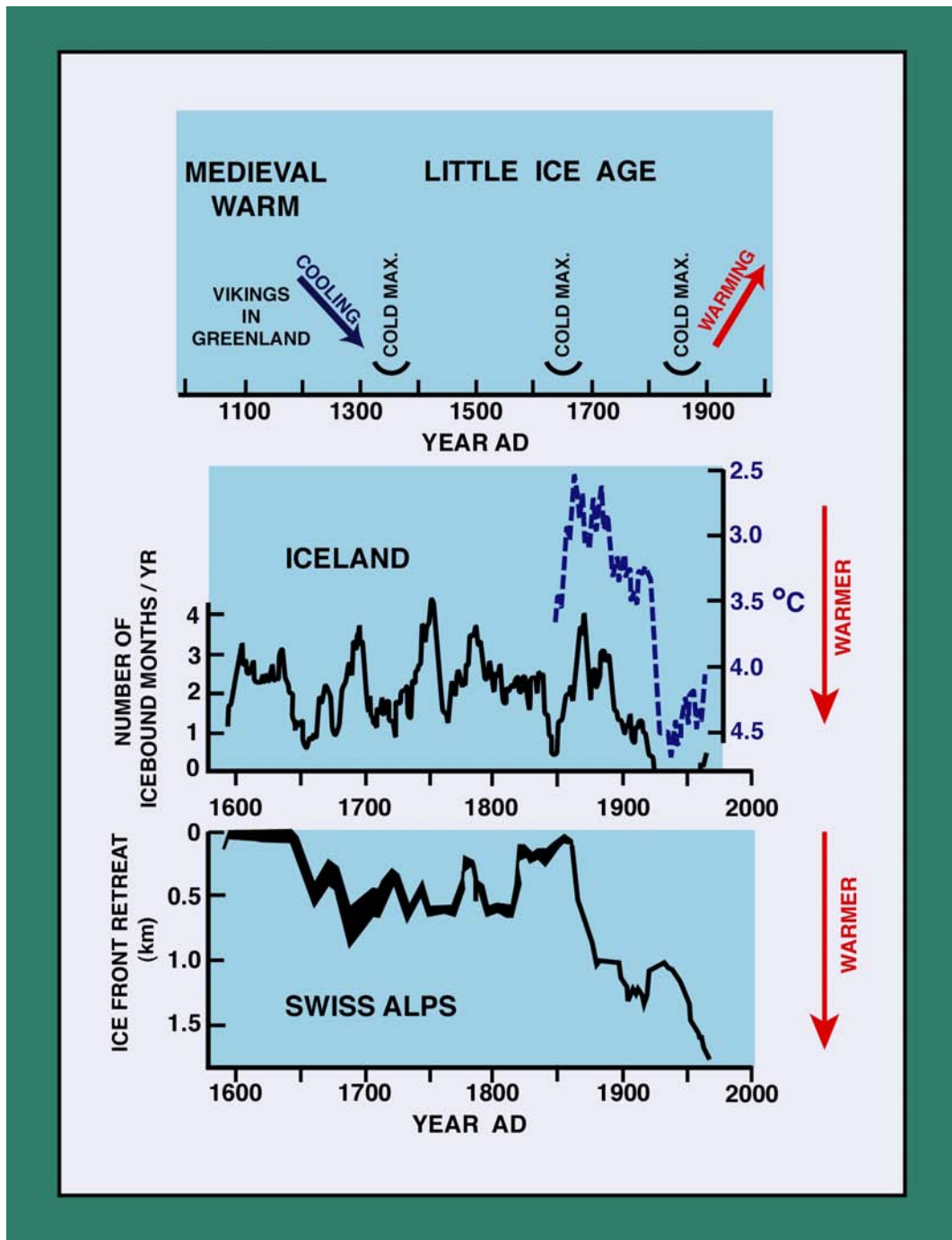


The so-called 8k event is marked by a brief (~80 year) cold snap in Greenland at about 8200 years ago. The oxygen isotope ratio dip suggests a 5°C cooling, and a thinning of the annual layers suggests a drop in snowfall; the increase in sodium chloride content suggests the expansion of sea ice cover in the Norwegian Sea, and the drop in methane content of the trapped air suggests a drying of wetlands. This event is clearly marked in the color record of a sediment core from the Cariaco Basin off the coast of Venezuela.

cooling which occurred during the Younger Dryas appears to have been a freeze-over of the northern Atlantic. There is ample reason to believe that such a freeze over would not occur were the Earth to have warmed by 4 to 6 degrees centigrade. One has only to consider that during the last couple of decades the Arctic Ocean appears to have lost 30 or so percent of its floating ice inventory.⁶⁰ During this period the globe has warmed by only a scant half degree centigrade. Models which reproduce this decline in sea ice predict that if the warming were to continue at its current pace for a few more decades, at least during the summer months, the Arctic would become largely free of ice. Hence, if predictions based on model simulations are valid, then a 4 to 6 degree centigrade global warming would pretty much insure that a freeze over of the northern Atlantic would not occur.

But, what if the Pentagon's projection of the current weakening of the conveyor were correct? It calls for a conveyor shutdown in a decade or so. On this time scale, the planet will have warmed by only another few tenths of a degree. Keeping in mind that there is no physical basis that such a shutdown is imminent, were it to occur, would it lead to a freeze over of the northern Atlantic?

There is paleoclimate evidence suggesting that, were a sudden shutdown to occur under current climate conditions, a partial winter freeze-up might occur. Punctuating the otherwise uneventful Holocene record in Greenland ice is a brief cold blip. It happened about 8200 years ago and lasted only about 80 years.⁶¹ Based on measurements of the isotopic composition of gases trapped in Greenland ice spanning this event, Jeff Severinghaus has convincingly demonstrated that, while brief, it was profound. Mean annual temperatures in Greenland dropped by a whopping 5°C! Such a dramatic cooling likely required at least a partial freeze-over of the northern Atlantic. Bearing witness to the existence of this ice are far field impacts including a brief drop in the atmosphere's methane content. As shown by John Chiang, sea ice in the northern Atlantic nudges southward the Inter-Tropical Convergence Zone leading to precipitation changes. That



The Little Ice Age was ushered in during the early part of the 14th century. Its beginning corresponds to the end of the Medieval Warm interval during which the Vikings colonized Greenland. Although historic evidence from Iceland and Greenland documents the latter half of the LIA, evidence for the first of the three cold maxima comes from stumps of trees knocked over by the 1350 A.D. advance of Swiss glaciers.

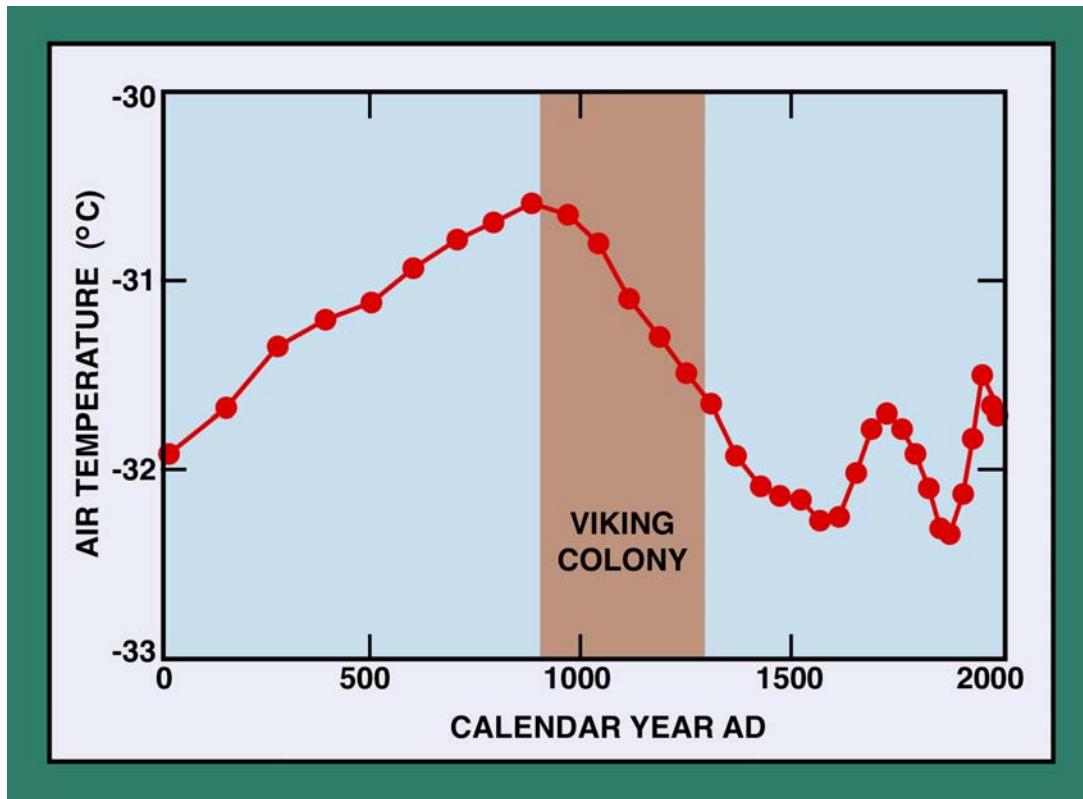
this occurred is suggested by the record in Cariaco Basin sediment. As global temperatures at the time of the 8k event were comparable to today's, one could argue that if a freeze up happened then, it could happen a decade or so from now.

We think we know what triggered this brief event. Eight thousand years ago, the once great Laurentian ice sheet was represented by only a small remnant draped around the perimeter of Hudson Bay. As had been the case during much of the ice sheet's shrinkage, a lake filled the moat which occupied the southern and western margins of the ice. A sudden drop in the level of this lake heralded the discharge of a very large volume of water.⁶² It appears that this water escaped by tunneling its way through the remnant ice into Hudson Bay and from there through Hudson Straits out into the northern Atlantic.

The fact that this cold snap lasted only 80 years implies that under interglacial climatic conditions the ocean prefers to be in its conveyor-on mode. Thus, once the waters from the great flood had spread throughout the Atlantic and beyond, the conveyor spontaneously restarted, eliminating the sea ice and therefore restoring warm conditions.

In order to evaluate claims that the weakening of the conveyor heralded by the decline in high latitude salinity during the last several decades heralds an imminent conveyor shutdown, it is necessary to put this decline into context. Is it possible, that it is merely one of many natural fluctuations which have been ongoing during the entire course of the Holocene? It is clear that, except for the brief interruption 8200 years ago, the conveyor has been operative throughout the Holocene. But has its strength remained unchanged? Could, as the result of global warming, the weakening reflect the melting of Arctic sea ice and the release to the northern Atlantic of this melt water and of the low salinity water stored beneath the ice? If so, because the amount of floating ice is finite, the impact will be short-lived.

But with regard to changes in tropical rainfall, is sea ice necessary? A recent modeling study by Zhang and Delworth⁶³ of the NOAA lab in Princeton suggests that by merely adding fresh water to the northern Atlantic, these tropical impacts can be created.



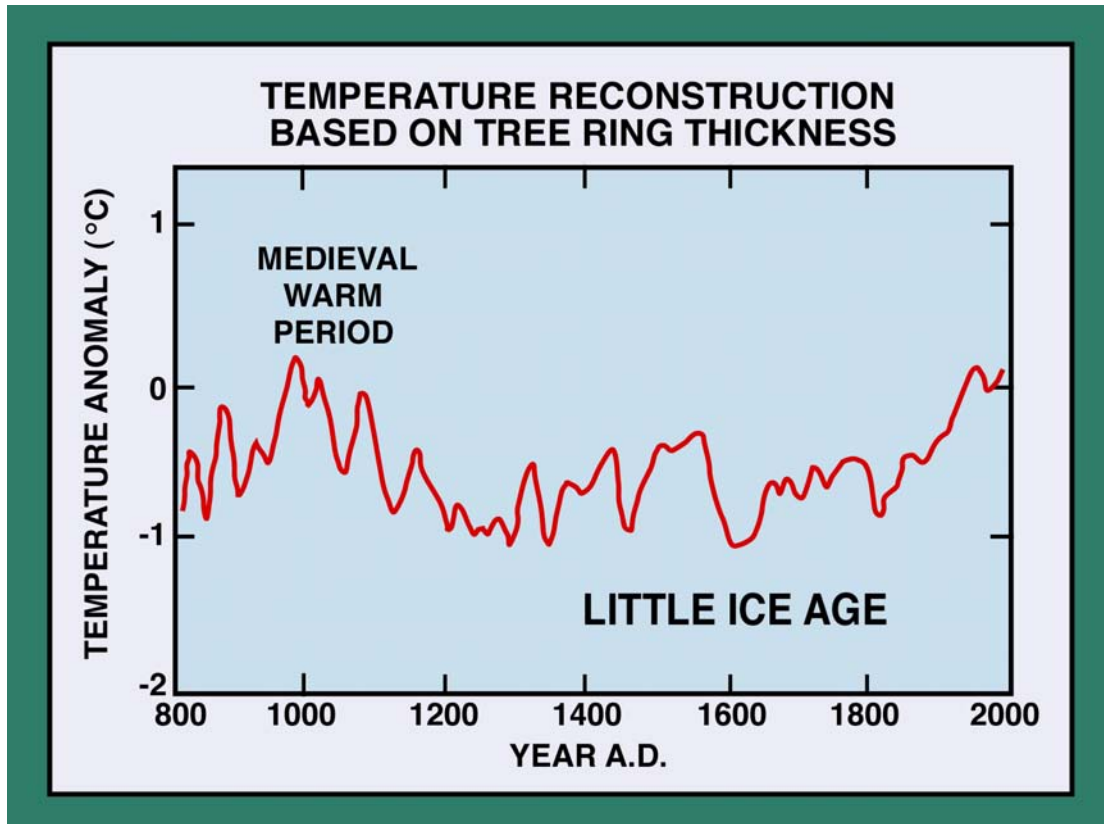
Reconstructed air temperature record for central Greenland based on a “deconvolution” of down-hole temperature measurements by Denmark’s Dorthe Dahl-Jensen. It suggests that at the peak of the Medieval Warm it was about 1.5°C warmer than during the coldest portion of the Little Ice Age. It should be noted that diffusion of heat within the ice has smoothed away any higher frequency variations.

We know for sure that temperature in the northern Atlantic basin has undergone small but important swings. During the Little Ice Age (1350 and 1850 A.D.) temperatures averaged about one degree colder than today's. The most reliable record of this cooling is kept by Europe's glaciers which reached their maximum Holocene size at three separate times during this interval.

Historical observations document two of these glacial maxima: one in the years around 1850 and the other in those about 1650. Tree stumps decapitated by advancing ice bear witness to an earlier maximum near 1350. The end moraines occupied by the larger of the Swiss glaciers (Rhône, Allègre, Gorner...) during the middle 1800s are massive horseshoe-shaped features standing 50 or so meters above the surroundings. So large are they that geologists are convinced that they had to be formed by more than one Holocene ice advance. Based on the morphology of the deposits created by numerous smaller alpine glaciers, it has been estimated that mountain temperatures at the time of the 1850 maximum were about 1° colder than today.

Additional support for the estimate of a one-degree-centigrade Little Ice Age cooling comes from temperature profiles in holes drilled deep into Greenland's ice cap. In a manner exactly analogous to that employed by Adkins and Schrag in their analysis of profiles in sediment pore water of salinities and ^{18}O to ^{16}O ratios, past temperatures can be teased out of temperature profiles in the ice. Although the memory of past cold periods is being gradually erased by diffusion of heat down into the ice, enough of the cold bump created by the Little Ice Age remains to allow the average temperature drop (relative to today's) to be reconstructed. The answer which comes out is that temperature averaged a bit more than one degree centigrade colder than during preceding warm period.⁶⁴

In the northern Atlantic region, the Little Ice Age was preceded by an episode of warmth comparable to today's. It lasted from about 900 to about 1300 A.D. and is referred to as the Medieval Warm Period. Most of us know about it because it was made



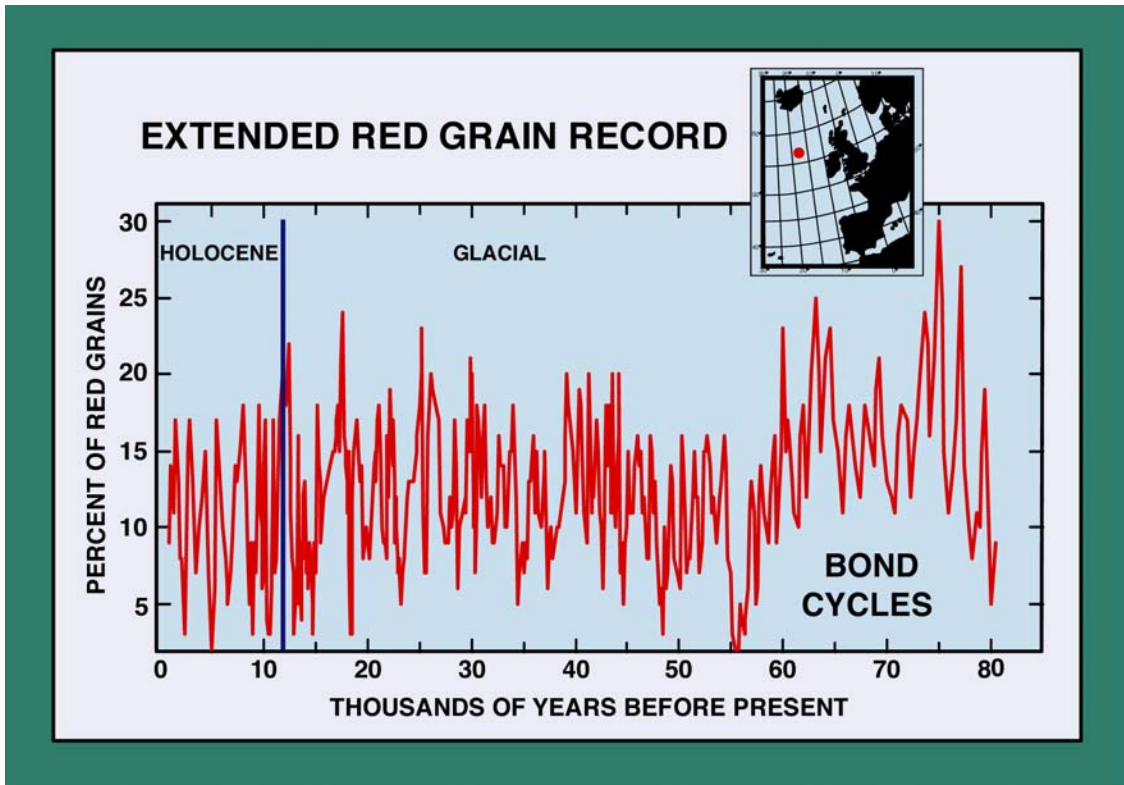
For trees living near their cold limit, the thickness of annual growth rings is influenced mainly by temperature. The temperature record shown in this diagram was constructed by Jon Esper based on a composite of 1800 thickness records from Siberia, Scandinavia, Canada and Alaska and also from north temperate mountains. His reconstruction suggests that temperatures at these locales were as much as 1°C colder than today's at times during the Little Ice Age, and that they reached levels comparable to today's at the peak of the Medieval Warm Period 1000 years ago.

famous by Eric the Red and his band of Vikings who, when driven out of Scandinavia, sailed their ships to southern Greenland and established a colony. Archeological studies reveal that this colony prospered during the first century or so of its existence. However, hard times came when a decline in conditions favorable for grain growth set in. The decline forced the colonists to turn ever more to the sea for sustenance. Carbon isotope measurements on bones from Viking burials show that the mix of food from the land and food from the sea started at about 80-20, then steadily declined until the last of the Viking settlers were getting only 20 percent of their food from the land. Early in the 14th century, starvation appears to have set in and by 1330 A.D., all contact with the colony was lost. So, as the glaciers in the Swiss Alps began their Little Ice Age advance, colder climatic conditions in Greenland squelched agriculture.

Additional evidence regarding the cycle from Medieval warmth to Little Ice Age cold comes from records kept in trees whose growth is temperature limited. Ian Esper, a German dendrochronologist, conducted a thorough analysis of ring thickness records from borings made in 1800 trees from across northern Siberia, Scandinavia, Canada and Alaska. He convincingly demonstrated that the thickness of the rings agreed very nicely with the evidence presented above. Rings formed during the time of the Little Ice Age were consistently thinner than rings formed during the preceding Medieval Warm.⁶⁵

A more dramatic piece of evidence comes from Russia's Kara Peninsula where a grove of dead trees was found above today's tree line.⁶⁶ Radiocarbon dates on wood from these trees places the time of forest growth during the Medieval Warm Period. Ring counts show that the forest was in existence for more than a century. Thus, it appears that during this time, temperatures may have been even warmer than today's.

Lamont-Doherty's Gerard Bond amassed a highly important data set on Holocene sediments from the northern Atlantic.^{67,68} These results portray an oscillation with a period averaging 1500 years. What he measured was the percentage of the sand-sized grains present in a given sediment sample which were iron-stained (i.e., red in color). His

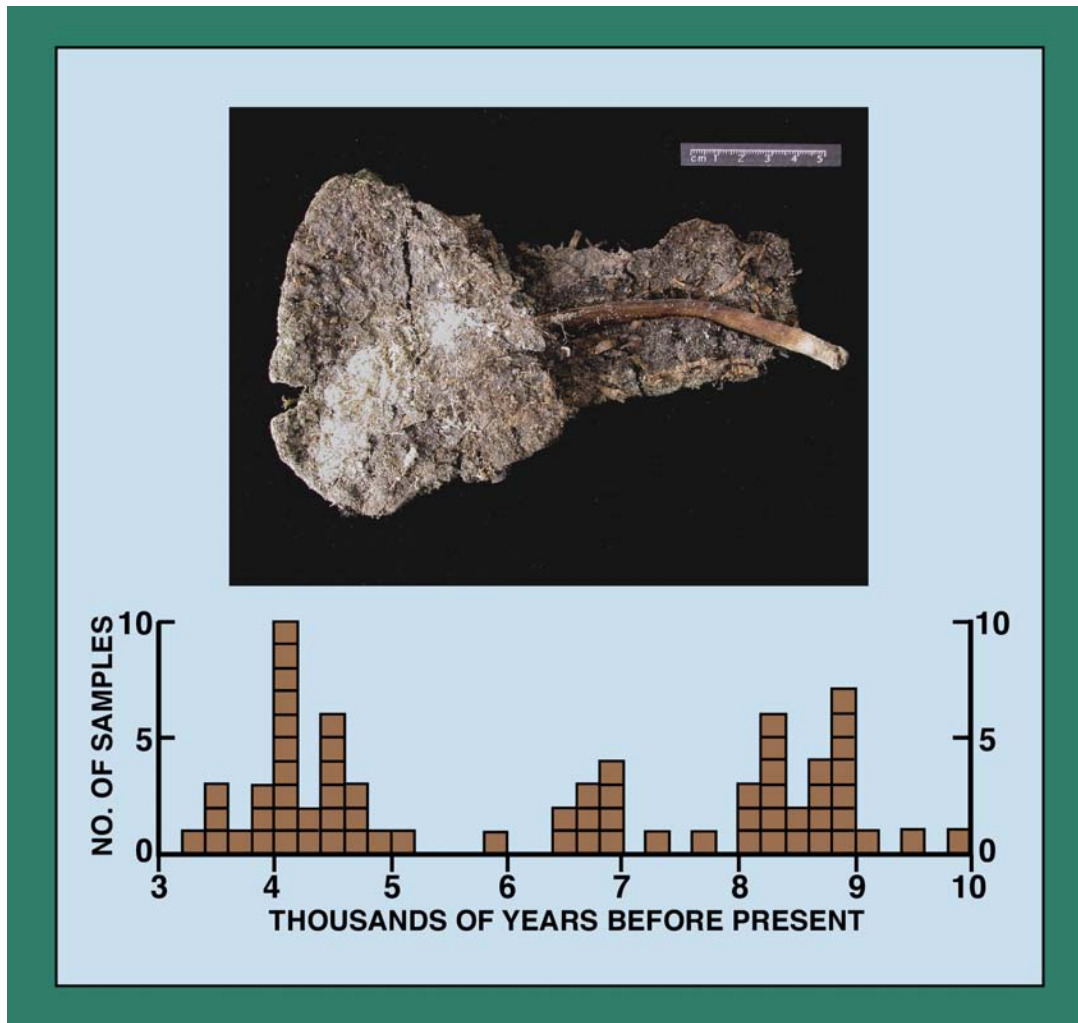


Percentage of iron-stained grains in the ice-rafted debris from a northern Atlantic sediment core for the last 80,000 years. On the average, the red-grain maxima are spaced at 1500-year intervals. Although the minima are not as low and the maxima a bit higher, the record for much of the last glacial period is remarkably similar to that for the Holocene.

results showed that this fraction swung back and forth from lows of 3 to 6 percent to highs of 15 to 20 percent. Because of their large size these grains could not have been transported to the site of his sediment core by either wind or water. Rather, they must have been dropped from melting ice. Bond subsequently showed that the red grains very likely originated in sea ice formed along the margins of islands in the Canadian Arctic where iron-stained sandstones occur and that the unstained grains originated, to a large extent, in ice from northern Atlantic glaciers (Greenland, Elsmere...). Hence, he postulated that the red-grain maxima represent relatively cold episodes during which sea ice originating in the Arctic could survive the long trip to site of his core. Conversely, he proposed that the red-grain minima represent relatively warm periods when the sea ice produced in the Arctic largely melted before reaching his core site. Consistent with this interpretation is Bond's demonstration that the time of the Medieval Warm Period was represented by a red-grain minimum and the Little Ice Age by a red-grain maximum.

Is there evidence confirming the existence of Bond's earlier Holocene warm intervals? Ideally such evidence would come from Europe's mountain glaciers. But, while maxima leave behind moraines, minima go largely unrecorded and, of course, any record which was left behind would be largely erased by subsequent glacial advances. Luckily, Christian Schlüchter of Bern University came up with a means of obtaining information about previous warm intervals. The evidence is in the form of chunks of twisted wood and battered peat which are carried out from beneath the retreating glaciers by each summer's melt water. These chunks represent trees and bogs which existed during times when the glaciers were even smaller than today's. While they do not tell us how much warmer, it is clear that the temperature must have been at least as warm as today's. The results suggest warm periods centered at 8500, 6700 and 4200 years ago.⁶⁹ The two older episodes match two of Bond's red-grain minima.

While the evidence for Holocene temperature fluctuations at high northern latitudes is impressive, as yet no smoking gun that links them to the Atlantic's conveyor



As shown by Ann Hormes and by Ueli Joerin while graduate students at the University in Bern, radiocarbon measurements on wood and peat, carried out from beneath Swiss glaciers with summer melt water, provide information regarding times during the Holocene when summer temperatures were even warmer than today's. The twisted shape of many of the wood fragments bears witness to the fact that they were overrun by advancing ice. Alerted to the importance of such data, efforts are now underway in many of the Earth's glaciated regions to seek and radiocarbon-date material formed in forests and bogs now covered by ice.

circulation has been found. In the case of the Younger Dryas, the rise in atmosphere –surface ocean ^{14}C to C ratio and the antiphasing between temperatures in Greenland and Antarctica provided a link to the conveyor. The Holocene temperature cycles lack the rectangular shape of the Younger Dryas and D-O events. Rather, they give the impression that they are more nearly sinusoidal. Hence, if the conveyor is involved, it has not been turning on and off; rather, it has been waxing and waning in strength.

Is there evidence that the conveyor was involved? Were there to have been an alternation in the relative strength of deep water formation in the northern and in the southern polar regions, it should show up as an alternation in the temperature fluctuations in Greenland and Antarctica. The record from one such borehole in Antarctic ice has been reported at several scientific meetings by Gary Clow of the U. S. Geological Survey (but never published). It suggests that air temperature in the southern polar region was three degrees centigrade colder during the time of the Medieval Warm Period than during the time of the Little Ice Age. It is this observation upon which my hunch is based. But, until the record from this borehole has been properly published and until it has been confirmed in borings at other Antarctic locales, it cannot be used to support the idea that oscillations in conveyor strength occurred.

What about the temperate and tropical regions of our planet? Did they undergo temperature changes in concert with the Medieval Warm Period – Little Ice Age high latitude changes? Only for the cold maximum centered at 1850 A.D. do we have adequate information. It comes from observations by humans of the extent of mountain glaciers. Except for locales experiencing very low snowfall, the planet's mountain glaciers stood at or close to their maximum Holocene extents during the middle of the 19th century (i.e., during the last of the three Little Ice Age cold maxima). Included are mountain glaciers in the tropics (Kenya and Colombia) and in the southern hemisphere (Chile-Argentina and New Zealand). Thus, if Gary Clow's borehole temperature record turns out to typify



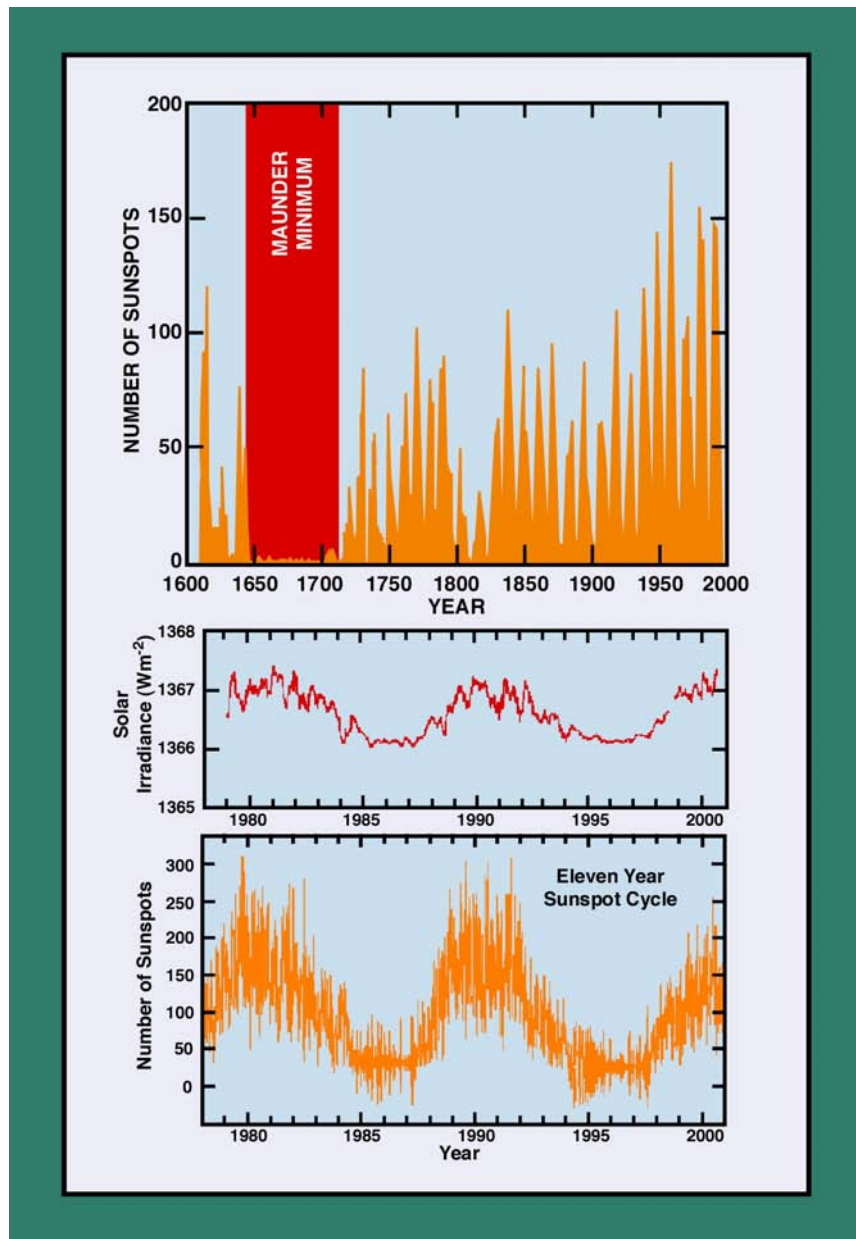
**West Walker River, California (recent photo)
Trees which grew during the Medieval Mega-Drought.**

One of four locales in California's Sierra Nevada where trees grew in areas now covered by water. In each case, the growth period was more than a century and the time of growth was the latter part of the Medieval Warm Period. Together, these fossil trees record a long-term drought more severe than even the short-term ones experienced during historical time.

Antarctica, then the boundary between cooling and warming during the Little Ice Age must have lain in the Southern Ocean rather than at the equator.

Information regarding climate conditions in temperate and tropical regions during the Medieval Warm Period is virtually non-existent. Our paleoclimate proxies for these regions are not sufficiently sensitive to allow 1°C changes in temperature to be reliably detected. Indications of rainfall changes do exist however. For example, Cal State's Scott Stine has documented two profound droughts in the western U.S.A. His case is based on the remains of trees which grew at sites now under water. Two are on lake bottoms, one is a river bed and one is a swamp. All these remains date from two time intervals 900 to 1100 A.D. and 1200 to 1350 A.D. The time is fixed by radiocarbon dates on the wood and the duration by ring counts. In each situation, these century-duration droughts exceeded in intensity even the most severe several year-duration droughts of historic time.

Working with Heidelberg's Bernd Kromer and Zurich's Jurg Beer, Gerard Bond threw the field of paleoclimate into a tizzy by making a case that the Holocene's millennial temperature oscillations were paced by the Sun.⁷⁰ While the Sun has always lingered in the wings as a possible driver of climate change, it had never before made a dramatic appearance. Bond et al. based their conclusion on the similarity between the red-grain record and reconstructions of the rates of production of the radioisotopes ¹⁴C and ¹⁰Be by cosmic-rays bombarding of our atmosphere. The reconstruction of the past rates of ¹⁴C production is based on measurements on wood samples precisely dated by ring counting and matching (dendrochronology). That for the production rate of ¹⁰Be was reconstructed by measurements of its concentration in ice from borings in the Greenland ice cap. The link to the Sun comes from the observation that both of these isotopes were produced at higher rates during what is known as the Maunder Minimum in sunspot activity. Galileo discovered sunspots in 1604 A.D. They were monitored in subsequent years, but in 1645, they disappeared and did not reappear until 1715 A.D. Ions, shot out

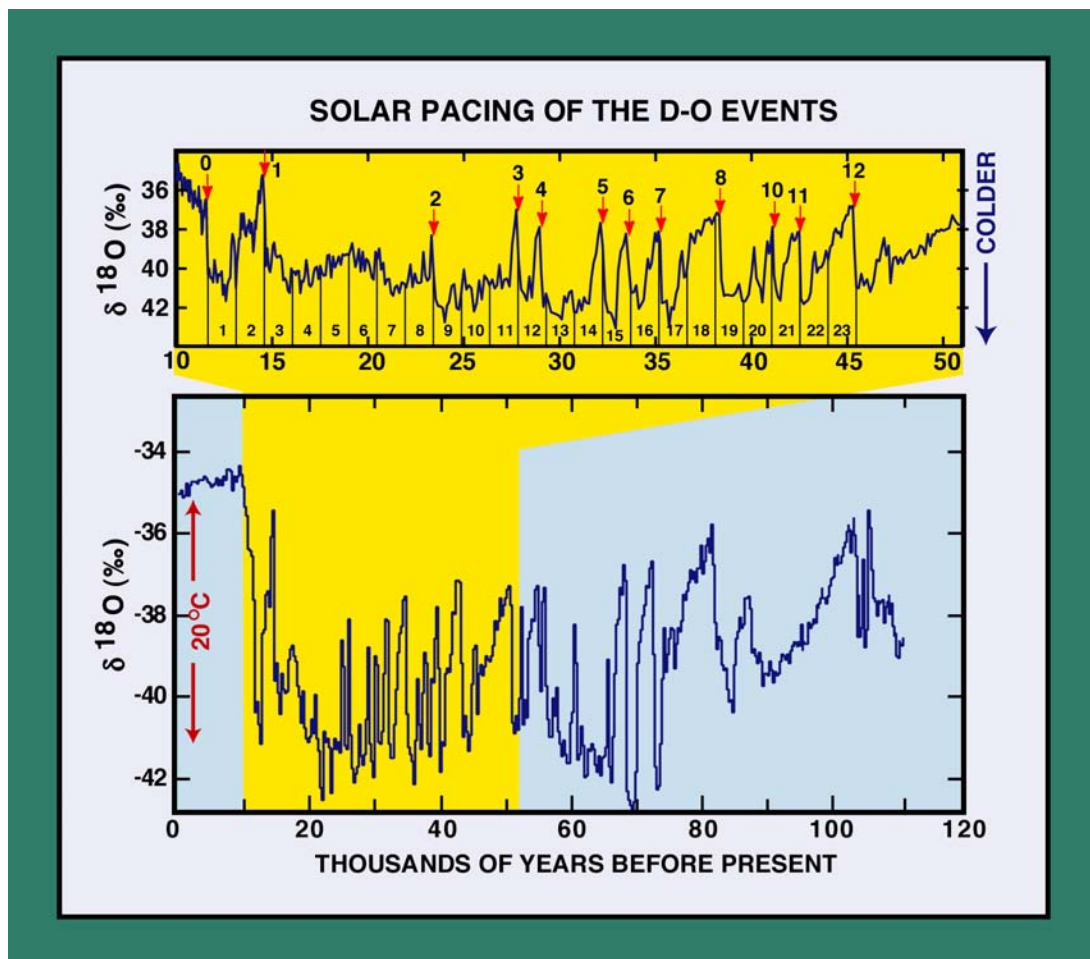


Galileo discovered sunspots in 1604 A.D. Since then, their number has been monitored revealing a strong 11-year cycle. Only during the period from 1645 to 1715 were these dark spots largely absent. Since 1978, measurements (by satellites) of sufficient accuracy have been conducted which allow changes in the Sun's irradiance during the course of these cycles to be assessed. During sunspot maxima the irradiance increases by a tiny amount (one part in 1300). Unless the change was considerably larger during times such as the Maunder Minimum when sunspot activity was much reduced, it is difficult to see how these irradiance changes could perturb the Earth's climate.

from the Sun's magnetic tangles (i.e., its dark spots), create a magnetic field which deflects cosmic rays away from our solar system. During the Maunder Minimum, this shield was largely shut down allowing more cosmic rays than usual to reach Earth and hence more ^{14}C and ^{10}Be to be produced.

Satellite-based measurements document that small changes in solar irradiance accompany the 11-year sunspot cycle. The irradiance was about one part in 1300 greater at the times of the last two sunspot maxima than at the times of the last two sunspot minima.⁷¹ But as these measurements commenced only 25 years ago, we have no way to reliably reconstruct the Sun's irradiance during the Maunder Minimum. In the absence of a long-term record, Bond, Kromer and Beer were forced to assume that the Sun's irradiance followed the rate of production of the cosmogenic nuclides ^{14}C and ^{10}Be and that somehow these admittedly very small irradiance changes were responsible for the temperature cycles at high latitudes in the Northern Hemisphere. But no one has come up with a reasonable scenario as to how tiny changes in solar irradiance produced one degree centigrade temperature shifts. Based on model simulations, their impact would be expected to produce changes of only about one tenth of one degree centigrade. One alternate proposal holds that the considerably larger changes in ultraviolet radiation associated with sunspot cycles changed the concentration of ozone in the stratosphere and that this change somehow impacted the rest of the atmosphere. Another calls on changes in the number of ions created in our atmosphere by cosmic bombardment; the idea being that these ions act as cloud condensation nuclei and hence impact cloud reflectivity. But, at this writing, none of these scenarios had gained particular favor. Perhaps the Sun drives Bond's red-grain cycle, but the physical link remains illusive.

More puzzling is what appears to be a tie between Bond's red-grain cycles and the initiation of D-O events. Not only was his red-grain cycle operative during the Holocene, but it continued back through the entire length of the last glacial period and beyond. Neither the average spacing between red-grain maxima nor their average amplitude



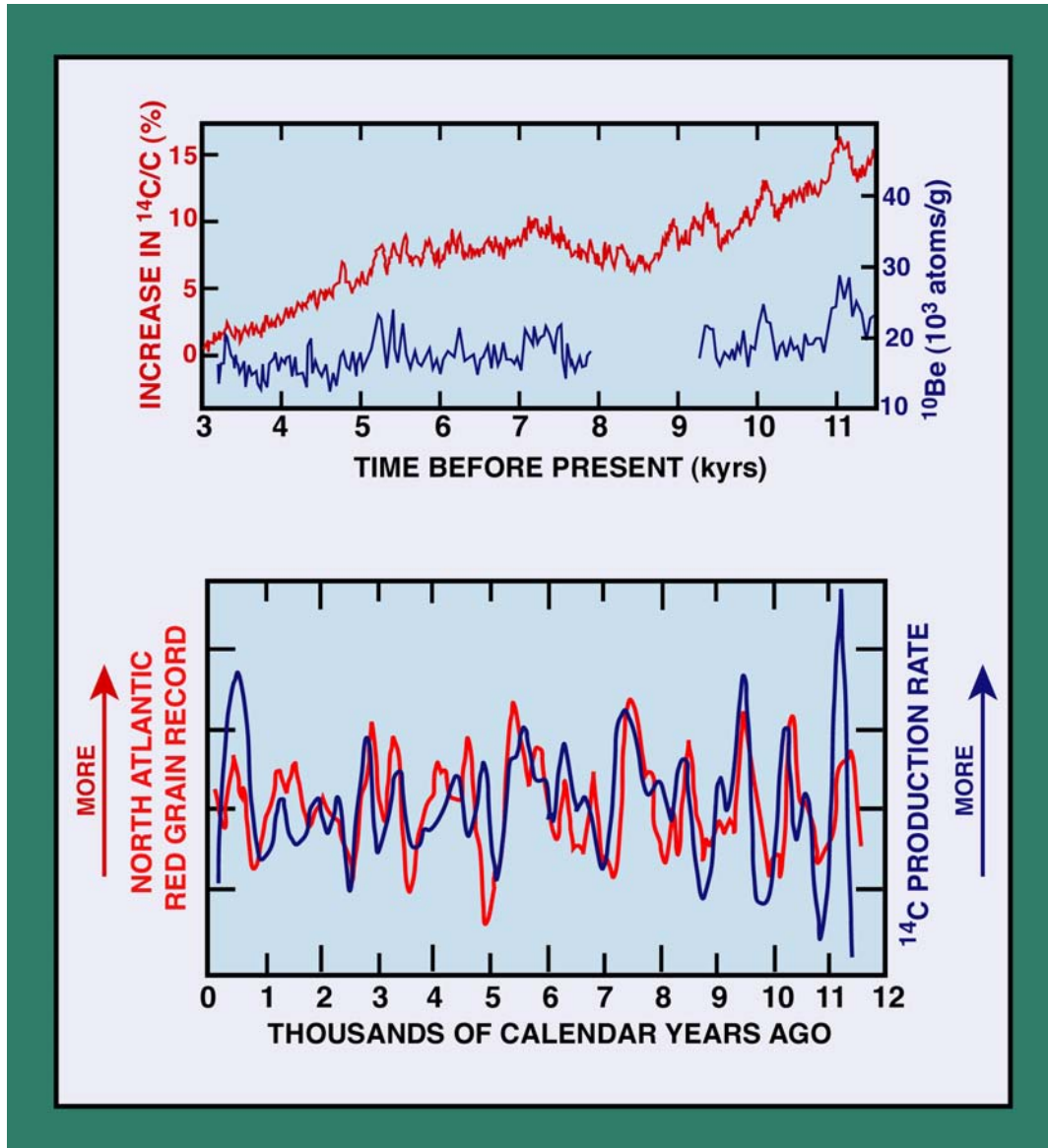
Stefan Rahmstorf pointed out an intriguing coincidence between the timing of the abrupt warmings which mark the onset of each D-O event (and also the end of the Younger Dryas). Starting with the end of the YD, he made 24 time marks spaced at intervals of 1470 years (i.e., the average duration of a Bond's red-grain cycle). He noted that each of the 12 abrupt warmings which occurred during the interval from 12,000 to 45,000 years ago fell close to one of these time marks. Based on this coincidence, he postulated that the small variations in solar irradiance were somehow capable of triggering jumps from one climate system state to another. In order to explain why only about half of the solar pulses succeeded in initiating a jump, he postulated that jumps can only occur when the system is close to its limit of stability.

underwent a significant change from glacial to post-glacial time. Bond shows that although the spacing between the maxima varies, any series of ten lasted close to 14,700 years.

Potsdam's Andrey Ganopolski and Stefan Rahmstorf⁷² picked up on Bond's periodicity and noted that the sharp warmings which initiated each of the D-O events fell uncannily close to time marks spaced 1470 years apart. To explain why there were only 12 such abrupt warmings in an interval spanning 24 of these time marks, Rahmstorf called on what is known to physicists as stochastic resonance. Only when the system was close to its bifurcation point did the nudge provided by the 1470-year cycle kick it into its alternate state of operation. As shown by Penn State's Richard Alley, if the system failed to respond to a particular kick, the record indicates that it was more likely to respond to the next one.⁷³

By postulating that whatever paces Bond's red-grain cycle also paced the D-O events, Rahmstorf certainly raised the ante. During glacial time some of the tiny impulses responsible for the red-grain cycle were able to kick the system into its intermediate mode (i.e., the mode represented by the warm phases of the D-O events). Hence, if the Sun paces the red-grain cycles, Rahmstorf would contend that it must also pace the D-O events. If so, then changes in solar luminosity, so tiny that they appear far too weak to explain the one degree centigrade swings during the Holocene temperature, somehow also led to order of magnitude larger D-O cycles.

As this stretches credibility, one might ask, could there be another way to explain the correlation between the red-grain record and the ^{14}C and ^{10}Be reconstructions? I say "reconstructions" rather than "production rates" because the only alternate explanation that has a chance of being correct is that the cycles in both these cosmogenic isotopes are the result of terrestrial rather than solar changes. As we have already seen, the ^{14}C to C ratio in atmospheric CO_2 is sensitive to changes in the strength of conveyor circulation. The ^{10}Be atoms produced in the atmosphere do not fall like hail stones. Rather, these



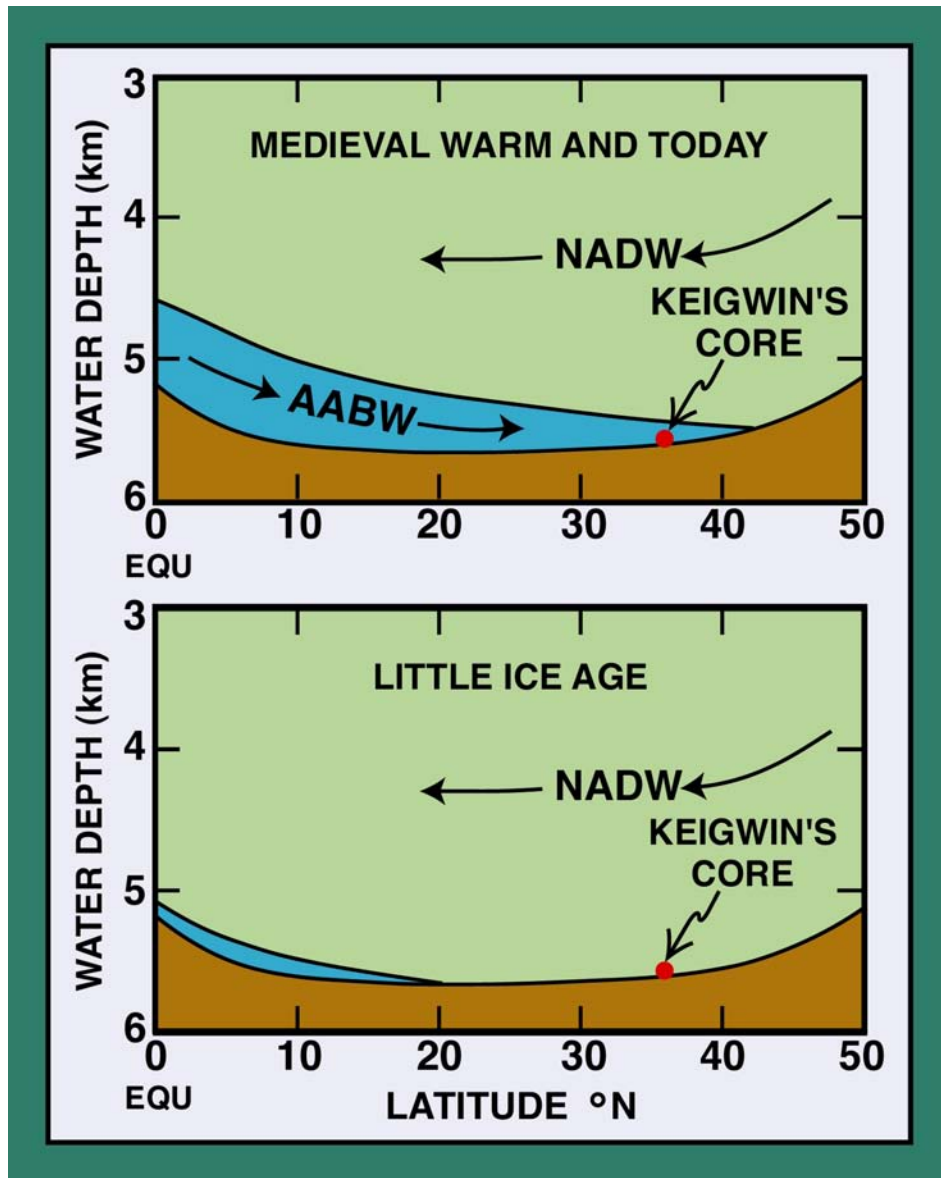
In the upper panel, the tree-ring-based reconstruction of the ^{14}C to C ratio in atmospheric CO_2 for the period 3000 to 11,500 years ago is compared with the ^{10}Be concentration measurements in Summit Greenland ice available for portions of this time interval. As can be seen, the peaks in the ^{10}Be record nicely match those in the ^{14}C record suggesting that both result from increases in the cosmic ray bombardment of our atmosphere (i.e., increases in production rate).

Gerard Bond compared his red-grain record with that of the production-rate radiocarbon atoms in our atmosphere (see lower panel). In order to do this, he had to remove the long-term downward trend from the record and focus on variations which occurred on a millennial time scale. As can be seen, the match between the variations in cosmic ray production and that in the percentage of red-stained grains is reasonably good. This match led Bond and his co-authors to conclude that the red-grain cycles were paced by the Sun.

atoms become attached to tiny aerosols and are carried by air currents over great distances before touching down on the planet's surface. Further, most of the ^{10}Be atoms reaching the surface of the Greenland ice cap arrive attached to snow flakes. It turns out that the number of ^{10}Be atoms deposited per square meter per year at the sites of Greenland's Summit ice cores is only one third of the average global production rate of this isotope. Because of the complexity of the routing to the ice cap and the association of the delivery to the ice cap with snowfall, this fraction could well depend on climate. Hence, were the temperature cycles at high latitude in the Northern Hemisphere associated with oscillations in the strength of the conveyor, then one might expect changes in both the concentrations of ^{14}C in atmospheric CO_2 and of ^{10}Be in Greenland ice. The sense would have to be higher ^{14}C and ^{10}Be during times when the conveyor was weaker and Greenland was colder.

Could this alternate scenario be the answer? Although the terrestrial explanation is certainly viable, one observation strongly favors the production explanation. The relative magnitude of the fluctuations in ^{10}Be compared to those ^{14}C are as expected if the cause were changes in cosmic ray production. Those favoring a terrestrial explanation would have to attribute this agreement to a coincidence. The proof of the pudding will come when a detailed ^{10}Be record for an Antarctic ice core becomes available. If it agrees with the Greenland record, then the production hypothesis will gain even greater credibility.

Scott Lehman of the University of Colorado has proposed another test. He eyes the bumps in the ^{14}C record in the 9 to 11 thousand-year age range and asks what a comparable record based on foraminifera from deep sea sediments would look like. He postulates that if ^{14}C production is the cause for these bumps, then the surface ocean record should lag the atmosphere record and have a smaller amplitude. On the other, if ocean mixing is the cause, the bumps should look much the same as those in the atmospheric record. Lehman hopes to conduct this test using shells from the annually



Penetration of Antarctic Bottom Water (AABW) into the western of the northern Atlantic. Radiocarbon measurements on benthic foraminifera shells by Lloyd Keigwin clearly demonstrate that during the Little Ice Age this tongue was pushed back by the North Atlantic Deep Water (NADW). Recently, the AABW tongue has pushed its way back into the northern Atlantic. It now reoccupies the “territory” it held during the time of the Medieval Warm.

layered sediment in the Cariaco Basin.

Why might the conveyor oscillate in strength? It would have to be postulated that for some reason the export of salt never quite matches the export of water vapor. If salt export were to be too slow, then salt would build up in the Atlantic forcing the conveyor to run faster. If this speed up eventually led to an overshoot in salt export, then the conveyor would be forced to weaken until it once again had failed to export salt fast enough. However, if, instead of undergoing overshoots, the conveyor strength merely adjusted itself to match the rate of salt buildup, then there would be no oscillation. In order to oscillate, there must be some delay mechanism which allows overshoots to occur. As the time constant of Bond's oscillation is on the order of 1500 years, the delay would have to be roughly half this long (i.e., 750 years).

To date, no one has articulated what this delay might be. I suspect that it might have to do with the time waters spend in the deep Pacific and Indian Oceans. As we have seen, radiocarbon tells us that this time is currently on the order of 800 years. Okay, but what's the connection? One possibility is that it involves an oscillation in salt content between the deep Atlantic Ocean and the deep Pacific–Indian Oceans. In a sense, the sites of deep water production in Southern Ocean are in competition with those in the northern Atlantic Ocean. The more dense the source water, the greater its advantage in its competition for space in the deep sea. Hence, one of the influences on the density of deep water produced in the Southern Ocean is the density the water re-circulated from the deep Pacific and Indian Oceans. As the re-circulating water spends many hundreds of years traveling through the deep realm of these two oceans, its salt content remembers the time when it formed. Hence, we have the makings of an oscillator.

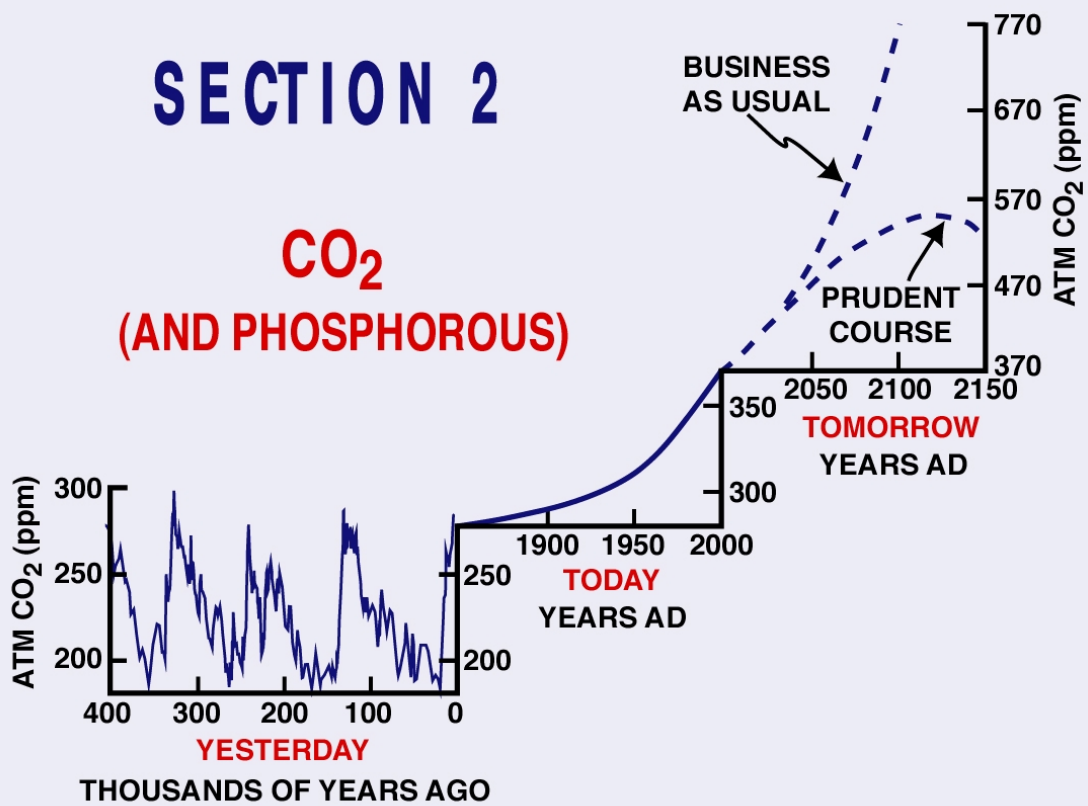
As this book was being written, Lloyd Keigwin of Woods Hole Oceanographic made an extremely important discovery. It involves measurements of the ^{14}C to C ratios in benthic foraminifera picked from a sediment core raised northeast of Bermuda. As the sedimentation rate at the site of this core is extremely large, events during the last one

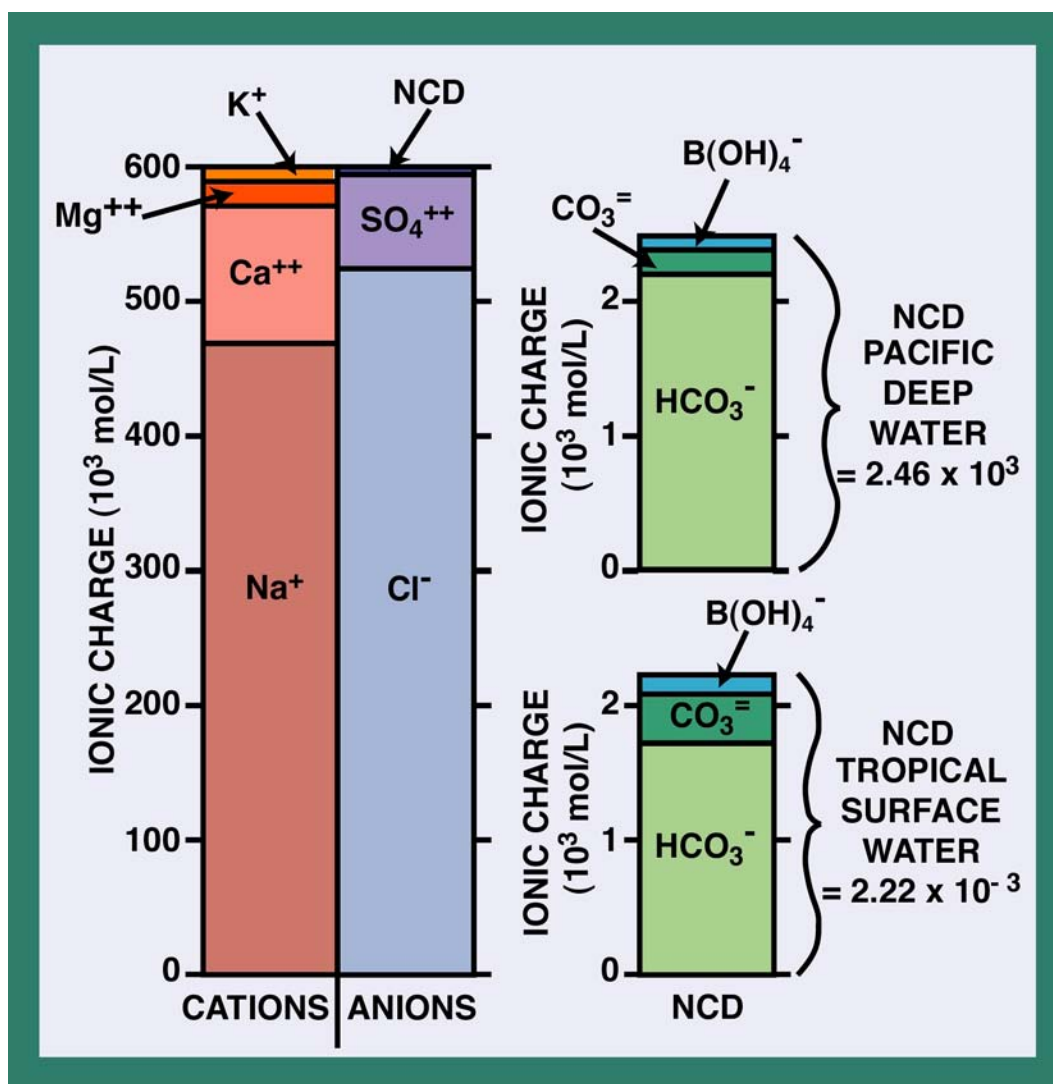
thousand years are well resolved. Keigwin found that during the time of the Medieval Warm Period, his measurements indicated that the core site was bathed in the tongue of low radiocarbon northward penetrating Antarctic Bottom Water. Then, with the onset of the Little Ice Age, this tongue must have retreated for the radiocarbon values in the benthic forams increased to a value typifying North Atlantic Deep Water. Then, at the close of the Little Ice Age, Keigwin's measurements indicate that the low radiocarbon tongue moved back over the site. The implications of this discovery are large. First, they suggest that indeed the relative strengths of deep water production in northern and southern source regions have oscillated in concert with temperature changes at high northern latitudes. Second, it suggests that during the Little Ice Age the deep water formed in the northern Atlantic was sufficiently dense to repel the invasion of waters from the Southern Ocean. While I had been thinking that the Little Ice Age might have been the result of a weakening of conveyor circulation and hence heat delivered to the surface of the northern Atlantic, Keigwin's discovery suggests the opposite. Colder conditions in the northern Atlantic caused the deep waters which formed there to become more dense. Hence, the bottom line appears to be that the atmosphere sent the message to the ocean rather than vice versa.

This has been a rather extensive detour from the question as to whether or not the conveyor is headed toward an imminent shutdown. The upshot is that we know for sure that temperatures at high northern latitudes have been swinging back and forth on a millennial time scale. As these changes likely involve fluctuations in the strength of the conveyor circulation, the reduction of salinity during the last half century may reflect just another of these natural fluctuations. However, considering the large gaps in our knowledge, it behooves us to intensify our efforts to monitor the ongoing status of the conveyor's strength!

SECTION 2

CO₂ (AND PHOSPHOROUS)





Balance between the positively-charged ions (i.e., cations) and the negatively-charged ions (i.e., anions) in sea water. The major ions have fixed charges as shown. The tiny imbalance between the total positive charge carried by the cations and the total negative charge carried by the anions ions (i.e., the negative charge deficit or NCD) is made up by ions of the elements carbon and boron. The ions of these elements can achieve more than one charge state. Carbon can assume the neutral carbon dioxide form, the singly-charged bicarbonate form or the doubly-charged carbonate form. Boron can assume the neutral form or the singly-charged form.

The NCD in deep water is larger than that for surface waters because Ca^{++} ions are incorporated into CaCO_3 in surface waters and released by dissolution of CaCO_3 in deep waters.

Of course, ions of all the other elements on the periodic table contribute to the charge balance. But, as their contributions are tiny, they are not shown here.

CHAPTER 4

TODAY'S CHEMISTRY

Unlike the majority of the constituents of sea salt, whose ratios to one another are everywhere the same, those constituents used as building blocks by marine organisms vary in concentration both with location and water depth. Our interest lies with the concentrations of the three species of dissolved inorganic carbon: i.e., bicarbonate ion (HCO_3^-), carbonate ion (CO_3^{--}) and carbon dioxide gas (CO_2). We will, of course, concentrate on the CO_2 concentrations in surface ocean waters for it is these concentrations which taken together dictate the atmosphere's CO_2 content. In this chapter, I deal with the ocean as it was before the Industrial Revolution. The reason is that by burning fossil fuels we have altered the ocean's chemistry.

Marine plants capture CO_2 molecules from the surrounding water and use the carbon atoms as building blocks for their soft tissue. Marine animals and bacteria consume this organic matter converting the carbon back to CO_2 . However, between the time of its formation in the sunlit upper ocean and its consumption, some of the organic tissue sinks (or swims) into the vast ocean interior before being eaten. The net result is that CO_2 is removed from surface waters and added to deep waters. So, in a sense, marine organisms are working to hold down the CO_2 content of surface waters and hence also of the atmosphere. Geochemists refer to this process as the ocean's biological pump.

What actually happens when CO_2 is removed from surface waters by plants is, however, more complicated. The reason is that CO_2 maintains an equilibrium with its companion HCO_3^- and CO_3^{--} ions



The relationship among the concentrations of these three species of carbon must fulfill the requirement that

PROPERTIES	TROPICAL SURFACE	DEEP PACIFIC	UNITS
WATER DEPTH	0	4000	meters
TEMPERATURE	25.0	1.5	°C
SALINITY	35.0	34.7	g/kg
P_{CO_2}	280	510*	10^{-6} atm
NCD	2216.0	2450.0	10^{-6} mol/kg
ΣCO_2	1858.0	2340.0	10^{-6} mol/kg
$(CO_2)_{aq}$	7.9	29.9	10^{-6} mol/kg
(HCO_3^-)	1601.5	2215.0	10^{-6} mol/kg
(CO_3^{2-})	248.5	95.0	10^{-6} mol/kg
ΣB	410.6	407.1	10^{-6} mol/kg
$B(OH)_3^0$	302.0	362.6	10^{-6} mol/kg
$B(OH)_4^-$	108.6	44.5	10^{-6} mol/kg
(OH^-)	8.8	0.4	10^{-6} mol/kg
pH	8.15	7.77	
* AT SEA SURFACE PRESSURE			

Comparison of the ionic compositions of a typical tropical surface water and a typical Pacific deep water. The difference in NCD reflects $CaCO_3$ formation in surface water and dissolution in deep water. The difference in ΣCO_2 reflects photosynthesis-respiration cycle as well as the $CaCO_3$ cycle. The CO_2 partial pressure in deep water cannot, of course, be measured; rather, the value listed here is that which would be measured were the sample brought to the surface and maintained at its *in situ* temperature. Because high accuracy is required, marine chemists express concentrations in units of moles per kilogram rather than moles per liter. The reason is that while the volume of a water parcel varies with temperature (i.e., expands when heated) its weight remains the same.

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

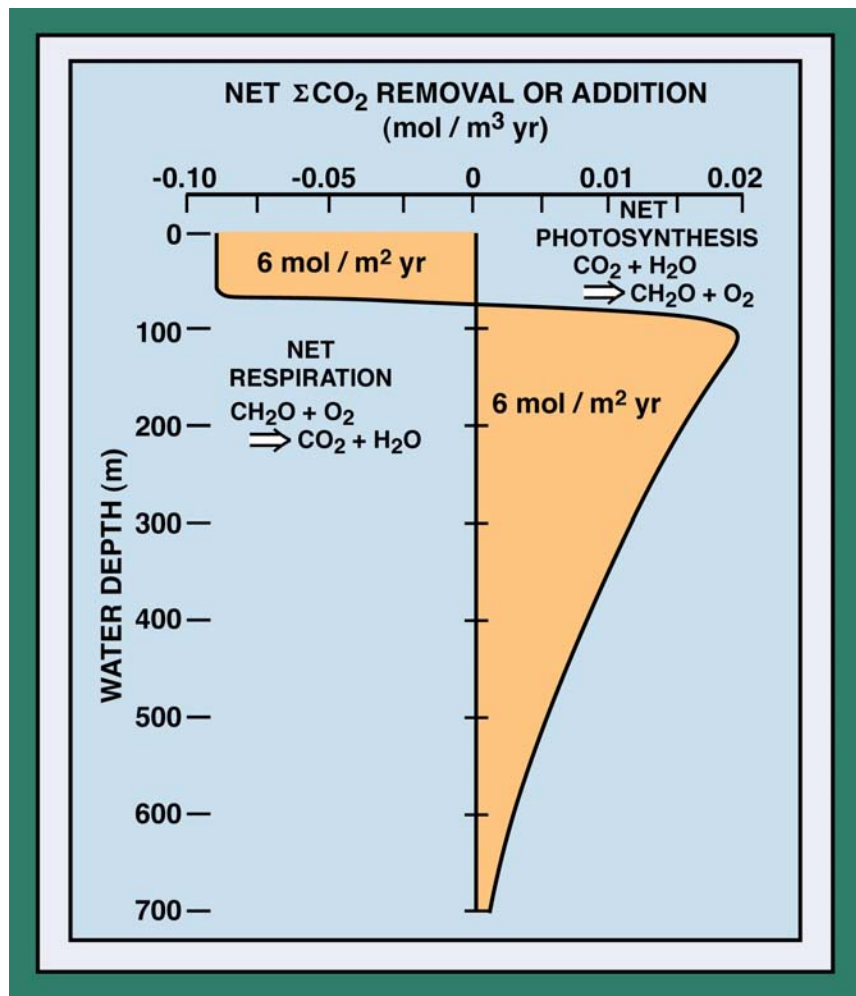
where k is a constant whose value depends on the temperature (and salinity) of the sea water.

Another requirement is that the sum of the negative charges on the anions dissolved in sea water must exactly match the sum of the positive charges on the cations. In other words, sea water must be electrically neutral. Most of the ions dissolved in sea water have a fixed electrical charge. Sodium and potassium ions have one positive charge (i.e., each has given up one of its orbital electrons). Magnesium and calcium ions have two positive charges. Chloride ions have a single negative charge (each has taken on one extra orbital electron). Sulfate ions have two negative charges. When totaled, the fixed charges on the positive ions (i.e., cations) exceed the fixed charges on the negative ions (i.e. anions) by a small amount. Chemical oceanographers refer to this deficit in negative charge as “alkalinity”. As the term “alkalinity” inevitably confuses students, I choose to give it another name which helps to keep in mind what it signifies. “Alkalinity” will instead be referred to as “negative charge deficit” or NCD. The negative charge deficit is compensated by ions which can exist in more than one charge state. The carbon species ($CO_3^{=}$ and HCO_3^-) and the boron species (HBO_3^- and H_2BO_3) serve in this role. In tropical surface water 95 percent of the NCD is made up by a combination of two carbon species and about 5 percent by the charged boron species. In Pacific deep water charged borate makes up only 2 percent of the NCD.

In order to keep the discussion manageable, I will assume that boron doesn’t exist. Hence in our simplified ocean

$$NCD = [HCO_3^-] + 2[CO_3^{=}]$$

So, based on the requirements that the species of inorganic carbon be at equilibrium with one another and that the water be electrically neutral, we can write down three equations



As photosynthesis requires light, it occurs only in the upper 100 or so meters of the water column. Everywhere in the ocean, there exists a wind-stirred and therefore chemically-homogenous surface layer. It is within this layer that most of the ocean's photosynthesis occurs (and also much of its respiration). As some sunlight penetrates through the mixed layer into the underlying stratified thermocline, photosynthesis also occurs beneath the wind-stirred layer. But, as the available light dwindles with depth, respiration gains the upper hand (shown here at 70 meters). Below about 100 meters, there is no further photosynthesis. As the organic matter which rains below this depth is efficiently "eaten," the amount of carbon returned to dissolved form drops off dramatically with water depth. So efficient are these consumers that only about one percent of the photosynthetic product reaches the deep sea (i.e., to depths greater than 1 km).

Since more than 99.9 percent of the organic carbon produced by photosynthesis is ultimately eaten, the amount of net respiration below the crossover depth (shown here as 70 meters) must match the net photosynthetic production above this depth.

Note that in order to make the diagram manageable, the scale to the left of zero differs by a factor of five from that to the right of zero.

which allow the concentrations of CO_2 , HCO_3^- , and $\text{CO}_3^{=}$ to be calculated. The first states the requirement that the solution be electrically neutral.

$$1) \quad \text{NCD} = [\text{HCO}_3^-] + 2[\text{CO}_3^{=}]$$

The second states the requirement that the concentrations of the three species of inorganic carbon add up to the total inorganic carbon (i.e., ΣCO_2) concentration.

$$2) \quad \Sigma\text{CO}_2 = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{=}]$$

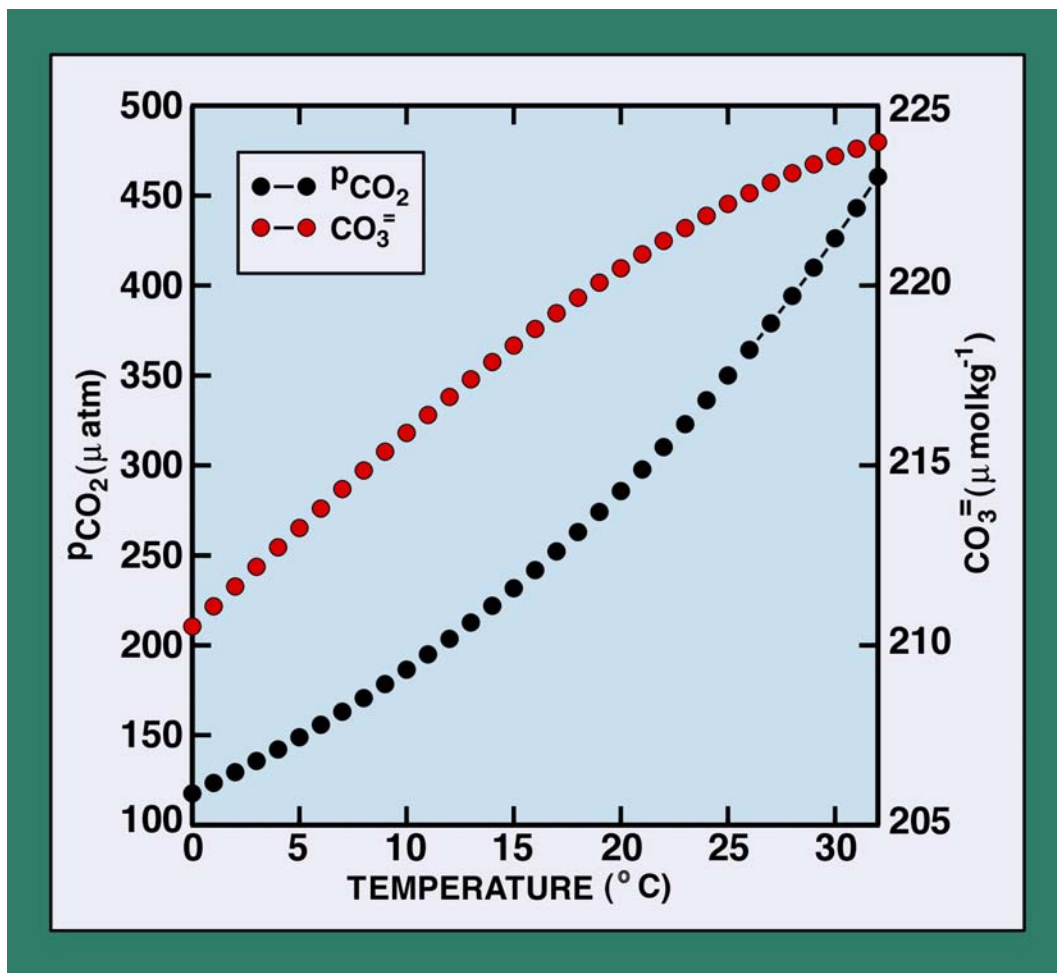
The third states the requirement that equilibrium must be maintained among the inorganic carbon species.

$$3) \quad k = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_2][\text{CO}_3^{=}]}$$

These three equations contain five unknown quantities and only one known quantity (i.e., k). Hence only if two of these quantities are measured can the other three be calculated. Marine chemists have techniques capable of measuring both the NDC and ΣCO_2 (the former by titration with acid and the latter by measuring the amount of CO_2 released when the water sample is acidified). It is also possible to directly measure the partial pressure exerted by the CO_2 gas dissolved in the water by equilibrating a large amount of sea water with a small amount of air and then measuring the CO_2 content of the air.

I drag the reader through this bit of chemistry because our discussion of what controls the CO_2 content of the atmosphere will revolve around changes in the concentrations of ΣCO_2 and NCD both with location in the sea and with time.

We have already seen that the ΣCO_2 concentration in surface sea water is reduced by photosynthesis and that in deep water it is increased by respiration. But in addition to forming soft tissue, some marine organisms form CaCO_3 hard parts (i.e., cages or shells). In so doing, they decrease both the ΣCO_2 content of the water and the NCD as well. The reason that the NCD decreases is that calcium is removed from the water and, of course, its positive charges are removed as well. Thereby the negative charge deficit is reduced.



The dependence on temperature of the carbonate ion concentration and the partial pressure of CO_2 gas for a water sample with a fixed ΣCO_2 concentration of 1935×10^{-6} moles per kilogram and a fixed NCD of 2250×10^{-6} moles per kilogram.

Photosynthesis removes CO₂ from the water reducing the partial pressure exerted by this gas on the overlying atmosphere. By contrast, even though calcite formation removes carbon from the water and thereby lowers its ΣCO₂ content, the partial pressure of carbon dioxide rises instead of falls. The reason has to do with the removal of calcium's two positive charges.

To see why calcite formation has the opposite impact on the CO₂ concentration in sea water as photosynthesis, let us consider the composition of a hypothetical warm surface water for which:

$$k = 1.45 \times 10^3$$

$$\Sigma\text{CO}_2 = 1910 \times 10^{-6} \text{ mol/L}$$

$$\text{NCD} = 2100 \times 10^{-6} \text{ mol/L}$$

$$\text{HCO}_3^- = 1700 \times 10^{-6} \text{ mol/L}$$

$$\text{CO}_3^{=} = 200 \times 10^{-6} \text{ mol/L}$$

$$\text{CO}_2 = 10 \times 10^{-6} \text{ mol/L}$$

Now let us assume that organisms remove 50×10^{-6} moles per liter of carbon via photosynthesis. The composition of sea water changes to:

$$\Sigma\text{CO}_2 = 1860 \times 10^{-6} \text{ mol/L}$$

$$\text{NCD} = 2100 \times 10^{-6} \text{ mol/L}$$

$$\text{HCO}_3^- = 1606 \times 10^{-6} \text{ mol/L}$$

$$\text{CO}_3^{=} = 247 \times 10^{-6} \text{ mol/L}$$

$$\text{CO}_2 = 7 \times 10^{-6} \text{ mol/L}$$

As expected, the CO₂ concentration drops. But while 50×10^{-6} moles per liter of CO₂ were removed, the CO₂ content dropped by only 3×10^{-6} moles per liter. The remaining 47×10^{-6} moles/liter come from the bicarbonate-carbonate ion pool. With fewer inorganic carbon ions, more carbonate ion is needed to match the NCD.

The next step is to assume that the organisms also remove 50×10^{-6} moles per liter of Ca and C from the water to produce calcite cages and shells.

RESPIRATION RATIOS <u>THROUGHOUT THE OCEAN INTERIOR</u> ORG (P) : ORG (N) : ORG (C) : ORG (H) : O₂ 1 : 16 : 130 : 52 : -175 $16 \text{ NH}_3 + 16 \text{ HCO}_3^- + 32 (\text{O}_2) \Rightarrow 16 (\text{NO}_3)^- + 16 \text{ CO}_2 + 32 (\text{H}_2\text{O})$ $130 (\text{CH}_2\text{O}) + 130 (\text{O}_2) \Rightarrow 130 (\text{CO}_2) + 130 (\text{H}_2\text{O})$ $52 (\text{H}) + \frac{13 (\text{O}_2)}{175 (\text{O}_2)} \Rightarrow 26 (\text{H}_2\text{O})$						
<u>IN THE DEEP PACIFIC</u> ORG C : CaCO₃ : SiO₂ 1 : ~1 : ~1						
<u>COMBINED RATIOS IN DEEP PACIFIC</u> PO₄ : NO₃ : SiO₂ : ΣCO₂ : NCD : Ca : O₂ 1 : 16 : 130 : 260 : 260 : 130 : -175						

Based on regressions of property against property (see page 89 for examples), it is possible to determine the average composition of the particulates being decomposed in the ocean's interior and the amount of O₂ required to accomplish their decomposition. Surprisingly, despite compositional differences among marine plants, the ratios obtained for deconvolutions carried out in the deep water of the cold Norwegian Sea and the deep water of the warm Red Sea are similar to those obtained for the deep Pacific and Indian Oceans and also for the thermoclines of the Atlantic Ocean and the Indian Ocean..

The ratio of CaCO₃ dissolution to organic carbon oxidation is obtained by regressing NCD against ΣCO₂. This allows the amount of excess ΣCO₂ derived from CaCO₃ dissolution to be subtracted from the ΣCO₂ excess to yield the amount derived from respiration.

The ratio of opal dissolution to CaCO₃ dissolution is obtained from the regression of NCD against dissolved silica.

As the O₂ demands required for the conversion of NH₃ bound in organic matter to NO₃⁻ dissolved in sea water and of carbon in organic matter to ΣCO₂ do not add up to the amount of O₂ lost, it is assumed that the remainder of the missing O₂ goes into the conversion of organic-bound hydrogen atoms into water molecules.

$$\Sigma\text{CO}_2 = 1810 \times 10^{-6} \text{ mol/L}$$

$$\text{NCD} = 2000 \times 10^{-6} \text{ mol/L}$$

$$\text{HCO}_3^- = 1820 \times 10^{-6} \text{ mol/L}$$

$$\text{CO}_3^{=} = 198 \times 10^{-6} \text{ mol/L}$$

$$\text{CO}_2 = 9 \times 10^{-6} \text{ mol/L}$$

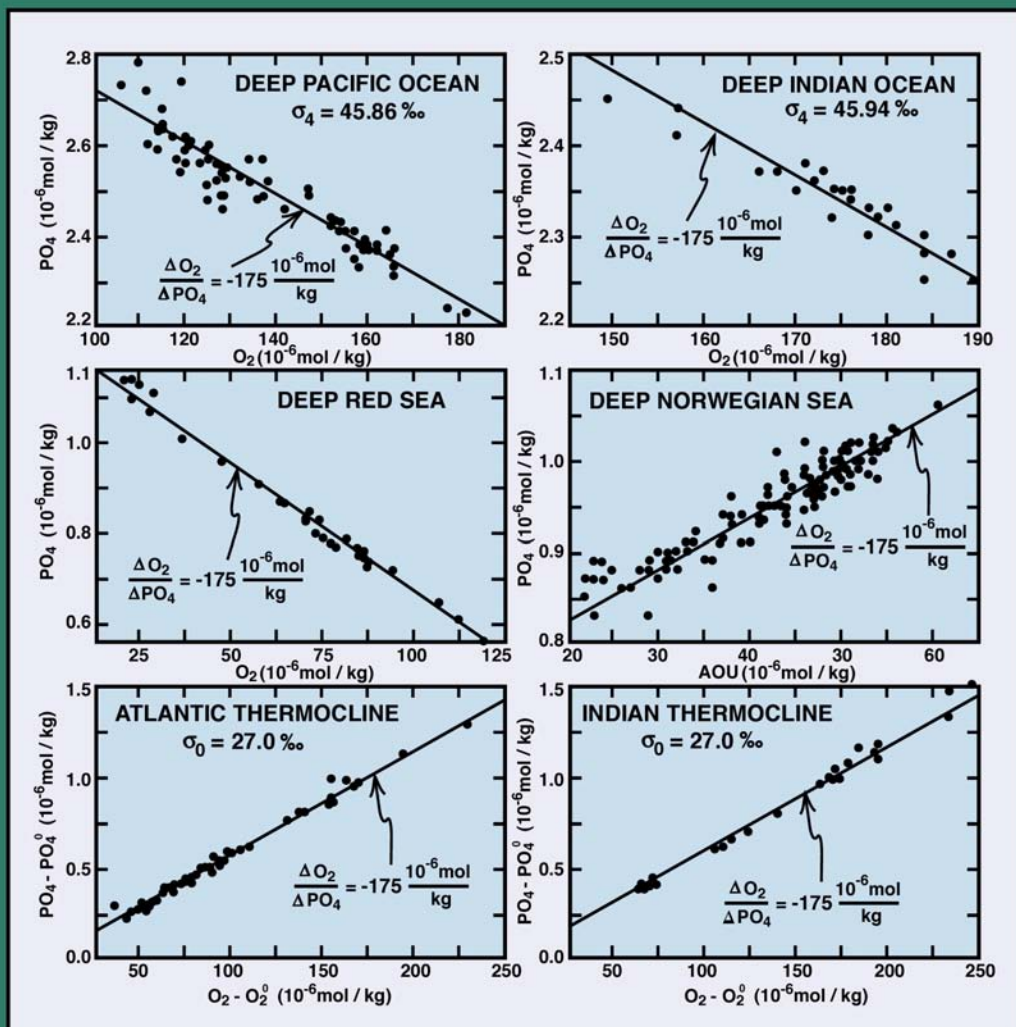
Despite the removal of 50×10^{-6} moles /liter of carbon from the water, its CO_2 gas concentration rises from 7 to 9×10^{-6} moles/liter. The reason is that as the negative charge deficit is reduced by the removal of 50×10^{-6} moles/liter of calcium (i.e., reducing the NCD by 100×10^{-6} moles per liter). Hence the $\text{CO}_3^{=}$ ion concentration drops and the CO_2 content rises.

It is interesting to note that the carbonate ion concentration increased from 200 to 247×10^{-6} moles per liter as the result of the photosynthetic removal of CO_2 . It then dropped back to very close to its original value as the result of the creation of calcium carbonate cages and shells.

This section of the book is entitled “Carbon and Phosphorus”. There is a good reason for this choice. Marine organisms require both nitrogen and phosphorus in addition to carbon. They need about one phosphorus atom and 16 nitrogen atoms for every 130 carbon atoms they incorporate into their organic tissue. In average ocean water, there are about 1000 molecules of ΣCO_2 for every molecule of PO_4 . Thus, as organisms have a glut of available carbon, their productivity is instead limited by the availability of nitrogen and phosphorus.

So, why was phosphorus chosen instead of nitrogen? The reason is that some marine organisms have the enzymes capable of converting dissolved N_2 gas to nitrate ion. By contrast, no means exists for marine organisms to enhance their phosphorus supply. Rather, they must rely on that delivered from the continents dissolved in river water.

One of the great puzzles in marine chemistry is why the ratio of nitrate to phosphate dissolved in the sea is close to the N to P ratio in marine organisms. The most



Regressions of PO_4 concentration against O_2 concentration for four regions of the deep ocean fed by a single source and for two of the oceanic thermocline isopycnal horizons where the compositions are influenced by the mixing of two end-members. In all six cases, a line with a slope of -175 moles O_2 per mole PO_4 provides an adequate fit to the measurements.^{74,75}

likely explanation holds that, as breaking the bond that binds N_2 molecules requires a lot of energy, organisms produce only enough nitrate to match the available phosphorus supply. But an alternate explanation lurks. It holds that it is nitrogen which limits plant growth and organisms “luxury” store any available phosphorus. As we shall discuss in the next chapter, it matters greatly which of these explanations is the correct one. In the discussions which follow, we will assume the first explanation to be the correct one.

The extent to which the phosphate supplied to surface waters by upwelling is utilized varies greatly from region to region. At temperate latitudes, little of the phosphate goes unused. By contrast, at high latitudes and in portions of the tropical ocean, much of the available phosphate goes unused. This distribution mirrors the pattern of upwelling of subsurface waters which carry with them phosphate (and the respiration CO_2) accumulated in the ocean’s interior. The primary reason phosphate is not entirely utilized is that it is supplied faster than the organisms can consume it. But, as we shall see, the sparsity of sunlight and surprisingly, a dearth of the element iron are likely important contributors.

It might be expected that exchange with the atmospheric CO_2 would lead to the same partial pressure of CO_2 in all surface waters. But this is not the case. For example, the CO_2 partial pressure in eastern tropical Pacific surface waters exceeds that in the atmosphere by as much as 50 percent. Even though the excess CO_2 tends to escape to the atmosphere, it turns out the rate of escape is too slow to eliminate the excess.

A surprise in this connection is that phosphate-rich surface waters in the Southern Ocean have CO_2 partial pressures similar to those for phosphate-free surface waters in the temperate regions. One might conclude from this that the respiration CO_2 associated with the phosphate upwelled into the Southern Ocean largely escapes to the atmosphere. But, that is not the answer. Rather, the answer has to do with the dependence of the partial pressure exerted by the CO_2 dissolved in the water on water temperature. Because the solubility of CO_2 increases with decreasing water temperature, for any given CO_2 content

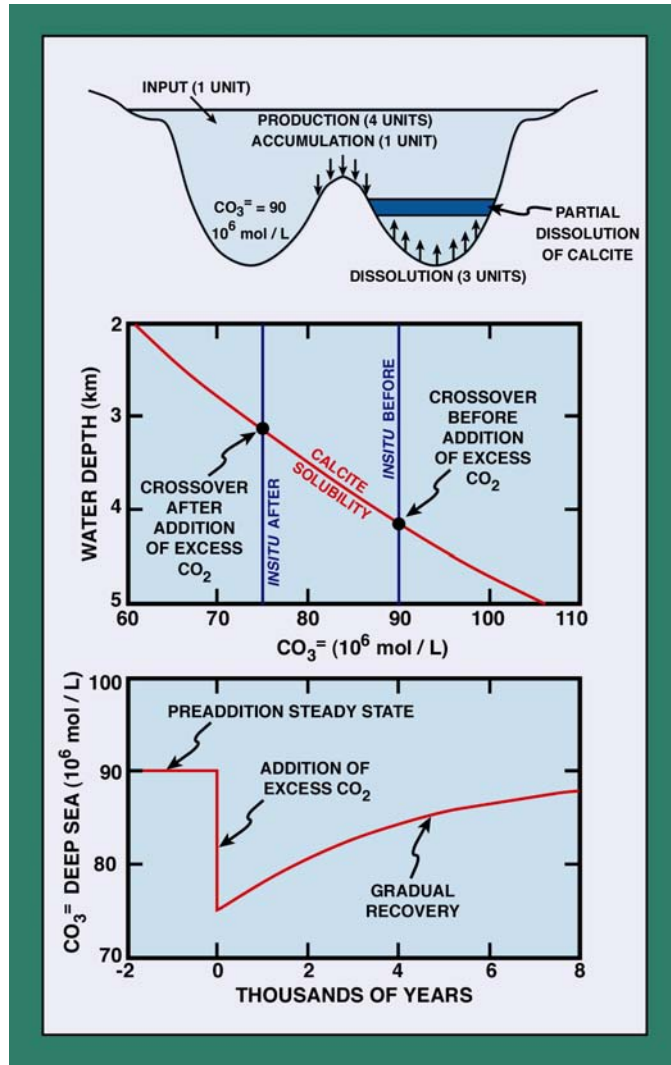
	SURF. TROPICAL OCEAN	NO- WHERE	SURF. NORTH. OCEAN	SURF. SOUTH. OCEAN	
TEMP.	25°	1°	1°	1°	°C
PO ₄	0.0	0.0	0.8	1.6	10 ⁻⁶ mol / L
RESP. CO ₂	0	0	100	200	10 ⁻⁶ mol / L
BEFORE UPTAKE OF CO₂ FROM THE ATMOSPHERE					
P _{CO₂}	280	90	160	280	10 ⁻⁶ atm
ΔΣ CO ₂	0	0	0	0	10 ⁻⁶ mol / L
AFTER UPTAKE OF CO₂ FROM THE ATMOSPHERE					
P _{CO₂}	280	280	280	280	10 ⁻⁶ atm
ΔΣ CO ₂	0	+200	+100	0	10 ⁻⁶ mol / L

Comparison of the CO₂ partial pressures in four buckets of sea water with the same NCD but at different temperatures and different phosphate contents (and hence different respiration CO₂ contents). The water in the warm bucket has been equilibrated with an atmosphere containing 280 parts per million CO₂. A batch of this water is cooled to 1°C. A second batch is cooled to 1°C and then receives a dose of 0.8 micromoles per liter of phosphate (and its companion respiration CO₂). The fourth bucket is cooled to 1°C and receives 1.6 micromoles per liter of phosphate (and its companion respiration CO₂). The cooling causes the partial pressure of CO₂ to plummet to 90 micro-atmospheres. The addition of respiration CO₂ raises the CO₂ partial pressure. It turns out that the amount of respiration CO₂ in present waters in the Southern Ocean bucket just compensates for the reduction in CO₂ partial pressure caused by cooling. If these buckets are then permitted to equilibrate with the overlying atmosphere, the middle two would take up CO₂. CO₂ uptake by waters in the northern Atlantic takes place in the real ocean.⁷⁶

cold waters exert a lower CO_2 partial pressure than warm waters (see page 82). For any given CO_2 concentration, cold polar waters exert only a quarter the CO_2 partial pressure as warm tropical waters. However, the excess respiration CO_2 present in Southern Ocean surface waters gives them four times the CO_2 gas content as warm temperate waters. Hence, the reason Southern surface waters exert a CO_2 partial pressure similar to that for temperate surface waters is that their lower temperature is compensated by their higher respiration CO_2 content.⁷⁶

We have seen that an upper limit on the production of organic tissue by marine plants is set by the availability of phosphate. Is there a comparable limit on the amount of CaCO_3 hard-part material that can be manufactured by organisms living in the upper ocean? The answer is no. Only a small fraction of both the available calcium and the available inorganic carbon are utilized in this way. Rather, the amount of CaCO_3 formed depends on the productivity of the organisms which house themselves in calcite shells or cages. As these organisms make only as much calcium carbonate as their hard-part houses require, they don't deplete the surface waters in which they live.

Although the amount of carbon going into the formation of CaCO_3 shells and cages is small compared to that going into soft tissue, the amount of CaCO_3 carbon which is buried in sea floor sediments greatly exceeds the amount of soft tissue carbon buried. The reason is that soft tissue is a valuable commodity; so valuable that a food web has evolved in the ocean which very efficiently utilizes this resource. Most of the organic matter produced in the upper ocean is consumed in the upper ocean. That which escapes to the interior is largely eaten by organisms living in the oceanic thermocline (100 to 1000 meters depth). Only a percent or so survives until it reaches the deep sea. That bit which falls all the way to the sediment is largely eaten by bacteria, worms and other sea floor creatures.

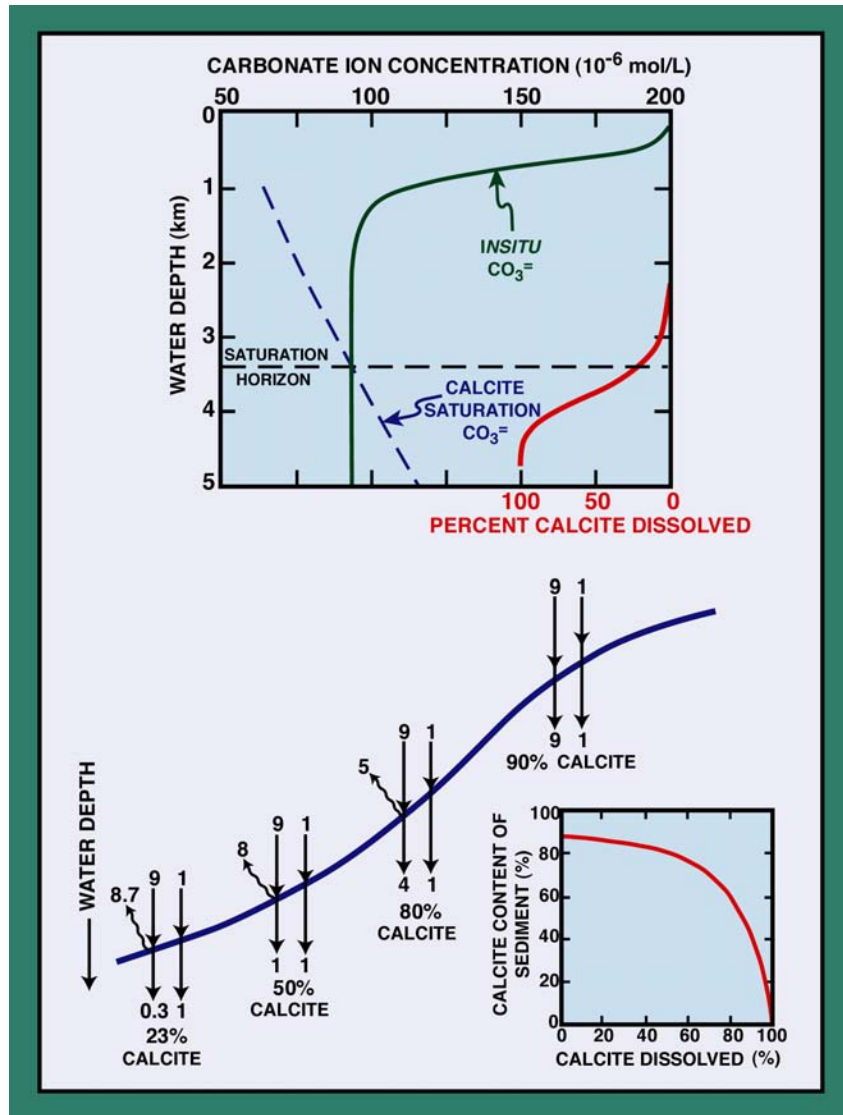


Marine organisms manufacture calcite about four times faster than its ingredients are delivered to the sea. In order to compensate for this overproduction, the carbonate ion concentration in deep sea water is driven to that value where about three quarters of the calcite raining to the sea floor re-dissolves. As the solubility of the mineral calcite increases with pressure (i.e., with water depth), this dissolution takes place in the deepest parts of the sea. Hence calcite accumulates on topographic highs and dissolves on the abyssal sea floor.

The destruction of forests and soils during the onset of each period of glaciations added excess CO_2 to the ocean and hence lowered the concentration of carbonate ion throughout the sea. This caused the saturation horizon to shoal and hence disrupted the balance between calcite burial and ingredient supply. The excess dissolution created in this way gradually neutralized the excess CO_2 thereby raising the carbonate ion concentration until a steady state was reestablished. The response time for such a recovery is on the order of 5000 years.

The high efficiency with which organic tissue is recycled is important to the ocean's phosphate inventory. This inventory depends not only on rate at which phosphate is supplied by rivers but also on how long the average phosphorus atom survives in the sea before being lost to the sediments. It turns out that this survival time is on the order of several tens of thousands of years. During this time the average phosphate atom is incorporated into marine soft tissue many hundreds of times and, of course, it is recycled many hundreds of times. Of importance to climate-induced changes in ocean operation to be discussed in the next chapter is that this large inventory of phosphorus provides a buffer against changes in the availability of life's limiting resource. It also ensures that the runoff in rivers of the phosphate and nitrate used to fertilize our farm lands will not significantly perturb plant productivity in the open ocean.

Unlike organic tissue, CaCO_3 has no nutritive value. Even so, roughly three quarters of that manufactured by marine organisms re-dissolves. The reason is that marine organisms manufacture CaCO_3 at a rate which exceeds that of the supply of its ingredients to the sea from rivers and volcanoes by something like a factor of four. Thus, in order for the oceans' carbon budget to be balanced (i.e., for loss to match input) this overproduction must be compensated by dissolution.⁷⁷ This dissolution takes place in the deep sea. Two factors dictate that this be the case. First, as we have seen, both the warming and the removal of CO_2 by photosynthesis raises the carbonate ion concentration in surface waters. Second, the cold temperature coupled with the release of CO_2 by respiration lowers the carbonate ion concentration in the deep sea. Finally, the solubility of the mineral calcite increases with pressure (and hence with water depth). By solubility, I mean that product of the Ca^{++} concentration and the $\text{CO}_3^{=}$ concentration at which calcite neither tends to dissolve nor precipitate. If the product of calcium and carbonate ion concentrations in a given sea water sample is smaller than the solubility product, then calcite will tend to dissolve. If it is larger than the solubility product, then



Depth profile of carbonate ion concentration in the tropical Pacific Ocean. Above a water depth of about 3.4 km the water is supersaturated with respect to calcite. Below this depth is undersaturated. However, as a result of the release of respiration CO_2 in sediment pore waters, their $\text{CO}_3^{=}$ concentration is lower than that in the overlying bottom water. Because of this, dissolution of calcite commences above the saturation horizon. A carbonate ion undersaturation of 15 or so micromoles per liter is required before all the calcite raining to the sea floor is dissolved (in other words, before the rate of dissolution matches the rate of supply).

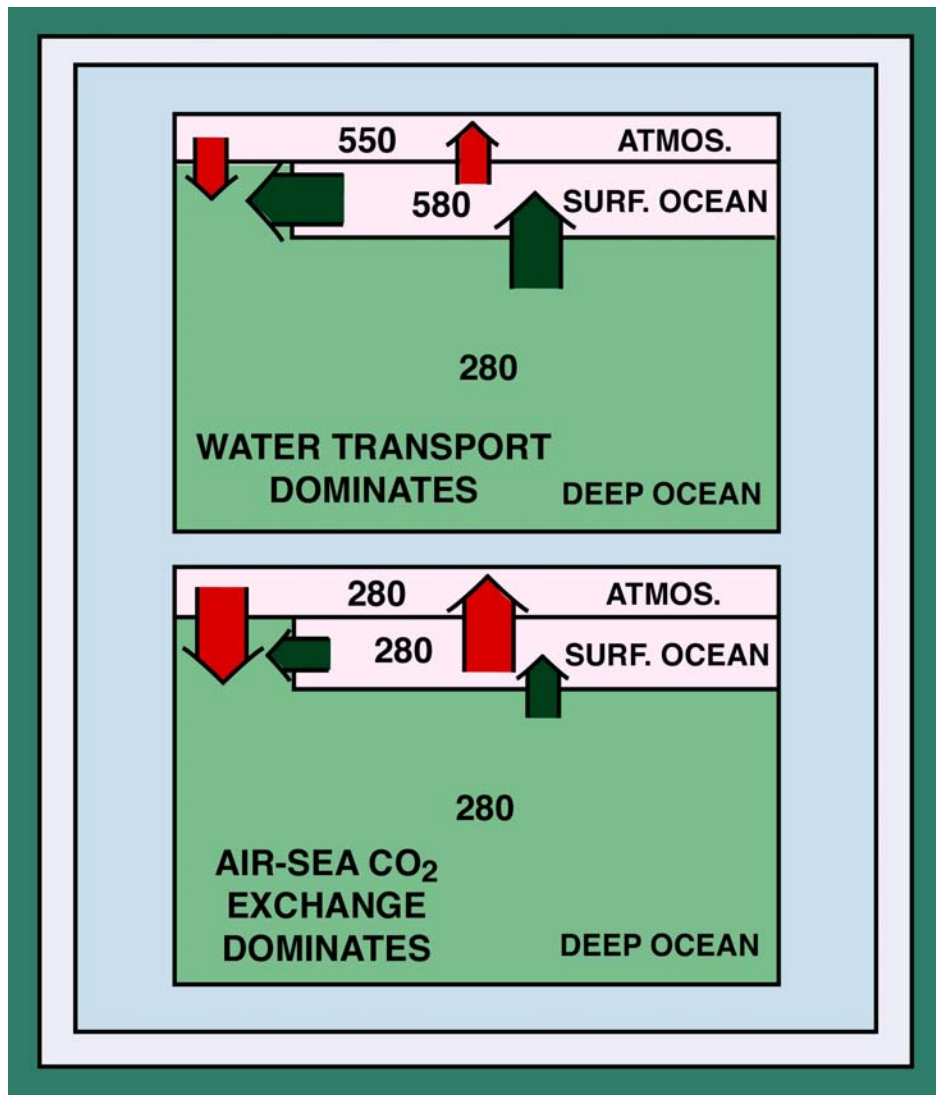
While the CaCO_3 content of sediments decreases with the extent of dissolution, the relationship between the calcite content of the sediment and the extent of dissolution is far from linear. The reason is that the rain rate of calcite greatly exceeds that of non-calcite (mainly soil debris delivered from the continents by rivers and wind). Because of this, more than 50 percent of the calcite must dissolve before the drop in sediment calcite content becomes significant.

the calcite will tend to grow. It turns out that inorganic growth of calcite is so severely kinetically inhibited that it doesn't happen. Only organisms have the secret required to overcome this kinetic barrier. So even though surface waters are highly supersaturated, calcite doesn't form spontaneously. By contrast, dissolution experiences no kinetic inhibition.

The large abundance of calcium in sea water makes the situation easier to understand. So large is it, that the formation and dissolution of CaCO_3 do not change its concentration significantly. On the other hand, the carbonate ion concentration ranges from as high as 240×10^{-6} moles per liter in warm surface water to as low as 70×10^{-6} moles per liter in the deep Pacific. Because of this we can treat the calcium concentration as if it were constant and focus our attention on the concentration of carbonate ion.

The ocean has a built in feedback system which drives its deep water carbonate ion concentration toward that value at which the over production by marine organisms is exactly balanced dissolution. This feedback is easy to understand. If CaCO_3 burial were to exceed the supply of inorganic carbon, then the carbonate ion inventory would be drawn down. This, in turn, would cause the saturation horizon to shoal and hence the fraction of the CaCO_3 falling into waters undersaturated with respect to calcite to increase. This situation would prevail until a balance between calcite burial and ingredient supply had been reestablished. The time constant for adjustment of the saturation horizon depth is on the order of 5000 years.

At this point, you may ask, how did we get enmeshed in what goes on in the deep sea? Isn't the goal of this section to understand how the ocean controls the atmosphere's CO_2 content? Right, but whatever causes the carbonate ion concentration in the deep sea to change will lead to a corresponding change in the carbonate ion concentration in surface waters, and hence also in the CO_2 concentration in surface waters and in the atmosphere's CO_2 content. Because the bicarbonate ion concentration in sea water is much larger than either the carbonate ion concentration or the carbon dioxide

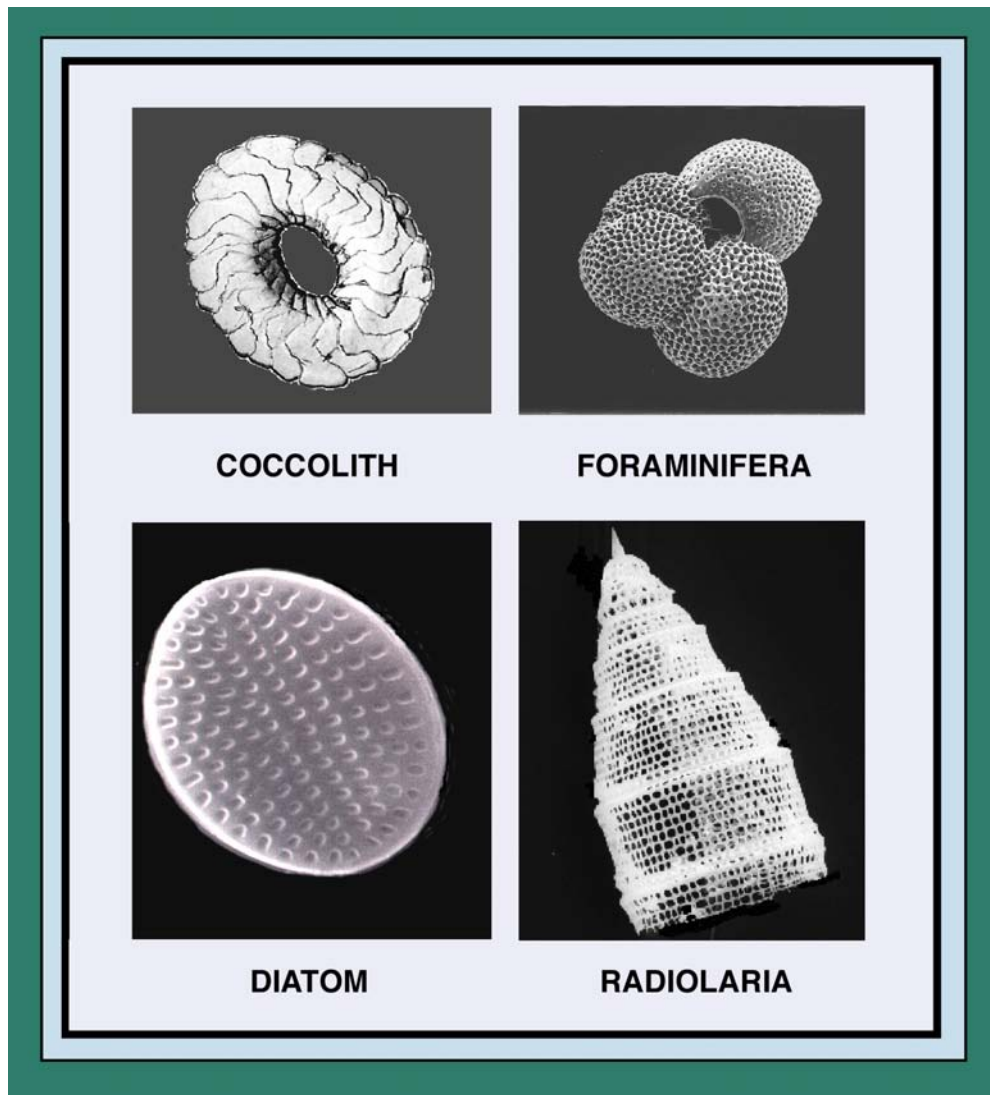


Extreme cases for a hypothetical abiotic two-box ocean. In the upper panel is shown the situation where the transport of inorganic carbon from the warm surface box to the outcrop of the deep ocean reservoir is far faster than the transport of CO₂ through the atmosphere. In this case, the CO₂ partial pressure in the warm surface ocean dominates and the atmosphere has a $p\text{CO}_2$ of 550 micro-atmospheres. In the lower panel is shown the other extreme where CO₂ transport through the atmosphere far outstrips that by water transport. In this case, the warm surface water and the atmosphere have the same CO₂ partial pressure (i.e., 280×10^{-6} atm) as the deep water reservoir (i.e., 280 micro-atmospheres).

concentration, to a rough approximation, the product of the carbonate ion concentration and the CO_2 concentration remains constant. Thus, if the carbonate ion concentration in the deep sea were to go down as a result of a need to rebalance the ocean's carbon budget, the CO_2 content of surface ocean waters and hence also of the atmosphere would rise. In the chapters which follow, we will see that during glacial changes in the depth of the deep sea's saturation horizon were potentially important and that these changes will certainly become important as the ocean takes up fossil fuel CO_2 .

The CO_2 concentration and temperature differences from place to place in the surface ocean give rise to differences in CO_2 partial pressure. Hence, the atmosphere's CO_2 content represents some sort of area-weighted average of the values for the underlying ocean. But, it turns out that those cold parts of the ocean which are linked to the deep sea potentially exert a greater influence on the atmosphere than their relatively small areas would suggest.

To illustrate why this is the case, let us consider a hypothetical two-box ocean. One box is a warm upper reservoir which occupies 90 percent of the ocean's surface but only a few percent of the ocean's volume. The other is a deep reservoir whose outcrop occupies the remaining 10 percent of the surface. Both reservoirs are well mixed: one with a temperature of 20°C and the other with a temperature of 0°C . This simple ocean is lifeless; hence, the only chemical differences between the reservoirs relate to temperature. The flow pattern is simple. Warm upper waters move laterally to the outcrop of the deep reservoir where they are cooled and then downwell. Cold waters from the deep reservoir upwell into the surface reservoir where they are warmed. The chemistry of the large deep-water reservoir is set so that it exerts a CO_2 partial pressure of 280×10^{-6} atmospheres. Thus, when deep water upwells and is warmed, its CO_2 partial pressure rises to let's say 580×10^{-6} atmospheres. It might then be expected that the CO_2 pressure in the well-mixed atmosphere above the ocean would be 550×10^{-6} atm (i.e., $0.10 \times 280 + 0.90 \times 580$). Wrong! The reason is that there is a tendency for CO_2 to escape to the atmosphere from warm reservoir and to be re-absorbed by the cold reservoir, thereby



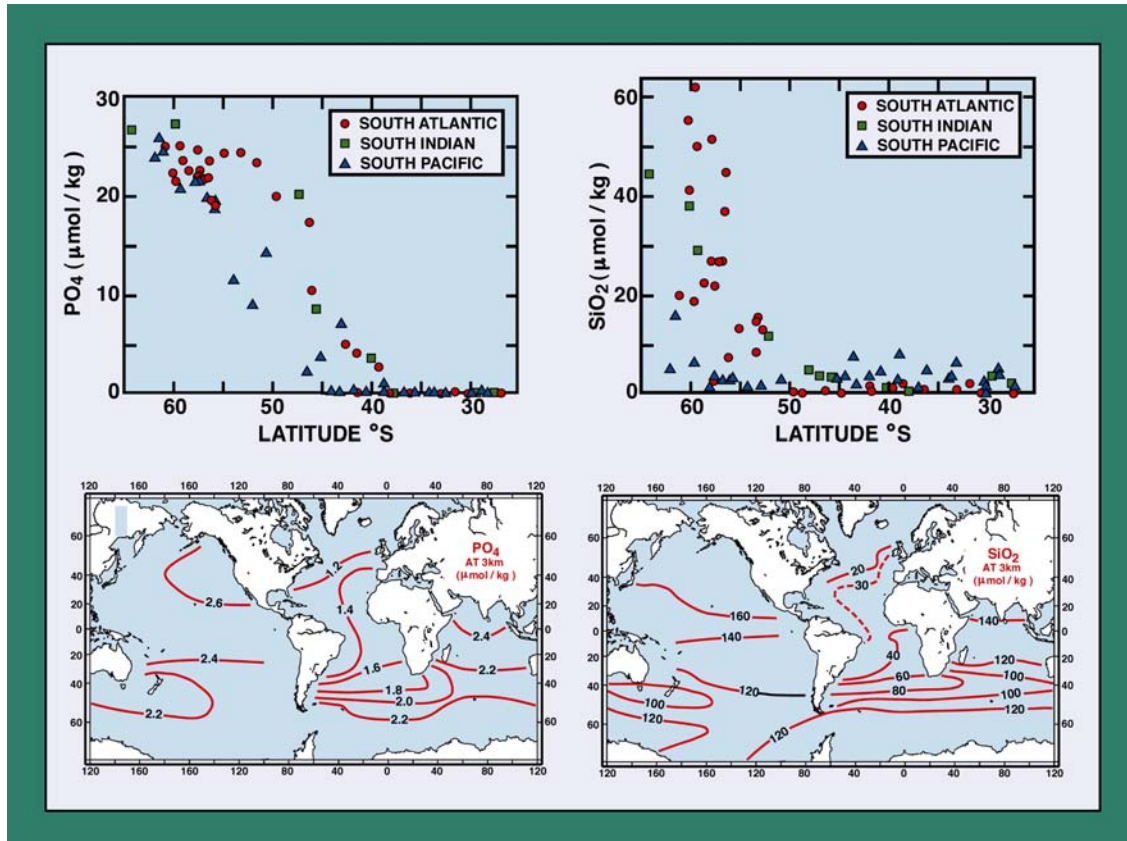
On the left are photomicrographs of marine plants which manufacture calcite houses (i.e., coccolithophoriads) and those which manufacture siliceous houses (i.e., diatoms). On the right are photomicrographs of single-celled animals which inhabit calcite houses (i.e., foraminifera) and those which inhabit siliceous cages (i.e., radiolarians). Photos courtesy of O. Roger Anderson, Lamont-Doherty Earth Observatory.

reducing the CO₂ partial pressure in the small upper reservoir without significantly altering that in the much larger deep reservoir. What actually happens depends on ratio of the rate of the overturning circulation to the rate of CO₂ exchange with the atmosphere. The 550 ppm prediction constitutes an upper limit corresponding to the situation where the rate of overturning greatly outstrips the rate of CO₂ transfer between the ocean and atmosphere. The lower limit of 280×10^{-6} atmospheres corresponds to the situation where the rate of CO₂ exchange with the atmosphere far outstrips the rate of the overturning.

So, where does the real ocean fall in this spectrum? The fact that Southern Ocean surface waters have a CO₂ partial pressure nearly matching that for major portions of the warm ocean makes this somewhat of a moot point for today's ocean. However, as we shall see, it becomes an important issue for the glacial ocean and perhaps for the ocean's future as well.

This issue was raised when box models of today's ocean which incorporated known CO₂ exchange rates and known deep water formation rates suggested that the Southern Ocean surface waters dominate the atmosphere's CO₂ content. However, when full-fledged simulations of the ocean driven by wind and density gradients are employed, the importance of the Southern Ocean in controlling the atmosphere's CO₂ content is much diminished.⁷⁸

One other hard part produced by marine plankton must be mentioned. Diatoms live in cages made of opaline silica. As dissolved silica carries no ionic charge, neither the manufacture nor the dissolution of these cages alters the NCD. Hence the silica cycle has no direct impact on carbon chemistry. But it does have an indirect impact, for diatoms compete with CaCO₃ producing organisms for resources. To the extent they are successful in this competition they alter the chemistry of both the surface and the deep ocean. If opal producers displace calcite producers, then the compensation provided by the change in NCD associated with CaCO₃ manufacture does not happen. Hence the CO₂



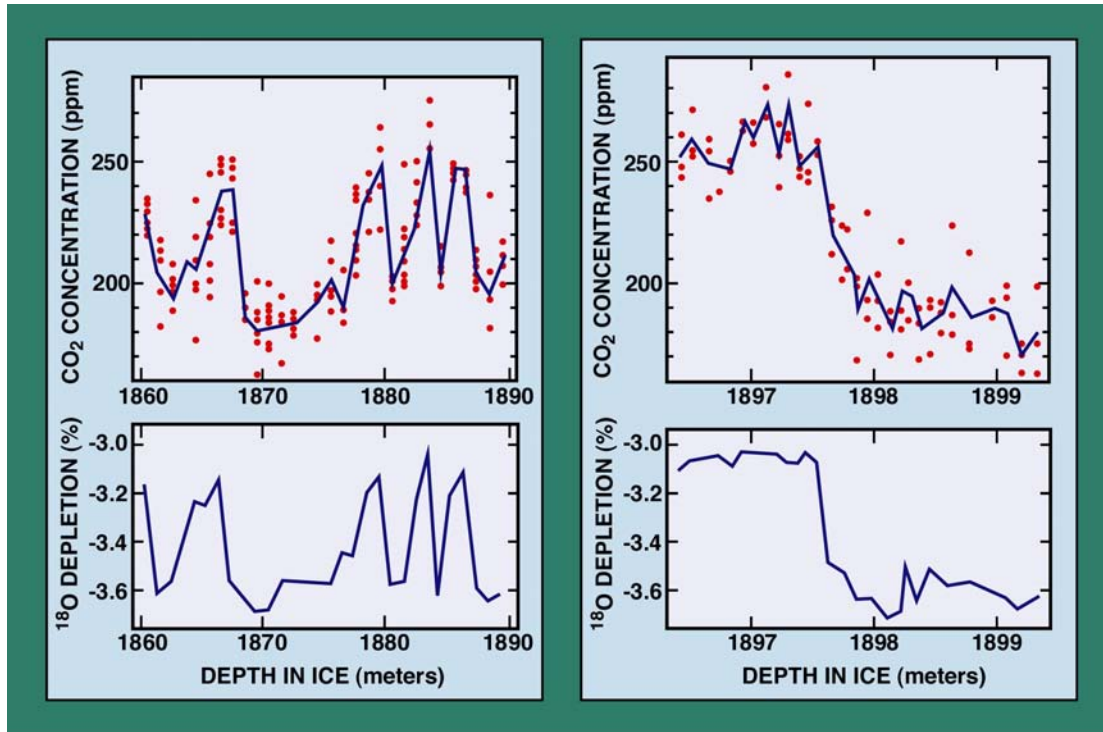
In the upper panel are shown the trends with latitude of the dissolved PO_4 and SiO_2 concentrations in summer surface waters of the Southern Ocean. As can be seen, the decline in silica content with distance from the Antarctic continent is much steeper than that for phosphate. As long as silica is abundant in surface waters, diatoms dominate.

In the lower panel are shown the distributions of dissolved PO_4 and SiO_2 at a depth of three kilometers in the world ocean. As can be seen, the depletion of SiO_2 in the Atlantic relative to the Pacific and Indian Oceans is far larger than that for phosphorus. This difference reflects the low SiO_2 to PO_4 ratio in the waters feeding the upper limb of the Atlantic's conveyor.

drawdown per unit of photosynthesis is greater for diatom-dominated communities than those dominated by calcite producers. Further, the displacement of CaCO_3 producers by diatoms reduces the excess production of calcite by marine organisms. The less production, the deeper the CaCO_3 saturation horizon will be.

Given abundant dissolved silica, diatoms dominate. Thus, they flourish in regions where upwelling occurs. It turns out that the ratio of Si to P required by diatoms is considerably greater than their ratio in upwelling waters. Hence silica always runs out before phosphorus. Once silica has been depleted, other organisms can come to fore. Because of this, the regions in which diatoms dominate are largely restricted to the Southern Ocean and northern Pacific. Calcite producers dominate in the remainder of the ocean. The boundary between these regions corresponds to the boundary between silica-rich surface waters and silica-depleted surface waters.

The phosphorus and silica contents of waters in the deep Atlantic are substantially lower than those in the deep Indian and Pacific Oceans. The phosphorus content is, on the average, twofold lower and the silica content tenfold lower. The magnitude of the Atlantic's deficiency has to do with the conveyor circulation. To understand this, one must first keep in mind that the residence times of phosphorus atoms and silica atoms in the sea (i.e., tens of millennia) are both far larger than the ventilation time of the Atlantic Ocean (i.e., a couple of centuries). Hence there can be no net gain or no net loss of either of these elements during a single pass around the Atlantic's conveyor loop. This being the case, the phosphorus and silica contents of waters entering the upper Atlantic must exactly match those in water exported in the conveyor's lower limb. Thus the reason why the deep Atlantic has a lower phosphorus and silica content than the deep Pacific and Indian Ocean is that the waters entering the upper-Atlantic (i.e., balancing the lower limb's outflow) carry less than the ocean-average nutrient concentrations. Further, as silica is efficiently removed close to the sites of upwelling, its deficiency in the water entering the upper Atlantic is much greater than that of phosphorus.



In the left-hand panel are plotted the CO₂ content of trapped air and the extent of ¹⁸O depletion in the ice itself for a several thousand-year period centered at about 30 thousand years ago. During this time interval, four Dansgaard-Oeschger (D-O) events occurred. As can be seen, during the warm phase (lower ¹⁸O depletion) of each D-O event, the CO₂ content of the bubbles rises from about 190 ppm to about 250 ppm. These increases were brought into question when CO₂ results from Antarctica ice cores became available. All the measurements on air from Antarctic ice cores for this same time period were in the range 190 to 200 ppm. The explanation appears to be that the high CO₂ values in the Greenland record were the result of the release within the ice of CO₂ generated as a result of a chemical reaction between the CaCO₃ and the acids contained in the ice. This explanation received strong support when it was shown by the Swiss group that the expected offset between the record in ice and that in air-bubbles did not exist (see right-hand diagram).

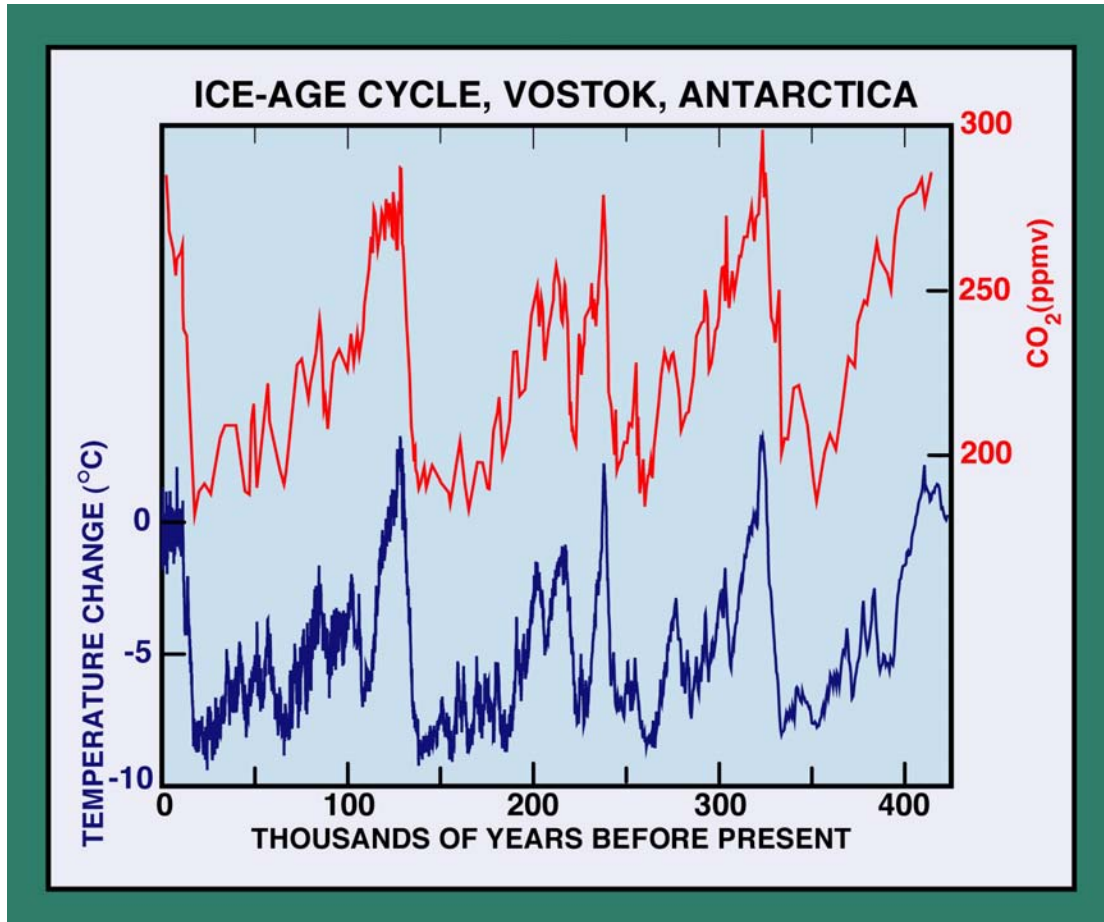
CHAPTER 5

YESTERDAY'S CHEMISTRY

It came as a big surprise when, based on measurements made on air trapped in Greenland ice, the claim was made that during glacial time the atmosphere's CO₂ content had dipped to 200 parts per million (ppm).⁷⁹ During the quarter of a century which has passed since this announcement was made, many ingenious scenarios purporting to explain this 80 ppm drop have been put forward. However, as yet, not one of them has gained wide acceptance.

Of course, before the stunning claim that the atmosphere's CO₂ content was only 70 percent that for pre-industrial time was accepted, the geochemical community had to be convinced that the low values were not the result of some artifact introduced during the long period of storage of the air in ice. To this end, scientists in Bern, Switzerland and Grenoble, France made CO₂ measurements air released by crushing the ice and on air released by melting the ice. The agreement of the results of these two measurement procedures demonstrated that the CO₂ had remained in the air bubbles rather than having diffused into the ice.

But, the grumbling resurfaced when the equivalents of the 250 ppm CO₂ contents found for ice representing the intermediate cold phases of the D-O events in Greenland ice⁸⁰ were not found in Antarctic ice.⁸¹ Clearly, one or both of the records had to be flawed. The Swiss group then made a set of measurements that clearly demonstrated that indeed flaws existed in the Greenland record. They zeroed in on what happened at the time of one of the abrupt D-O warmings (i.e., CO₂ increases from 200 to 250 ppm) and found that the CO₂ change occurred at exactly the same depth in the ice as the abrupt changes in ¹⁸O to ¹⁶O ratio and dust content.⁸² If the CO₂ changes were real, this should not have been the case, for the closure of bubbles in which the air is trapped takes place at the base of the firn 70 or so meters below the snow surface. Hence, were the CO₂

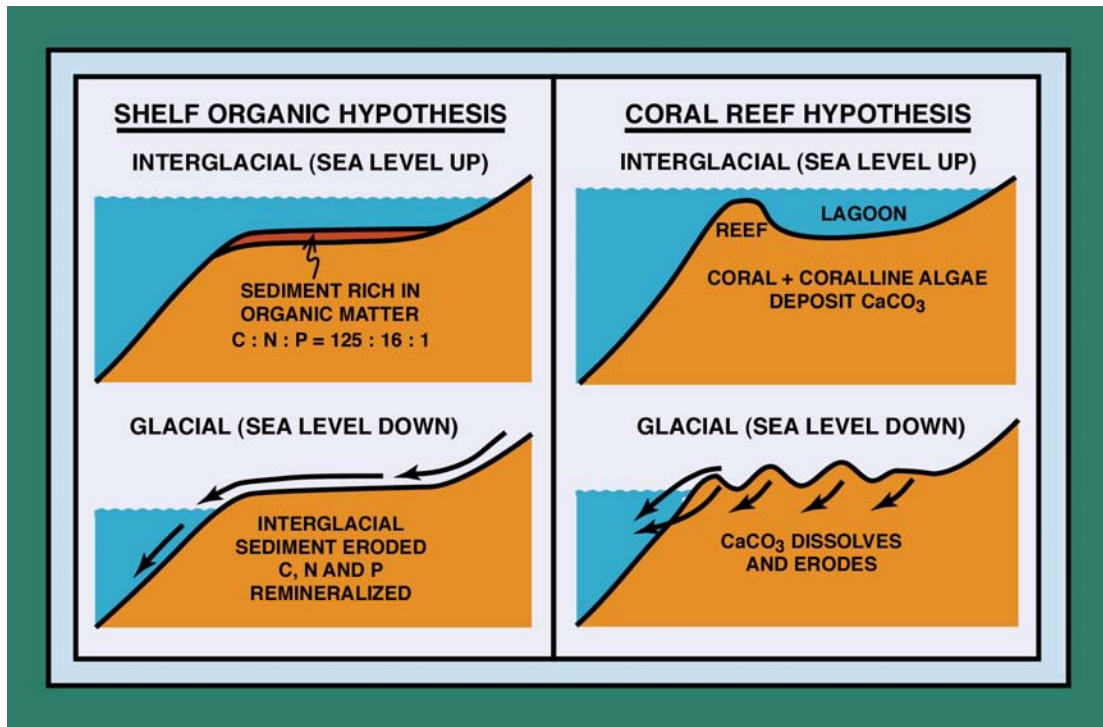


Records of CO₂ content of trapped air and of temperature (based on stable isotope measurements in the ice itself) from a long ice core raised at the Russian Vostok Station in the interior of the Antarctic ice cap.⁸³ Each cycle is characterized by a long decline toward colder and lower CO₂ content conditions modulated by a 20,000-year cycle. Each long decline was terminated by an abrupt return to interglacial conditions.

changes real, the abrupt CO₂ rise should have been displaced down core from those for ¹⁸O and dust. As it wasn't, the focus turned to processes occurring within the ice. In particular, the high content of CaCO₃ bearing dust in glacial-age ice from Greenland was viewed as the likely villain. Were the CaCO₃ to encounter the acid present in the ice, it would decompose and CO₂ gas would be released. While this appears to be the explanation, it is puzzling that during the coldest and hence dustiest times, the CO₂ results from Greenland ice agree with those from Antarctic ice. So there must be something about the ratio of acid to CaCO₃ during the intermediate cold phases of the D-O events that makes them different from the ultra cold periods. Perhaps during periods of intense cold, the ratio of CaCO₃ rain to acid rain was so high that the acid was entirely neutralized in the firn before the bubbles are sealed off. In this case, the CO₂ released by the decomposition of CaCO₃ would escape to the atmosphere through the web of firn pores.

The publication of the CO₂ record from the Vostok Antarctica ice core⁸³ largely quelled the grumbling. This record covered four full 100,000-year cycles. Each cycle showed the same temporal sequence, i.e., a step-wise decline from an interglacial high of 280 parts per million to a glacial low of about 190 parts per million followed by an abrupt rise back to 280 parts per million during the termination. Because the CaCO₃ dust and airborne acid concentrations in Antarctic ice are extremely low, release of CO₂ within the ice is not an issue. Further, it proved exceedingly difficult for critics to dream up a scenario based on some other artifact of storage. Hence, with the publication of the Vostok record, there could no longer be any doubt that the atmosphere's CO₂ content dropped during glacial time. Further, because the ocean holds 60 times more carbon than the atmosphere, the cause had to involve the ocean.

I had a head start on this problem because in my classes, I posed the question as to what might have caused the atmosphere's CO₂ content to be different during glacial time. So, I was ready to pounce when the new results were announced, and shortly thereafter, I



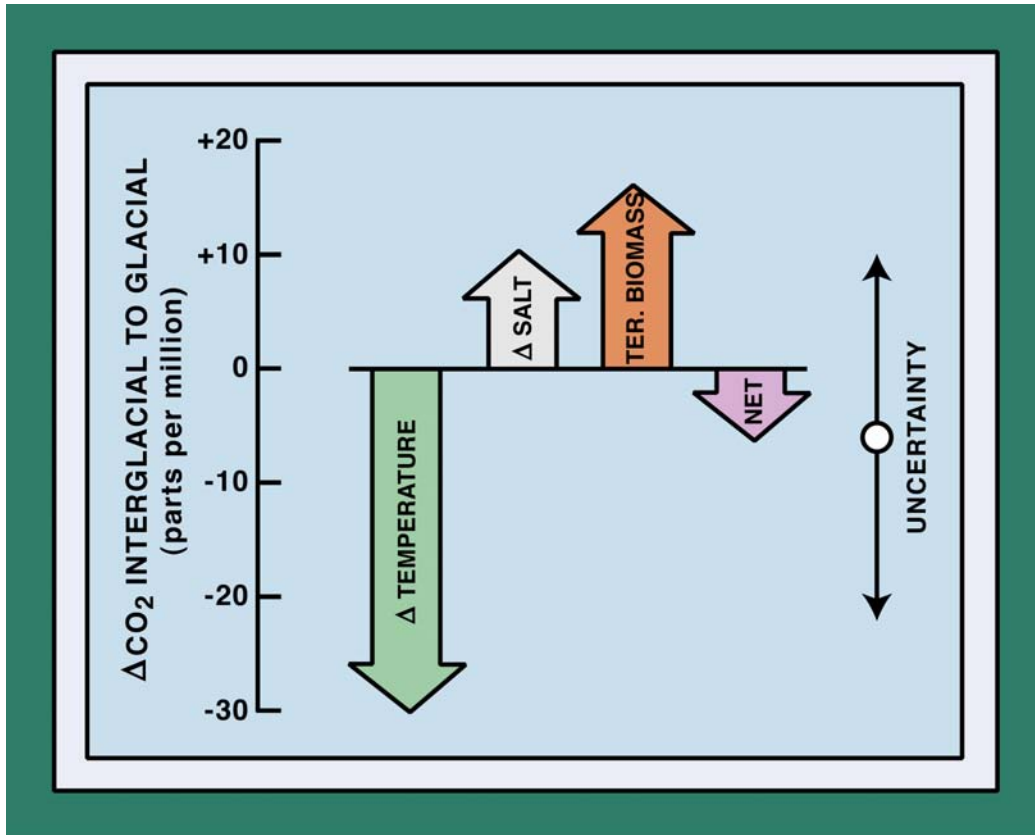
Two of the early hypotheses put forth to explain the lowered CO_2 content of the glacial atmosphere. While clever, each was soon shown to violate observation.

The key to the shelf organic hypothesis⁸⁴ was that the removal of PO_4 and NO_3 to sediment deposited during interglacials on the flooded continental shelves reduced the power of the biologic pump. When, during the subsequent glacial period, this organic-rich material was eroded back into the sea and the nutrients it contained were “remineralized” (i.e., returned to dissolved form), the biologic pump was correspondingly strengthened.

The key to the coral hypothesis⁸⁵ is that the manufacture of CaCO_3 leads to a rise in the CO_2 content of sea water. Thus, formation of CaCO_3 in tropical reefs and lagoons during interglacial high sea stands led to an increase in atmospheric CO_2 . Conversely, when sea level dropped during the subsequent glacial period, rain water charged with soil CO_2 dissolved away the exposed CaCO_3 much as it does in karst regions.

published a scenario which purportedly explained the 80 parts per million glacial-age CO₂ rise at the close of the last glacial period.⁸⁴ It involved deposition of organic matter on the continental shelves as they were flooded by the sea level rise associated with the melting of the glacial ice caps. I assumed a carbon to phosphorus ratio of 100 to 1 for the organics so buried. The CO₂ rise caused by the removal of phosphorus and hence a weakening of the biological pump outweighed the drop in CO₂ associated with the burial of organic carbon. Because of this, the atmosphere's CO₂ content was higher during times of interglaciation than during times of glaciation. Then when sea level dropped during the subsequent glacial period, the organic-rich sediment was assumed to have been eroded away and the carbon and phosphorus they contained was released to solution. The extra phosphorus would have strengthened the biological pump drawing the atmospheric CO₂ content back down. As part of this scenario, I introduced the use of carbon isotope ratio changes in the ocean's dissolved organic carbon as a constraint on scenarios purporting to explain the CO₂ change. While this first scenario was perhaps clever and innovative, its deficiencies far outweighed its strengths. Hence, it soon bit the dust.

Another early scenario, put forth by Wolfgang Berger of Scripps, proposed that it was the CaCO₃ manufactured by corals during the periods of rising sea level that caused the CO₂ content of the atmosphere to rise.⁸⁵ As we have already learned, when CaCO₃ forms, the reduction in NCD associated with the removal of calcium ions from sea water outweighs the reduction in inorganic carbon. So, the CO₂ content of ocean water rises and hence also that of the atmosphere. Then when sea level drops during the subsequent glaciation, these coral reefs are presumed to be eroded away and their CaCO₃ is returned to solution. In this way, the atmosphere's CO₂ content is drawn back down. But as was the case for my shelf-storage scenario, this one soon bit the dust. Its major flaw is that it requires a very large shift in the depth of the CaCO₃ saturation horizon (much deeper during glacial time than today). No evidence for such a large downward shift is seen in



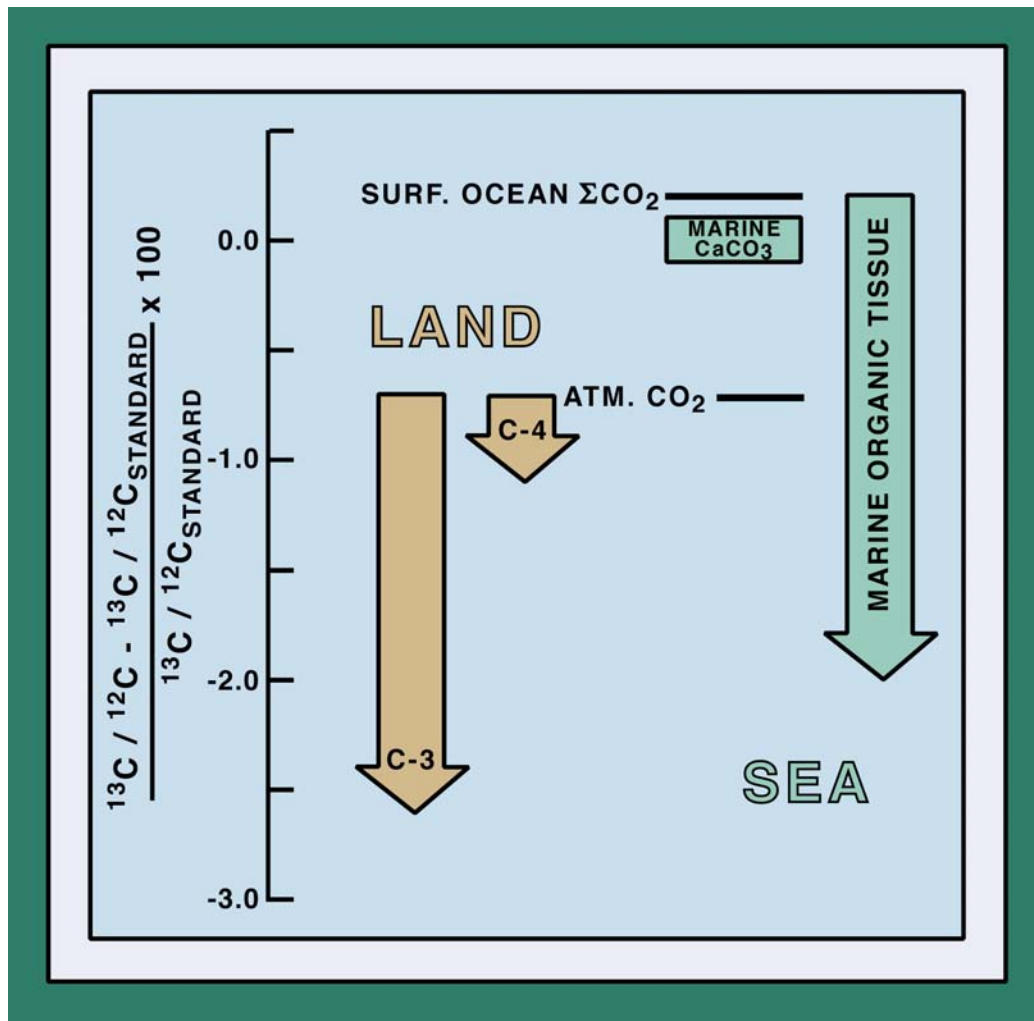
Impacts of a surface ocean cooling ($\sim 3^{\circ}\text{C}$), of an increased ocean saltiness ($\sim 1 \text{ g/lit}$) and of a decreased terrestrial biomass ($\sim 500 \times 10^9 \text{ tons carbon}$) on the atmosphere's CO_2 content.⁸⁶ The latter impact is calculated assuming that the addition of the biomass-derived CO_2 to the sea was compensated by excess CaCO_3 dissolution. Together, the three impacts are somewhat of a wash, for the increases in CO_2 resulting from higher saltiness and the addition of biomass-derived CO_2 largely cancel the decrease resulting from the cooling of the sea surface. While the uncertainty in these estimates is fairly large, no matter what assumptions are made, the combined contribution of these three changes can account for only a small fraction of the 90 ppm glacial CO_2 reduction recorded in ice cores.

the sedimentary record.

With the demise of the shelf storage and coral reef scenarios, the challenge went out to come up with others. MIT's Ed Boyle published the first of these.⁸⁷ He proposed that during glacial time more of the ocean's phosphorus was stored in the abyssal ocean. This proposal is referred to as the nutrient deepening scenario. Because there was no compelling evidence that this nutrient reorganization actually occurred, initially Boyle's idea failed to gain momentum. But, as we shall see, the discovery by Jess Adkins of Caltech of a glacial-age deep sea reservoir whose salt content appears to have been enhanced by the release of brine from forming sea ice will perhaps give new life to the Boyle's scenario.

Much excitement was created in the world of ocean chemistry by the simultaneous publication of three papers which independently proposed a scenario based on the nutrient content of polar ocean surface waters. One was authored by Harvard scientists,⁸⁸ a second by Princeton scientists⁸⁹ and a third by scientists at the University in Bern.⁹⁰ I dubbed it the Harvarton Bears scenario. Based on simple three-box ocean models, each group independently postulated that the planet's cold surface waters controlled the atmosphere's CO₂ content. Hence, if during glacial time, the presently high nutrient content of these cold surface waters could somehow have been drawn down, so also would the CO₂ content of the atmosphere. However, as no convincing explanation could be given regarding the cause of the nutrient decline, enthusiasm for this idea eventually waned. However, when the late John Martin of the Moss Landing Laboratory came out with his iron fertilization hypothesis,⁹¹ interest in this hypothesis was rejuvenated. Perhaps, Martin proposed, the excess dust carried aloft by enhanced glacial storminess provided the iron required for more efficient nutrient utilization in Southern Ocean surface waters.

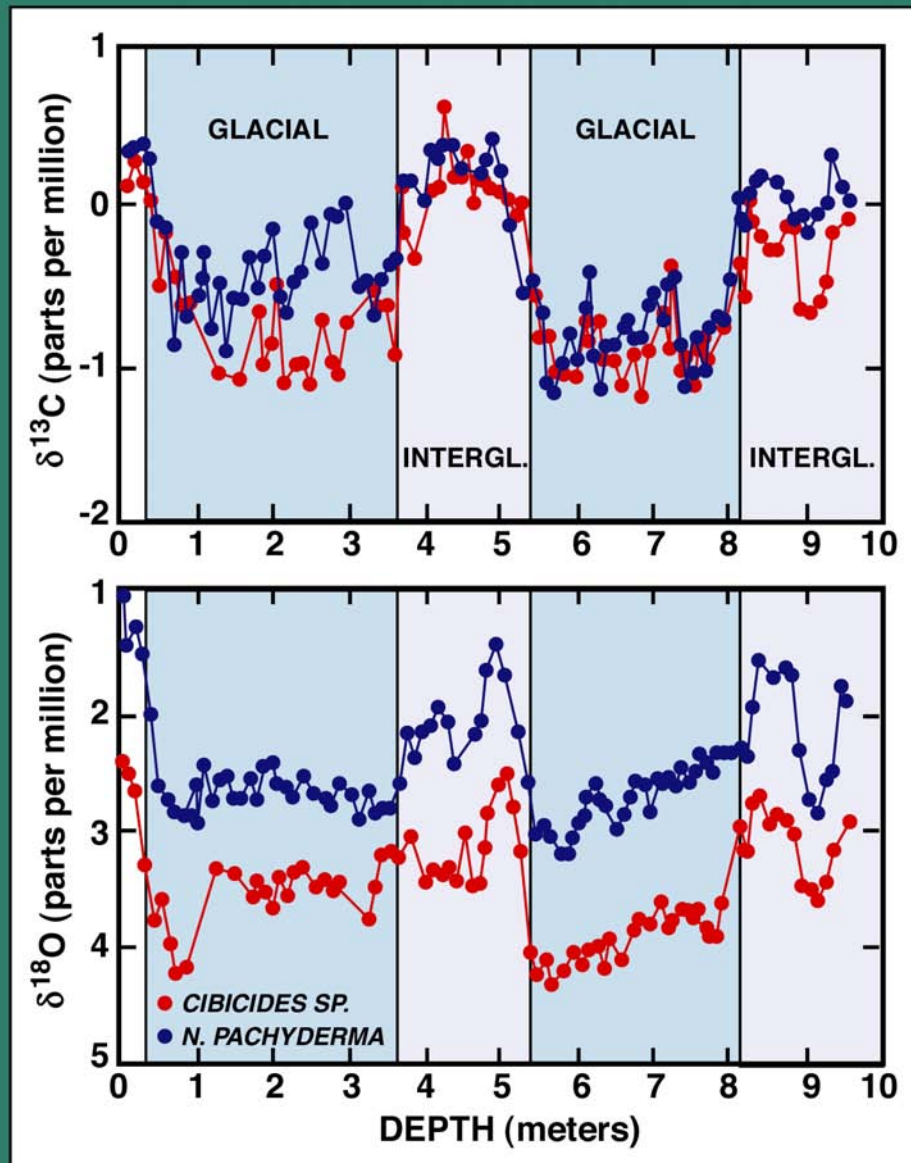
Before going on, a couple of obvious drivers of CO₂ change must be mentioned. The surface ocean was colder during glacial time. Other things being equal, this would



Guide to the separations between carbon's heavy isotope (^{13}C) and its light isotope (^{12}C) occurring in nature. The 0.9 percent lower ^{13}C to ^{12}C ratio in atmospheric CO_2 compared to that in surface ocean ΣCO_2 is the result of an equilibrium separation of these isotopes between the CO_2 gas dissolved in sea water on one hand and the ionized forms of inorganic carbon (i.e., HCO_3^- and CO_3^{2-}) on the other. The depletion of about 2.0 percent in the isotopic composition of those land plants using the C-3 photosynthetic pathway and of most marine algae is the result of a kinetic preference by the photosynthetic enzyme for the CO_2 containing the light carbon isotope. By contrast, the fractionation for plants using the C-4 photosynthetic pathway is much smaller. The reason is that these plants pump CO_2 to the enzyme forcing all the carbon to be utilized. The zero on this scale is arbitrary. It was adopted by Nobelist Harold Urey who fathered stable isotope measurements on natural materials.

have lowered the atmosphere's CO₂ content. Also the ocean was saltier during glacial time. Other things being equal, this would have raised the atmosphere's CO₂ content. Based on ¹³C measurements on glacial-age benthic foraminifera from throughout the deep sea, it appears that during glacial time the amount of carbon stored in trees as wood and in soils as humus was 30 or so percent smaller than now.⁹² This missing carbon would have taken up residence in the ocean and atmosphere as CO₂. Not only would it have raised the CO₂ concentration in all ocean waters but it would have driven down their carbonate ion concentrations throughout the sea, thus disturbing the balance between carbon gain and loss. The CaCO₃ saturation horizon would have shoaled increasing the extent of CaCO₃ dissolution. Much, but not all, of the impact of extra CO₂ would have been compensated by the consequent increase in NCD. When all three of these impacts (i.e., that from temperature, that from salt content and that from terrestrial biosphere) are added together, the result is pretty much a wash. The CO₂ drop due to glacial cooling is more or less balanced by a combination of the ocean's extra salt and the terrestrial biosphere-derived CO₂.

I have already mentioned carbon isotopes but have not, as yet, explained why they are useful. The reason has to do with two separations that occur between the 'light' (¹²C) and 'heavy' (¹³C) isotopes of carbon. One occurs during photosynthesis. Plants take up ¹²CO₂ with a slight preference to ¹³CO₂. Because of this, the organic matter manufactured by terrestrial plants has a ¹³C to ¹²C ratio averaging 1.8 percent lower than that in atmospheric CO₂. The second occurs because the CO₂ gas dissolved in sea water has a 0.9 percent lower ¹³C to ¹²C ratio than its companion bicarbonate ions. Because of this, the CO₂ in the atmosphere has a 0.9 percent lower ¹³C to ¹²C ratio than the inorganic carbon dissolved in sea water. The photosynthetic isotope separation is a kinetic phenomenon (i.e., a rate of reaction). The CO₂ - HCO₃⁻ isotope separation is a thermodynamic phenomenon (i.e., chemical equilibrium). Together the kinetic separation and the thermodynamic separation give rise to 2.7 percent depletion in ¹³C in terrestrial

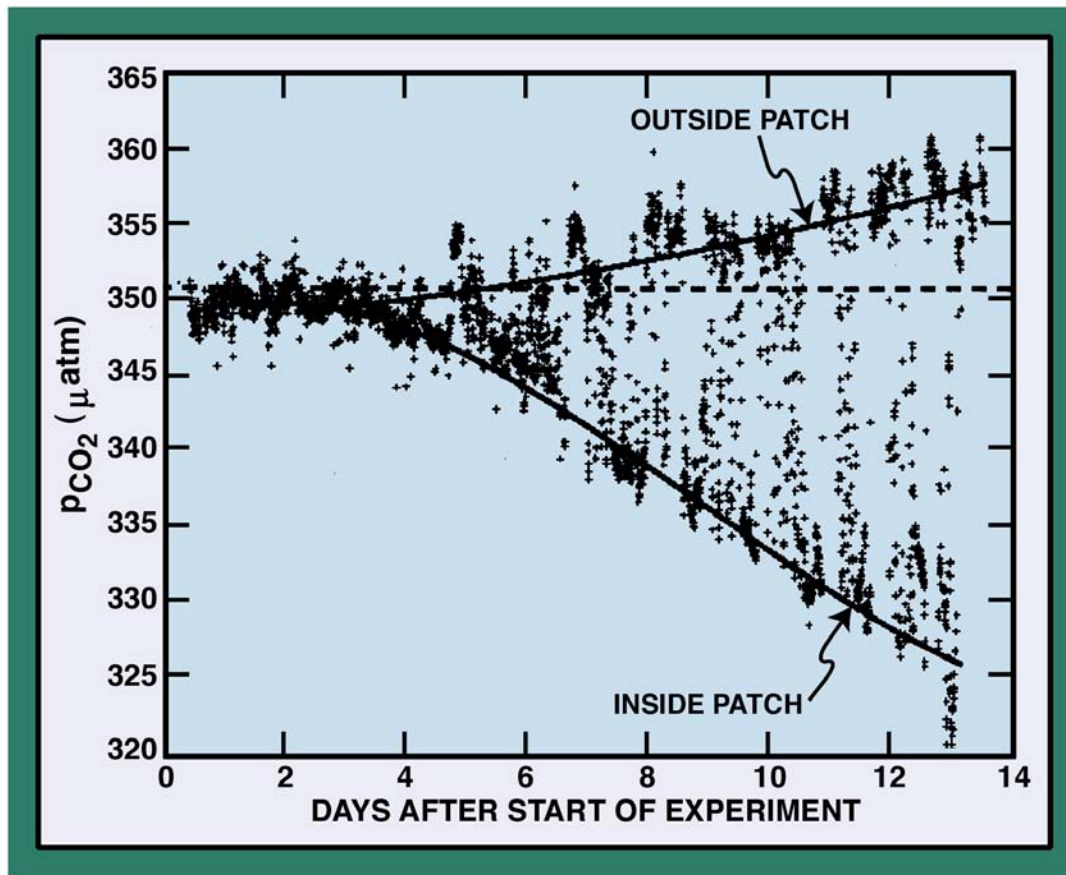


Records of ^{13}C and ^{18}O preserved in planktic (*pachyderma*) and in benthic foraminifera (*cibicides*) from a Southern Ocean sediment core (43°S, 3°W, 4.2 km) covering the last two 100,000-year duration climate cycles.⁹³ The point of the diagram is that no significant increase in the difference between the ^{13}C and ^{12}C ratio in surface and deep water took place during glacial time suggesting that there was no large increase in the efficiency of nutrient utilization in Southern Ocean surface waters.

organic matter (i.e., wood and soil humus) relative to the inorganic carbon in surface sea water. Hence the addition during glacial time of CO₂ derived from the release of carbon stored as wood and humus lowered the ¹³C to ¹²C ratio in the ocean-atmosphere inorganic carbon reservoir. Measurements of the change in ¹³C to ¹²C ratio in the benthic (i.e., bottom dwelling) foraminifera shells between glacial and Holocene time tells us that this reduction was about 0.035 percent. If this drop is attributed entirely to the introduction of CO₂ derived from terrestrial biomass, then during glacial time, there must have been 500 billion tons less carbon stored in wood and humus than today. This amount is comparable to that in the wood in today's forests and to about 30 percent of today's reservoir of terrestrial organic carbon (i.e., wood and humus). One reason for this reduction is the destruction during glacial time of the Northern Hemisphere's extensive boreal forests and bogs. These ecosystems were displaced by either glaciers or tundra.

Carbon isotope ratios also provide a means of assessing past strengths of the ocean's biologic pump. The organic matter produced by marine microorganisms is depleted in the heavy carbon isotope by about 2 percent relative to the ΣCO₂ in surface sea water. Hence the transfer of organic matter from the surface to the interior of the ocean raises the ¹³C to ¹²C ratio in the dissolved-inorganic carbon remaining behind in surface water. The isotopic composition of surface water and deep water inorganic carbon are recorded respectively in the shells of planktic and benthic foraminifera. Carbon isotope ratios recorded in foraminifera shells provide a paleo proxy for the difference between the phosphorus content of bottom and surface water, and hence allow us to determine whether or not the biologic pump was more efficient during times of glaciation. Measurements on foram shells from the Southern Ocean sediments suggest no significant increase in nutrient utilization efficiency.⁹³

One might ask, doesn't the formation and dissolution of calcite also impact the carbon isotope composition of the sea's inorganic carbon? The answer is no. The reason is that the isotopic composition of marine CaCO₃ is almost identical to that for the



Response of carbon dioxide partial pressure to iron additions to a patch of surface water at 61°S in the Pacific sector of the Southern Ocean. Measurements of a tracer SF_6 added along with the iron allowed a distinction between water samples taken inside and outside the drifting and spreading patch.⁹⁵

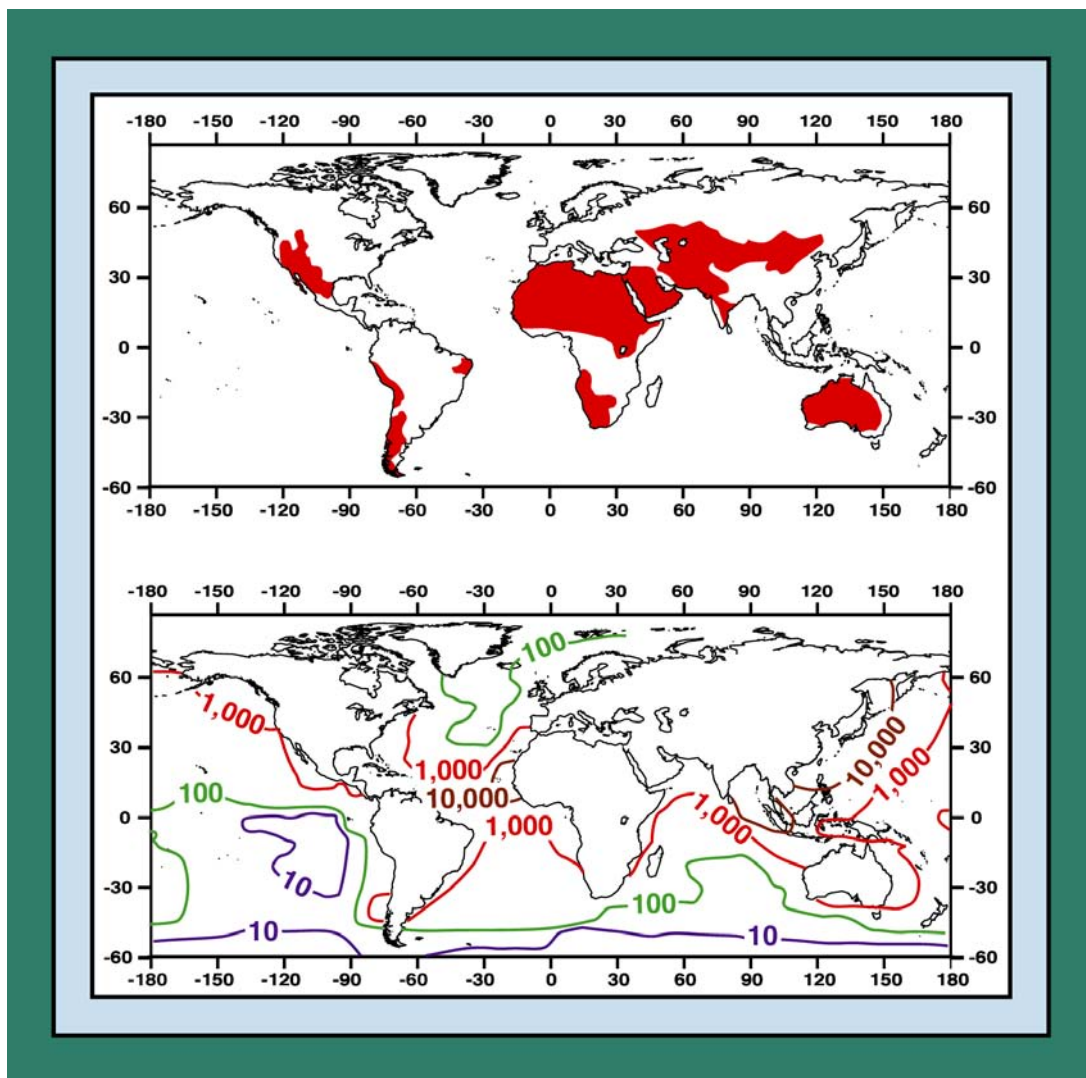
inorganic carbon dissolved in sea water.

As already mentioned, the late John Martin created a revolution in the field of marine biology by suggesting that in those areas of the ocean where phosphate is only partly utilized, plant productivity is retarded by an inadequate supply of dissolved iron. Key enzymes require iron atoms. Without these enzymes, plants can't function. As iron is our planet's most abundant element, Martin's claim came as a big surprise. But, like thorium, iron ranks with the least soluble elements. So low is its concentration in sea water that, until relatively recently, all measurements were erroneously high. The iron being measured was the result of contamination. As all oceanographic ships are made of iron, avoiding this contamination proved to be a significant challenge.

When these analytical problems were finally surmounted, it was demonstrated that the iron content of sea water was indeed exceedingly low. Having learned to avoid contamination, Martin added tiny amounts of iron to flasks of sea water and showed that relative to control samples, those with added iron underwent increases in chlorophyll concentration and decreases in phosphate concentration.

Martin's critics chose to discount his flask experiments claiming that the absence of the organisms which feed on the plants biased the results. This debate continued until an in situ experiment was conducted in the phosphate-rich surface waters of the eastern equatorial Pacific.⁹⁴ The spreading of the iron-enhanced surface water patch was monitored using an SF₆ tracer gas. Lo and behold, it worked. The phosphorus content and CO₂ partial pressure were drawn down and the chlorophyll concentration increased. Since then, in situ experiments have been conducted in the Southern Ocean⁹⁵ with similar results.

Meanwhile, scientists were busy making measurements to see how much iron there is in deep sea water. They found that small amounts were indeed present and also that these small amounts were there only because they were bound to a special "designer" enzyme secreted by marine organisms!⁹⁶ Binding to this enzyme prevented the iron atoms



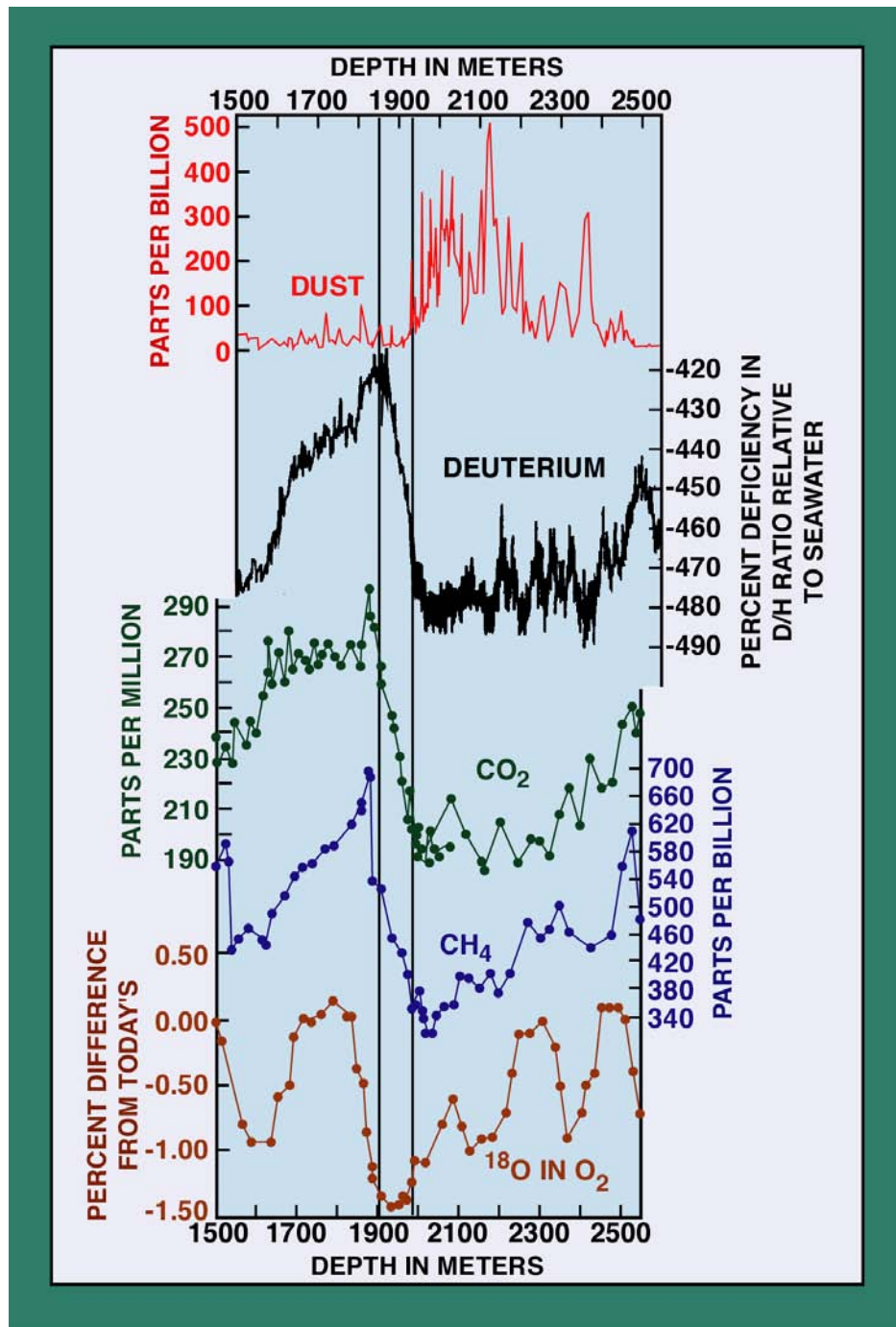
The map in the upper panel shows regions of the planet from which dust is supplied to the atmosphere. The map in the lower panel shows estimates of the contemporary flux of dust to the ocean surface (in milligrams per square meter per year). As this rain of dust is thought to be the major supplier of iron to the sea, it is clear that due to the absence of land masses at high southern latitudes, Southern Ocean surface waters are iron starved.

from being absorbed onto raining particulate matter. It seems incredible that these microorganisms conscious of the need to guarantee at least a minimal supply of iron learned to manufacture an enzyme capable of holding iron in solution. Of course, these organisms also had to develop the where-with-all to pull the iron away from this enzyme when they needed it. Jim Lovelock would call this Gaia in action.

Could iron hold the key to our glacial enigma? The records in ice cores from Antarctica show that, as was the case in Greenland,⁹⁷ the rate of dust infall was an order of magnitude higher during glacial time than during the Holocene.⁹⁸ Perhaps the iron contained in this excess dust permitted the phosphorus content and CO₂ partial pressure in Southern Ocean surface waters to be drawn down and consequently also the CO₂ content of the atmosphere.⁹¹

But why focus on the Southern Ocean? The obvious reason is that it is by far the largest region of the surface ocean where phosphorus goes largely unused. Further, because of the sparsity of land at high southern latitudes, the rain of iron-bearing dust onto the Southern Ocean is far smaller than anywhere else on the planet. Hence Southern Ocean waters are likely subject to severe iron limitation.

An indication of the importance of the Southern Ocean comes from the record in Vostok ice. In particular, the record as for the events surrounding Termination II (i.e., the penultimate deglaciation centered at 128,000 years ago). The first indication of the approaching deglaciation was a drop in the rain of dust onto the Antarctic plateau.⁹⁹ Following close on the heels of the drop in dustiness were rises in air temperature (as recorded by the isotopic composition of the ice), and rises in both the CO₂ and CH₄ contents of the air trapped in the ice. Only after these rises had been largely completed did the ¹⁸O content of the O₂ gas in the trapped air begin to rise. This strongly suggests that melting of the great northern ice sheets did not commence until Antarctica had warmed and until methane production in tropical wetlands had been ramped up. The basis for this claim is that as the ¹⁸O to ¹⁶O ratio in O₂ gas is tied to that in sea water and hence



Sequence of events as associated with Termination II as recorded in ice from the Vostok Antarctica boring.⁹⁹ The depth scale for properties recorded in trapped air (i.e., CO₂, CH₄ and ¹⁸O in O₂) has been displaced from that for properties recorded in the ice itself (dust and deuterium) in order to account for the close-off depth for the air bubbles.

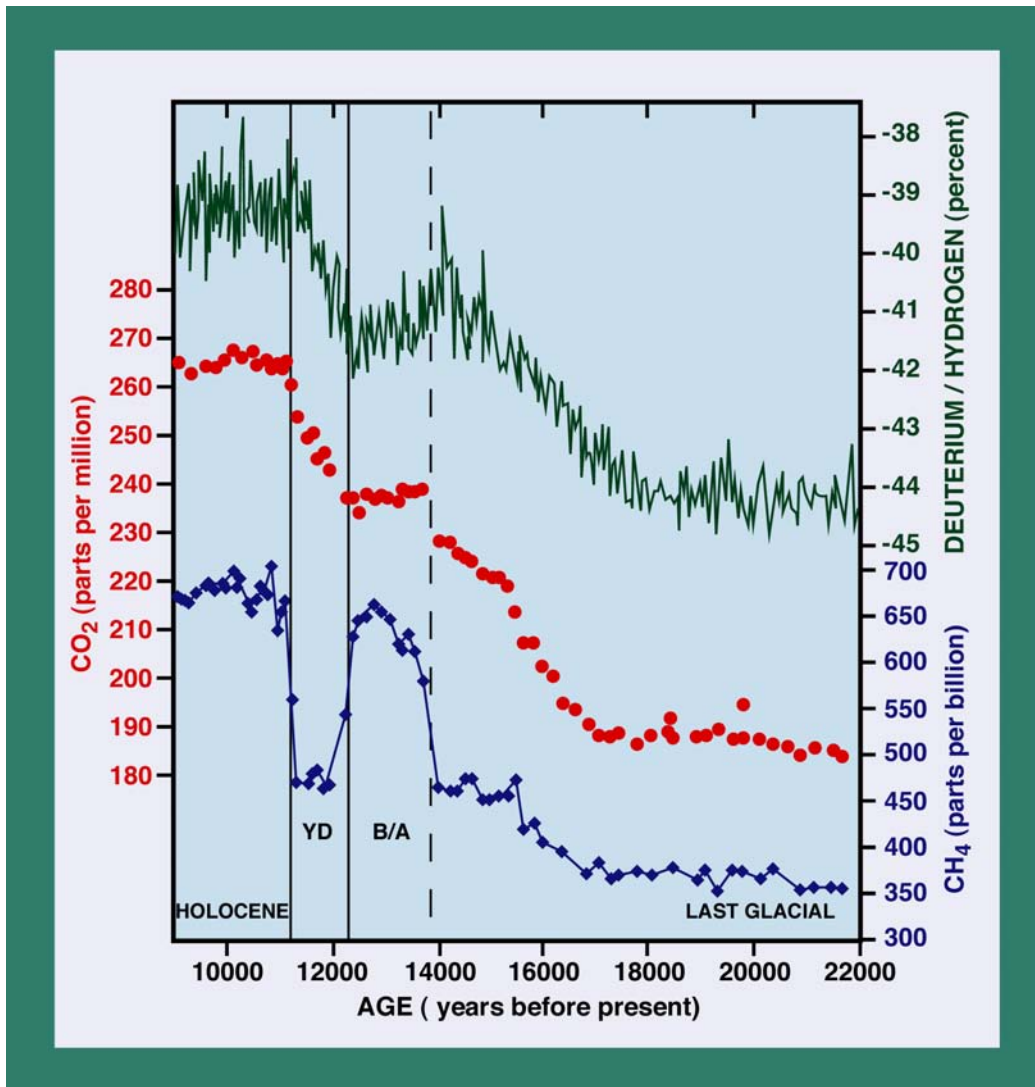
also to the amount ^{18}O -depleted water tied up in the glacial ice sheets.¹⁰⁰ Although there is a delay in imprinting the ocean's ^{18}O to ^{16}O ratio on the atmosphere's O_2 , it is quite small. The entire inventory of O_2 in the atmosphere is replaced once each millennium by photosynthesis. As all the water used in photosynthesis ultimately comes from the sea, the isotopic composition of O_2 is tied to that in sea water.

As the demise of the northern ice is tied to the rebirth of conveyor operation, the record in Antarctic ice tells us something extremely important about the rise in atmospheric CO_2 content. It was not triggered by the turn on of conveyor circulation. Rather, it was largely completed before this rejuvenation occurred.

One thing that has been learned from studies of the sediments beneath the Southern Ocean is that during peak glacial time winter sea ice extended 8 or so degrees latitude farther away from the Antarctic margin than it does today. One might imagine that the thermal isolation produced by this excess sea ice cover played a major role in cooling the interior of the Antarctic continent. Or the inverse could be true; the cooling of the south polar region allowed sea ice to expand. In any case, the warming of Antarctica and the reduction in the extent of sea ice cover went hand in hand. So perhaps our old friend sea ice, which played such an important role in the northern Atlantic, did so in the Southern Ocean as well.

But an even better reason exists for focusing on the Southern Ocean. As you remember in Chapter 2, we saw that the record of Antarctic air temperature during the period of deglaciation was antiphased with the record in Greenland. So a hot clue would be to determine whether the rise in atmospheric CO_2 content at the end of the last glacial period followed the Antarctic or the Greenland temporal pattern. The distinction is clear; the rise in atmospheric CO_2 content exactly mirrors the warming in Antarctica.¹⁰¹ This match cries out that CO_2 is controlled by something going on in the Southern Ocean. Sea ice cover is the likely villain!

While these observations clearly point to the Southern Ocean, iron fertilization is

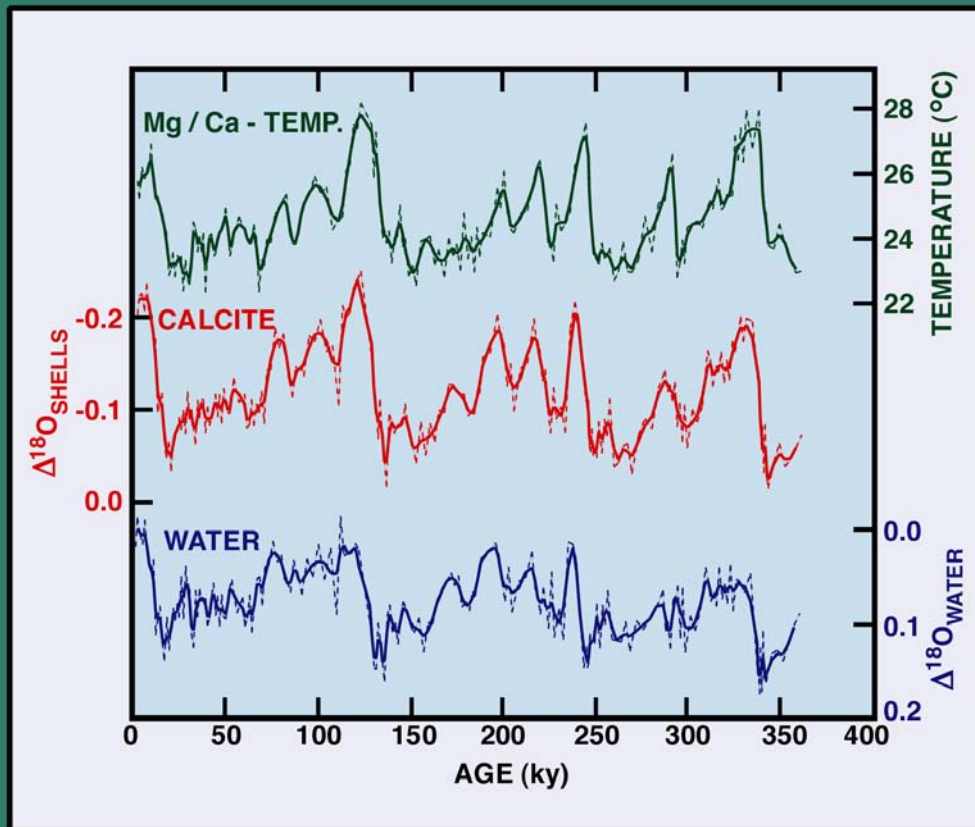


Records for air temperature (based on D to H ratio in the ice itself) and of CO₂ and CH₄ contents of the air bubbles in the Siple Dome Antarctica ice core.¹⁰¹ The time scale is based on the methane record which can be tied to the chronology based on the counting of annual layers in Greenland ice. The point is that the rise of CO₂ beautifully mimics that of Antarctic air temperature and is very different from the Greenland temperature record. This strongly suggests a Southern Ocean control for atmospheric CO₂ content!

not the only possible mechanism. Two others have been put forward. One involves Adkin's deep salty reservoir. Might it accumulate respiration products and thereby draw down the ΣCO_2 content of sea water and hence also the CO_2 content of the atmosphere? Unlikely! If the C to P ratio in the organic matter decomposed in this reservoir were on the order of 125 to 1, then the loss of phosphorus would weaken the biologic pump and thereby raise the CO_2 content of the atmosphere. Nice try, but no cigar.

Another suggestion is that the excess sea ice served as a barrier, preventing the respiration CO_2 brought to the surface by upwelling from escaping to the atmosphere.¹⁰² In this case, the loss of heat necessary for the redensification of the upwelled deep water would occur through the sea ice rather than by direct contact with the cold atmosphere. While in some ways this is appealing, one could counter by asking why when exposed during summer months the respiration CO_2 in surface water didn't lose its CO_2 to the atmosphere. If so, the winter sea ice lid would lose its effectiveness.

A further complication must be mentioned. Research by Harry Elderfield at Cambridge University¹⁰³ and by David Lea at the University of California¹⁰⁴ demonstrated that the trace incorporation of the element magnesium in foraminifera shells depends on their growth temperature: the warmer the water in which the calcite forms, the higher the amount of magnesium incorporated. A second method for the reconstruction of past surface ocean temperatures is to measure the ratio in the bulk sediment of two nearly chemically identical alkenones.¹⁰⁵ These compounds are produced by a calcium carbonate precipitating plant (coccolithophoridae). Both measurements on laboratory cultures and sediment core tops demonstrate that in the ocean's coldest water these organisms make only one of these alkenones and in the ocean's warmest waters they make only the other.¹⁰⁶ At intermediate temperatures, they make both in proportions which vary linearly with temperature. Application of these paleo thermometers to sediment cores at a number of sites in the southern hemisphere ocean reveal that surface ocean temperatures during the last interval of deglaciation followed the Antarctic

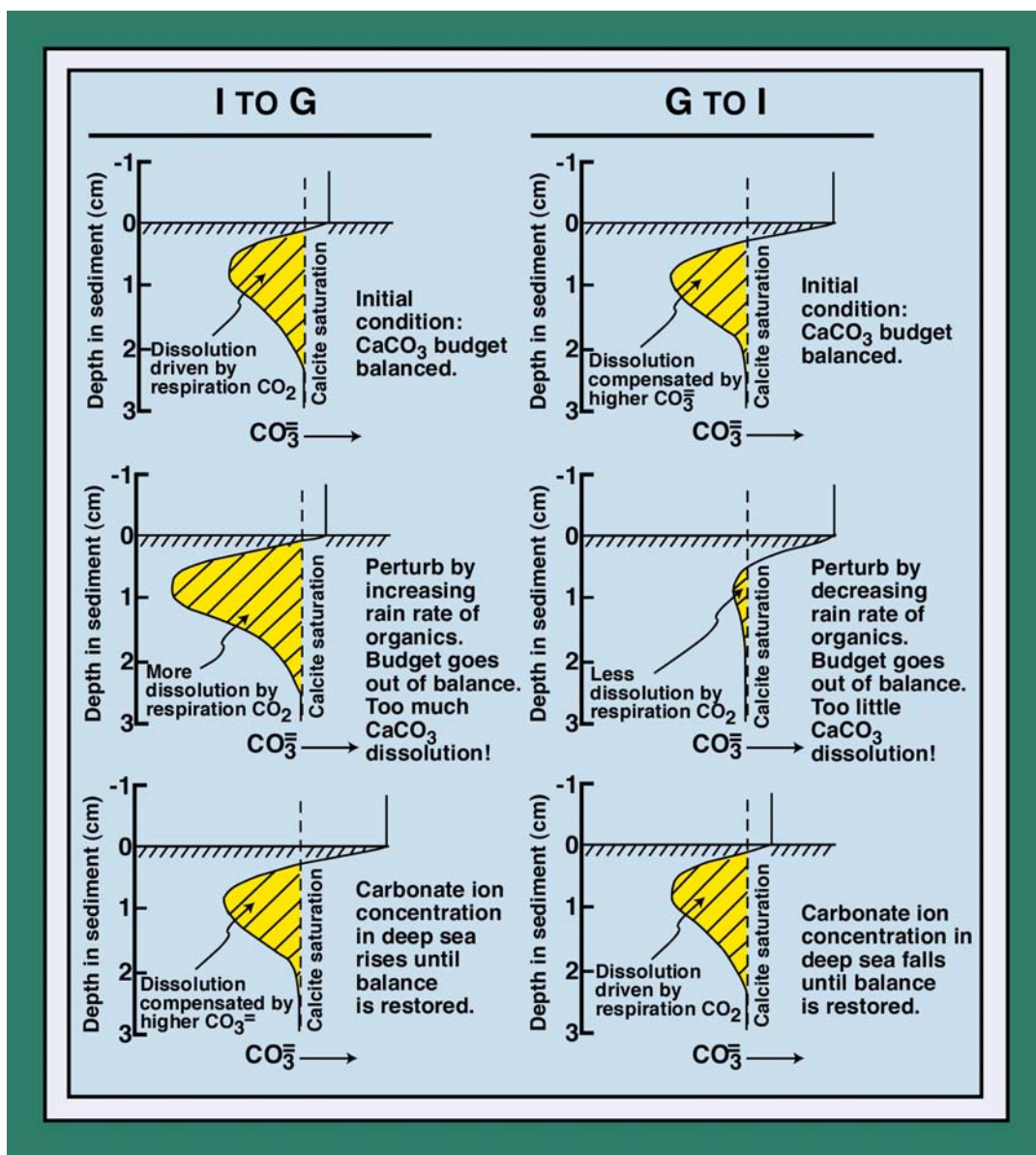


Measurements of Mg to Ca ratio and ^{18}O to ^{16}O ratio on samples from a core from the Cocos Ridge in the eastern equatorial Pacific made by Harry Elderfield of Cambridge University and David Lea of the University of California, Santa Barbara. The Mg measurements record the temperature of the water in which the shells grow. The ^{18}O measurements on the same shells record a combination of growth temperature and isotope composition of the water in which the shells grew. Based on the Mg record, the temperature component can be extracted creating a record of the ^{18}O to ^{16}O ratio in the surface water.

temporal pattern.

One other scenario must be mentioned. David Archer of the University of Chicago¹⁰⁷ proposed a very clever means by which a disruption of the ocean's CaCO_3 cycle might lower the atmosphere's CO_2 content without deepening the transition zone separating sediments rich in CaCO_3 and those poor in CaCO_3 . As discussed in Chapter 4, in today's ocean this transition zone is displaced somewhat deeper than the saturation horizon. The reason for this displacement is that beneath the saturation horizon the rate of dissolution increases with water depth. Only below that depth at which the rate of dissolution becomes large enough to match the rate of calcite rain will the CaCO_3 content of the sediment approach zero. In between the saturation horizon and this depth, only a fraction of the raining calcite dissolves. Archer recognized a complication in this scenario. Some of the organic matter which falls to the sea floor is stirred into the sediment before it is consumed by worms and bacteria. Its consumption then raises the CO_2 content of the uppermost sediment pore waters and correspondingly reduces their $\text{CO}_3^{=}$ concentration. Hence, the calcite saturation horizon in pore waters is displaced to a shallower depth than that in bottom waters. Because of this, calcite dissolution begins at a depth somewhat shallower than the bottom water saturation horizon.

Archer's proposal was that during glacial time the displacement between the depth of the pore water saturation horizon and the bottom water saturation horizon was greatly increased. This increase was postulated to have resulted from a much larger rain of organic matter to the sea floor. The increase in dissolution intensity in sediment pore waters generated by this excess respiration CO_2 initially created a large imbalance in the ocean's CaCO_3 budget. The amount of carbon entering the ocean would have temporarily exceeded the amount being buried in sediments. This would have led to a continuing buildup in the ocean's carbonate ion concentration and a corresponding decrease in the atmosphere's CO_2 content. After 5 to 10 thousand years, the balance between carbon loss and carbon gain would have been reestablished. If Archer's scenario is called upon to



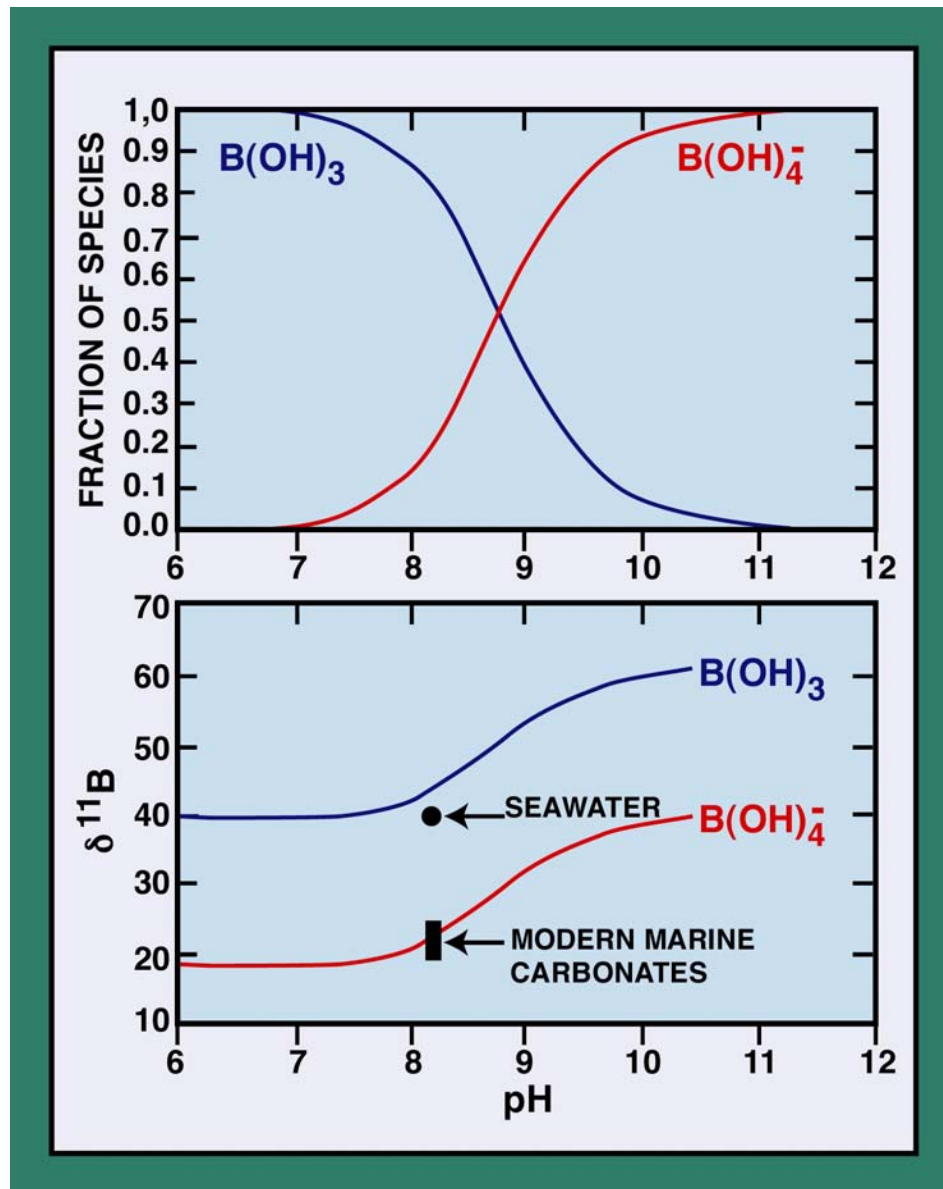
David Archer of the University of Chicago proposed that during glacial time an increase in the rain of organic carbon to the sea floor led to a decrease in the carbonate ion content of sediment pore waters thereby increasing the extent of sea floor dissolution of calcite.¹⁰⁷ This would have caused calcite dissolution to exceed the supply of ingredients thereby disrupting the balance in CaCO_3 throughput. The consequent buildup of the carbonate ion concentration in deep sea water would eventually have countered the pore water reduction in carbonate ion thereby restoring the CaCO_3 cycle to a steady state. This increase would have drawn down the CO_2 concentration in the ocean and consequently that in the atmosphere as well. The situation would have been reversed at the onset of interglacial time.

explain the full glacial drawdown of the atmosphere's CO_2 content, then the offset between the bottom water saturation horizon and pore water saturation horizon would have to have increased from a few hundred meters to several thousand meters.

Archer's hypothesis received a boost from boron isotope measurements made by Lamont-Doherty's Abijit Sanyal who followed up on research conducted by Gary Hemming, as part of his Ph.D. research at Stony Brook University. Hemming had demonstrated that the ratio of ^{11}B to ^{10}B in marine CaCO_3 depends on the pH (i.e., H^+ ion concentration) of the water in which it formed. Sanyal applied this method to benthic foraminifera. His reasoning was that as the H^+ concentration is proportional to the CO_2 concentration and since the product of the CO_2 and CO_3^- ion concentrations remains nearly constant, the carbonate ion concentration must be inversely proportional to the hydrogen ion concentration. Thus, his boron isotope measurements on benthic foraminifera shells potentially had the capability of demonstrating whether the large increase in the carbonate ion concentration in the glacial ocean demanded by Archer's scenario actually took place. To this end, Sanyal measured the isotopic composition of the trace amounts of boron contained in Holocene and glacial-age benthic foraminifera shells from both equatorial Atlantic and equatorial Pacific sediment cores.¹⁰⁸ In both cases, the shift in boron isotope ratio indicated that the carbonate ion concentration in the glacial deep ocean was higher than that for the Holocene. Not only was it higher, but it was higher by the amount needed to explain the entire 90 parts per million drop in atmospheric CO_2 content!

Problem solved? Unfortunately, no. Several questions dog Archer's scenario. One of these concerns had to do with the cause of the greatly increased rain rate of organic matter to the sea floor. If it was increased plant productivity, then it should show up as a corresponding increase in the carbon isotope difference between glacial-age planktic and benthic foraminifera shells. It didn't. Further, if the increase in organic matter rain to the sea floor was matched by an increase in CaCO_3 rain, then the excess respiration CO_2 so

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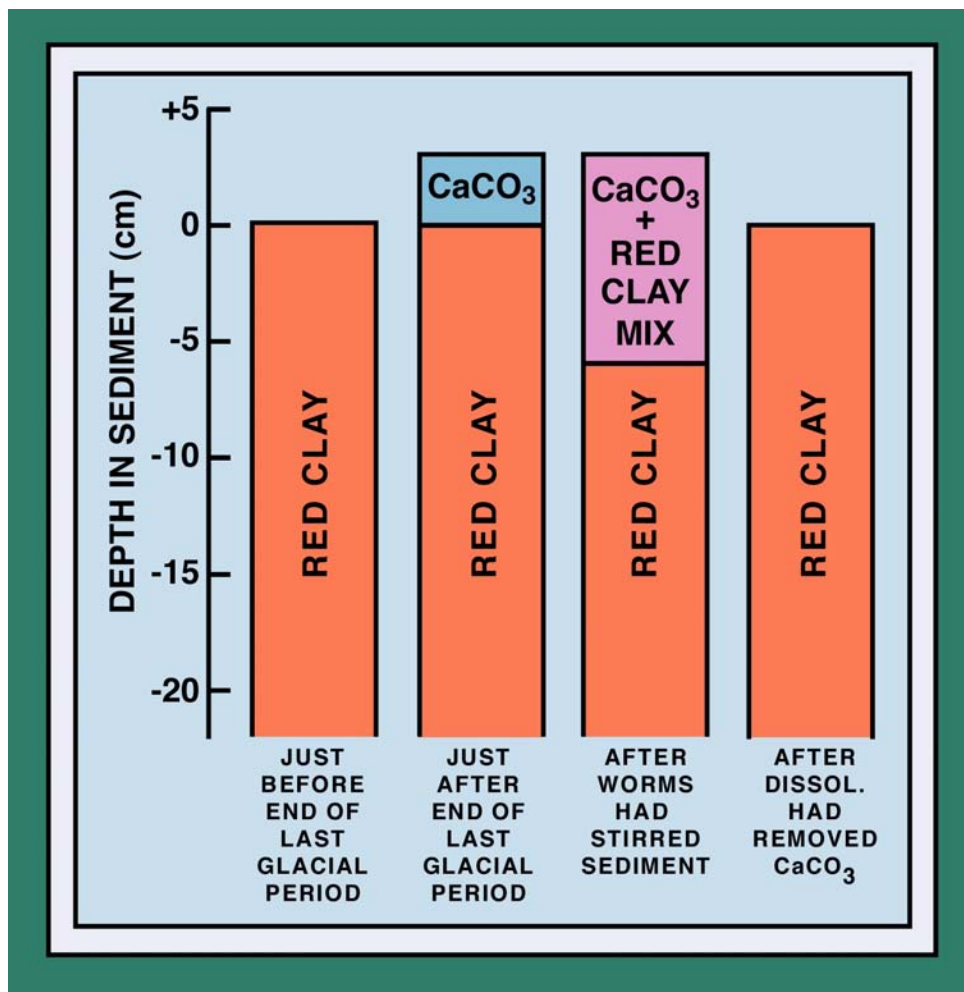
As shown by Gary Hemming and Abijit Sanyal, the ratio of the heavy (^{11}B) to the light (^{10}B) isotope of the element boron contained as traces in foraminifera shells varies with the pH (and hence also with carbonate ion concentration) of the sea water in which they formed. The reason is that neutral borate dissolved in sea water is enriched in ^{11}B by about two percent relative to charged borate. As the isotopic composition of the total borate is fixed, as the pH changes so also must the isotopic composition of each of these two species. The idea is that only charged borate ions are incorporated in the calcite. Hence their ^{11}B content increases as the pH of the ocean water rises (i.e., as the carbonate ion concentration increases).

generated would have been neutralized by CaCO_3 dissolution and the desired carbonate ion increase would not have occurred. One way in which both of these problems might be circumvented is to postulate that the domain of diatoms was greatly expanded during glacial time. This would eliminate the CaCO_3 problem and also provide dense entities needed to transport a greater fraction of the organic matter to the sea floor. But where did the extra silica come from? Why aren't the remains of diatoms found in glacial-age sediment? And why was the accumulation rate of calcite in deep sea sediments more or less the same during glacial time as during the Holocene?

Another question has to do with the fate of the large excess of carbonate ion stored in Archer's glacial ocean. At the termination of the glacial period, his scenario calls for a shutdown of the excess flux of organic matter to the sea floor. When this happened, the pore water saturation horizon would deepen by several kilometers. The depth of both horizons would exceed that of abyssal sea floor and hence both bottom waters and pore waters throughout the deep sea would find themselves supersaturated with CaCO_3 . In this situation, all the calcite manufactured by marine organisms would accumulate on the sea floor creating a large imbalance between carbon burial and carbon input. This excess accumulation of CaCO_3 across the entire sea floor would gradually draw down the ocean's excess carbonate ion. The saturation horizons would move back up the water column until a balance between carbon burial and input had been restored. The time required of this to happen would be 5 to 10 thousand years.

The amount of CaCO_3 deposited during this carbonate ion dump would have produced a layer of calcite averaging about 3 cm in thickness. But no vestige of this layer is to be found. Core-top sediment on the abyssal planes contains less than 0.1 percent CaCO_3 . Considering that the ever-present sea floor worms would have mixed this CaCO_3 into the pre-existing clays, it is inconceivable, at least to me, that none of the CaCO_3 should remain. Its absence constitutes strike two against the Archer scenario.

As if two strikes weren't enough, Princeton's Daniel Sigman tossed a third.¹⁰⁹



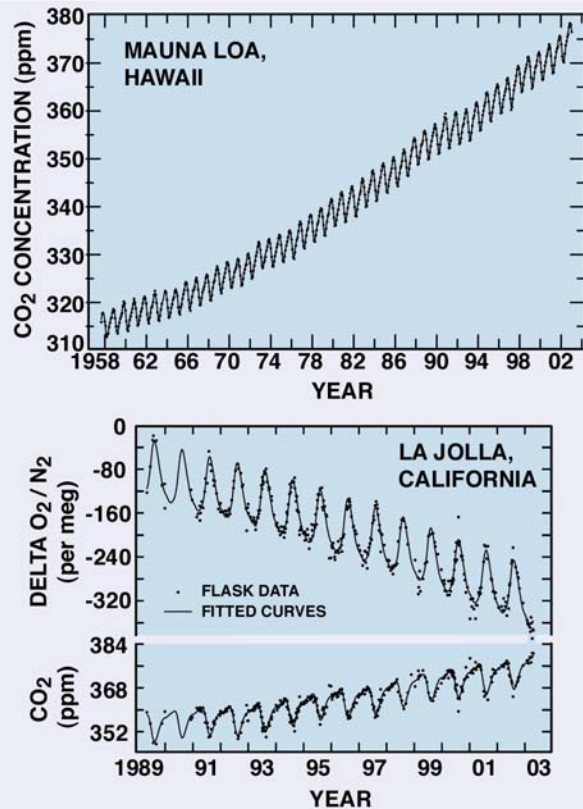
If Archer's pore-water scenario were responsible for the entire reduction of CO_2 in the glacial atmosphere, then the composition of sediment at 5000 meters depth in the Pacific Ocean would evolve as shown. As the sediment would have pore water highly undersaturated with respect to calcite, no CaCO_3 would have accumulated during glacial time. Then, when the extra flux of organic matter to the sea floor was shut down, the pore water saturation horizon would plummet to a depth greater than that of the abyssal ocean. This would allow CaCO_3 to accumulate over the entire sea floor. This deposition would continue until the excess CO_3^{2-} ion built up in the glacial deep sea had been dissipated. As a result, a layer of CaCO_3 averaging 3 km in thickness would have been created. Worms would have stirred this CaCO_3 into the underlying sediment. However, as no vestige of this CaCO_3 exists today, it would have had to totally dissolve during the last 10,000 or so years. I find this difficult to believe.

He showed through modeling that the several kilometer separation between the pore water and bottom water calcite saturation horizons demanded by Archer's scenario could not have been maintained.

So, as have all the other clever scenarios put forth to explain the low glacial atmospheric CO₂ content, that by Archer fell victim to its apparent short comings. Because of this, the quest goes on. Key in this regard are repeats of Sanyal's boron isotope measurements on benthic foraminifera. If the answer keeps coming up the same, then Archer's scenario will have to be rethought. How could the three strikes against it be erased? Can Archer's scenario be linked to Martin's iron fertilization? Can it be linked to the Antarctic sea ice record?

So, as is so often the case, nature carefully guards her secrets. Despite a number of hot clues and 25 years of clever ideas, no one has come up with an explanation which meets all the constraints.

ATMOSPHERIC CO₂ AND O₂ RECORDS



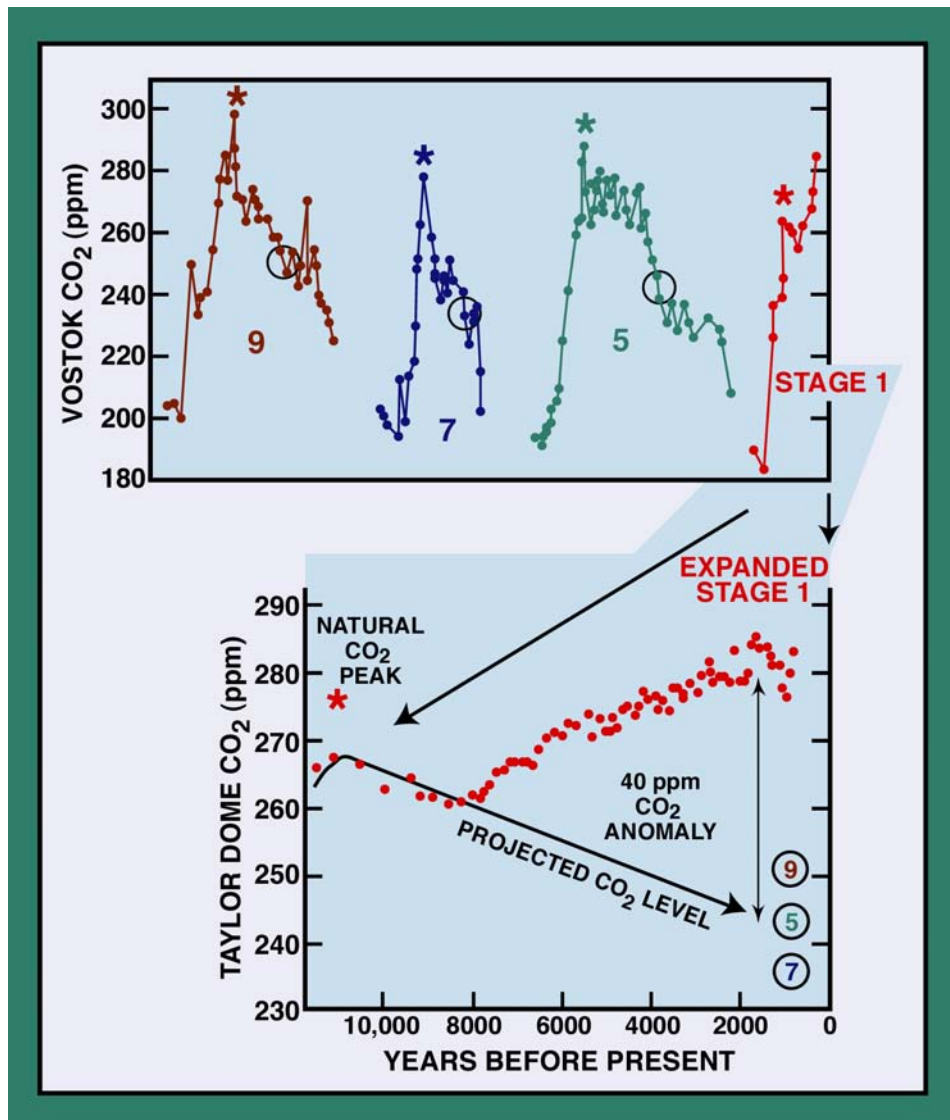
Records of the buildup of the atmosphere's CO₂ content and of the drawdown of its O₂ content. The Mauna Loa record was initiated by father, Charles David Keeling, in 1958. The La Jolla record was initiated by son, Ralph Keeling, in 1989. The seasonal fluctuations in these records reflect the alternation between the dominance of photosynthesis during warm months and respiration during cold months.

CHAPTER 6

TOMORROW'S CHEMISTRY

Over the last century, by burning coal, oil and natural gas, a half trillion tons of CO₂ has been released to the atmosphere. About 50 percent of this CO₂ remains airborne. Much of the other 50 percent has been sucked up by the ocean and, surprisingly, some has gone into an increase in the inventories of wood and soil humus. Although the reserves of oil and perhaps also of natural gas will run short during the next half century, enough coal, tar sand and oil shale await mining to supply cheap fossil-fuel energy for another century or so.

In 1850, the CO₂ concentration in the atmosphere was 280 parts per million. As sufficiently accurate measurements on atmospheric samples commenced only in 1958 when the CO₂ content had already risen to 316 parts per million, the content prior to the onset of the Industrial Revolution had to be determined through measurements on air bubbles trapped in polar ice. As depicted in Chapter 5, during the previous three interglacials, the CO₂ content peaked, as it did in the present interglacial, at 280 ± 20 ppm. However, as pointed out by Bill Ruddiman of the University of Virginia, there is a puzzling difference between the record for these earlier interglaciations and that for the present one.¹¹⁰ In the previous three, the CO₂ content peaked early in the interglacial and then steadily declined. While this was also the case in the present interglacial, the decline which followed the maximum continued for only about four thousand years after which the trend reversed and the CO₂ content started back up again. During the last 8000 years, it rose from 260 to 280 parts per million. Ruddiman contends that this rise is the result of forest cutting and burning by humans. Based on an analogy with the previous interglacials, he proposes that in the absence of human intervention the atmosphere's CO₂ content would have dropped during the course of the present interglacial to about 240



Bill Ruddiman of the University of Virginia noted that the CO₂ record for the Holocene differed from those for the previous three interglacials in that instead of undergoing a steady decline following an early interglacial maximum (see *s in upper panel) it reached a minimum about 8000 years ago and then started back up again. As shown in the lower panel, Ruddiman attributes this renewed rise to purposeful deforestation by humans. However, the extent of deforestation required to produce a 40 ppm rise is enormous: i.e., comparable to the extent of existing forests. Further, as the drop in oceanic ¹³C to ¹²C ratio in ocean-atmosphere carbon expected from this immense release of ¹³C-depleted carbon is not seen in the record kept in ice cores or in foraminifera shells, most of us geochemists firmly reject Ruddiman's explanation. We eagerly await the results for the stage 11 interglacial, expecting it to show a pattern similar to that for the Holocene.

parts per million. So Ruddiman is claiming that the human-induced CO₂ rise began 8000 years before the onset of the Industrial Revolution!

While an intriguing idea, it leaves geochemists howling. No way, they counter, for the extent of deforestation required would be comparable to the extent of existing forests. Were Ruddiman correct, this release of biospheric CO₂ should stand out like a sore thumb in the ¹³C record. The ¹³C to ¹²C ratio in atmospheric CO₂ and in oceanic dissolved inorganic carbon should have decreased by 0.3 to 0.4 percent during the last 8000 years. But, measurements on CO₂ trapped in Antarctic ice¹¹¹ and on CaCO₃ in planktic foraminifera shells¹¹² do not show this decrease.

My explanation for the rise in atmospheric CO₂ content is that it is the result of a compensation for the removal of CO₂ from the oceans to replace the forests and soil humus destroyed during glacial time.¹¹² This removal of the CO₂ led to an increase in the ocean's CO₃⁼ ion concentration unbalancing the ocean's carbon budget causing extra calcium carbonate to accumulate on the sea floor. The result would be a drawdown of the CO₃⁼ concentration until balance was restored. This reduction would have been accompanied by a corresponding increase in CO₂ content of the ocean and atmosphere. Importantly, CaCO₃ compensation would not have led to a ¹³C change.

So why no rise in CO₂ during the previous interglaciations? While I can't give a compelling answer, I suspect that it has to do with a difference in seasonality induced by the Earth's 20,000-year precession cycle. The situation for the present interglacial is much like that for interglacial stage 11. Hence, bets are out that when the CO₂ record for the next further back interglacial becomes available, that it will look much like that for the Holocene, providing proof that the CO₂ rise during the last 8000 years was not induced by man.

At the time this book was written, the atmosphere's CO₂ content had risen to 375 parts per million and will, in the near future, continue to rise at a rate of about 20 parts per million per decade. With population headed from 6.5 to 9.5 or so billion and with the

ATM CO ₂ = 280 x 10 ⁻⁶ atm		ATM CO ₂ = 360 x 10 ⁻⁶ atm		Δ
[NCD]	= 2216.0	[NCD]	= 2216.0	0.0 x 10 ⁻⁶ mol/L
[CO ₂]	= 9.6	[CO ₂]	= 12.3	+ 2.6 x 10 ⁻⁶ mol/L
[HCO ₃ ⁻]	= 1702.5	[HCO ₃ ⁻]	= 1779.5	+ 77.0 x 10 ⁻⁶ mol/L
[CO ₃ ⁼]	= 203.7	[CO ₃ ⁼]	= 173.1	- 30.6 x 10 ⁻⁶ mol/L
[Σ CO ₂]	= 1915.8	[Σ CO ₂]	= 1964.9	+ 49.1 x 10 ⁻⁶ mol/L
[B(OH) ₃ ⁰]	= 308.9	[B(OH) ₃ ⁰]	= 323.9	+ 15.0 x 10 ⁻⁶ mol/L
[B(OH) ₄ ⁻]	= 101.7	[B(OH) ₄ ⁻]	= 86.7	- 15.0 x 10 ⁻⁶ mol/L
[Σ B]	= 410.6	[Σ B]	= 410.6	0.0 x 10 ⁻⁶ mol/L
[OH ⁻]	= 4.4	[OH ⁻]	= 3.6	- 0.8 x 10 ⁻⁶ mol/L

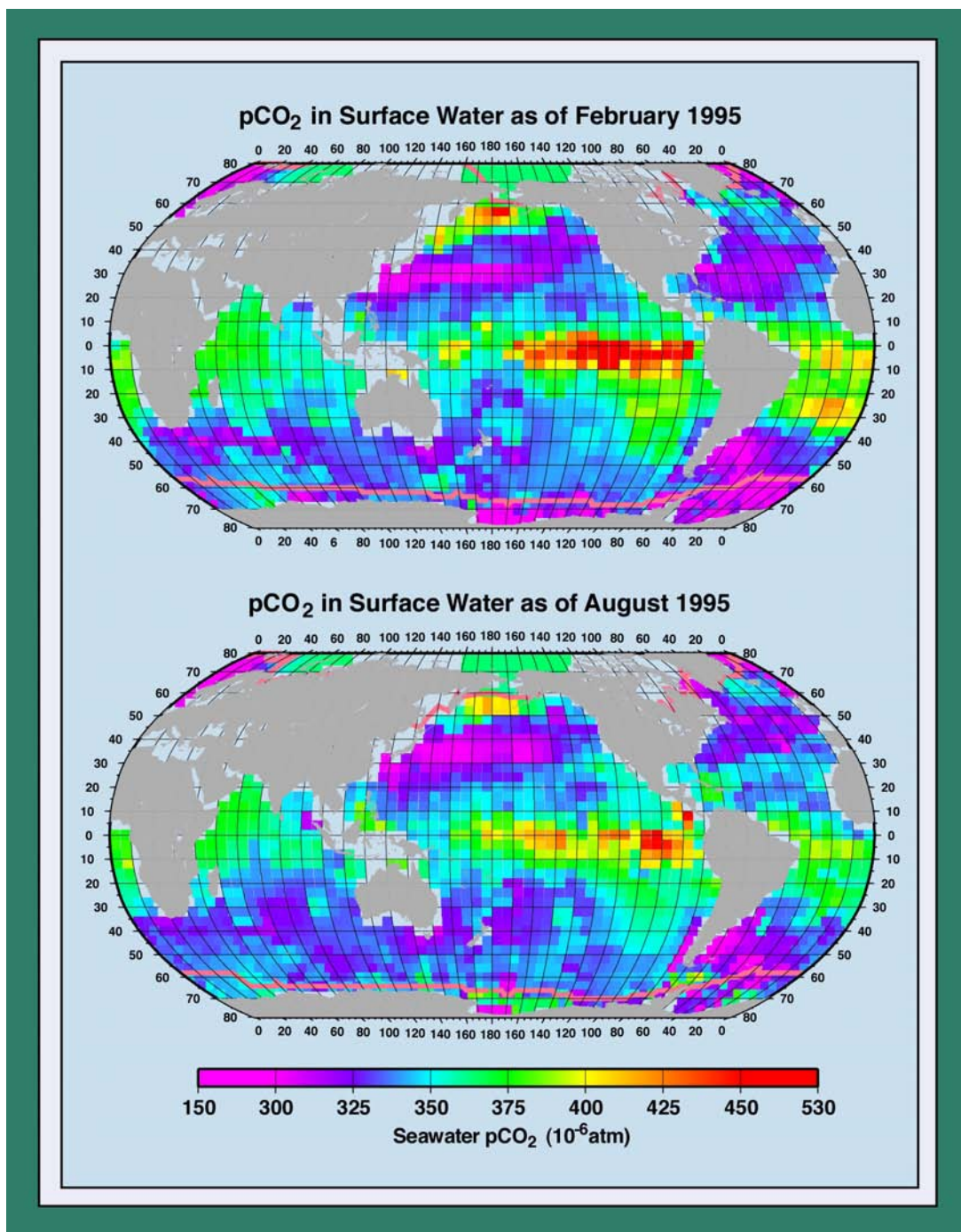
The change in the composition of a sea water sample initially equilibrated with air containing 280 x 10⁻⁶ atm CO₂ and then reequilibrated with air containing 360 x 10⁻⁶ atm CO₂. Note that the rise in dissolved CO₂ gas content (2.6 x 10⁻⁶ mol/liter) accounts for only 5 percent of the CO₂ taken up by the water (i.e., 49.1 x 10⁻⁶ mol/liter). Rather, the bulk of the uptake is accomplished by the conversion of CO₃⁼ to HCO₃⁻ (CO₂ + CO₃⁼ + H₂O → 2HCO₃⁻) and the conversion of B(OH)₄⁻ to B(OH)₃⁰ (CO₂ + B(OH)₄⁻ → HCO₃⁻ + B(OH)₃⁰). Of course, the negative charge deficit (NCD) and the total boron (ΣB) remain unchanged.

world's traditionally poor countries rapidly industrializing, were fossil fuels to remain our primary energy source, then the rise in atmosphere's CO₂ content would accelerate. It could well reach triple its pre-industrial level (i.e., 840 parts per million) early in the 22nd century. Most scientists agree that the consequences to climate of such a buildup would be unacceptable. Hence, efforts are in progress to find an escape hatch which would allow the world's energy demand to be met without driving up the atmosphere's CO₂ content to an objectionable level. Two pathways toward this end are being pursued: 1) a transition to alternate sources of energy and 2) purposeful capture and storage of the CO₂ produced by burning fossil fuels.

Our interest in man-made CO₂ rise is threefold. First, as time passes, how will its partitioning between the ocean and atmosphere evolve? Second, could CO₂ captured from electrical power plant exhausts and retrieved from the atmosphere be safely stored in the deep sea? And third, what will be the impact of the CO₂ taken up by the ocean on its chemical cycles and ecosystems?

In order to answer the first of these questions, three pieces of information are needed: 1) the thermodynamic capacity of sea water to take up excess CO₂, 2) the rate of transfer of excess CO₂ from the atmosphere to the surface ocean and 3) the rate at which surface waters charged with excess CO₂ are mixed into the ocean's interior. The bottom line is that to date only about 15 percent of the ocean's capacity to take up CO₂ has been utilized. The hold-up is mainly the result of the sluggishness of ocean mixing. Were no more fossil fuel CO₂ to be released to the atmosphere, given enough time (i.e., many centuries), about 85 percent of the excess CO₂ already produced would end up in the ocean. But, as more and more CO₂ is produced, the thermodynamic capacity for CO₂ uptake by the ocean will be correspondingly depleted. The reason is that we are using up the ocean's inventories of CO₃⁼ and B(OH)₄⁻.

Dissolved CO₂ gas itself accounts for only about 5 percent of the ocean's uptake. The remaining 95 percent of the uptake has been accomplished by a reshuffling of the

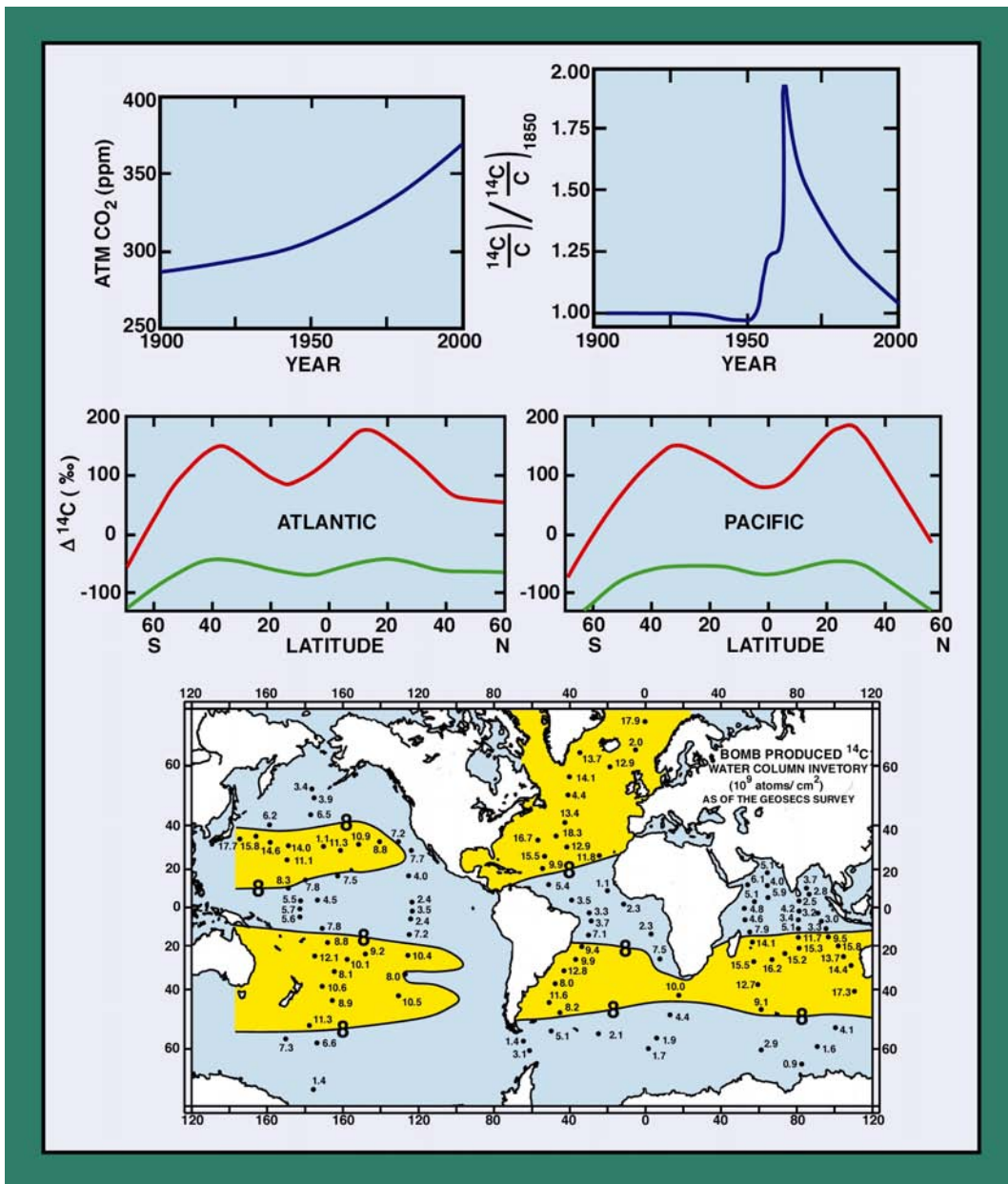


Maps showing the distribution of the CO₂ partial pressure in surface ocean water in the months of February and August. The blue-green tones represent areas where the partial pressure is close to that in the atmosphere. The orange-red tones represent areas where the pressure is higher than that in the atmosphere and the purple-maroon tones areas where it is lower. These maps were prepared by Lamont-Doherty's Taro Takahashi and Stew Sutherland.¹¹³

ions which balance the NCD. As the result of CO_2 uptake, the bicarbonate ion concentration rises and the carbonate ion and borate ion concentrations fall. Also, the concentration of hydroxyl ion undergoes a small decrease making the ocean more acidic. So, it is clear that our ocean is endowed with the capability to take up large amounts of CO_2 . It is also clear that by adding ever more CO_2 to the atmosphere we are depleting a natural resource. Interestingly, the amount of carbon locked up in fossil fuels, if burned, is more than enough to neutralize all the $\text{CO}_3^{=}$ and B(OH)_4^- in the sea.

The first step in the uptake of CO_2 by the sea involves its transfer from the atmosphere to surface ocean. Prior to the Industrial Revolution, CO_2 molecules in the atmosphere were continuously trading places with those in the surface ocean. As the CO_2 content of the atmosphere was at that time close to steady state with that in the surface ocean, over the course of a year, the number of CO_2 molecules entering the sea very closely matched the number leaving the sea. But, with the onset of fossil fuel burning, this balance was disrupted. More CO_2 molecules now invade the sea than escape from it. The excess invasion has gradually raised the partial pressure of CO_2 in the surface ocean. But the ocean is playing catch up. The reason is that each year the CO_2 content of the atmosphere rises a bit and each year the ocean's surface waters mix with underlying waters deficient in excess CO_2 .

Geochemists have come up with a number of ways to assess the extent of this lag. Taro Takahashi of Columbia's Lamont-Doherty Earth Observatory has pulled together the measurements of surface ocean CO_2 partial pressure made by his group and by those from other institutions.¹¹³ Takahashi had to take into account the sizable variations with location and with season. The bottom line is that, as of the 1990s, the surface had on the average an $8 \pm 2 \times 10^{-6}$ micro-atmosphere's lower CO_2 partial pressure than the atmosphere. Considering that between the 1880s and the 1990s the atmosphere's CO_2 content rose by about 80 parts per million (i.e., 280 to 360 ppm), this demonstrated that the surface ocean has been doing a pretty good job of "catching up". Its rise of 72 parts



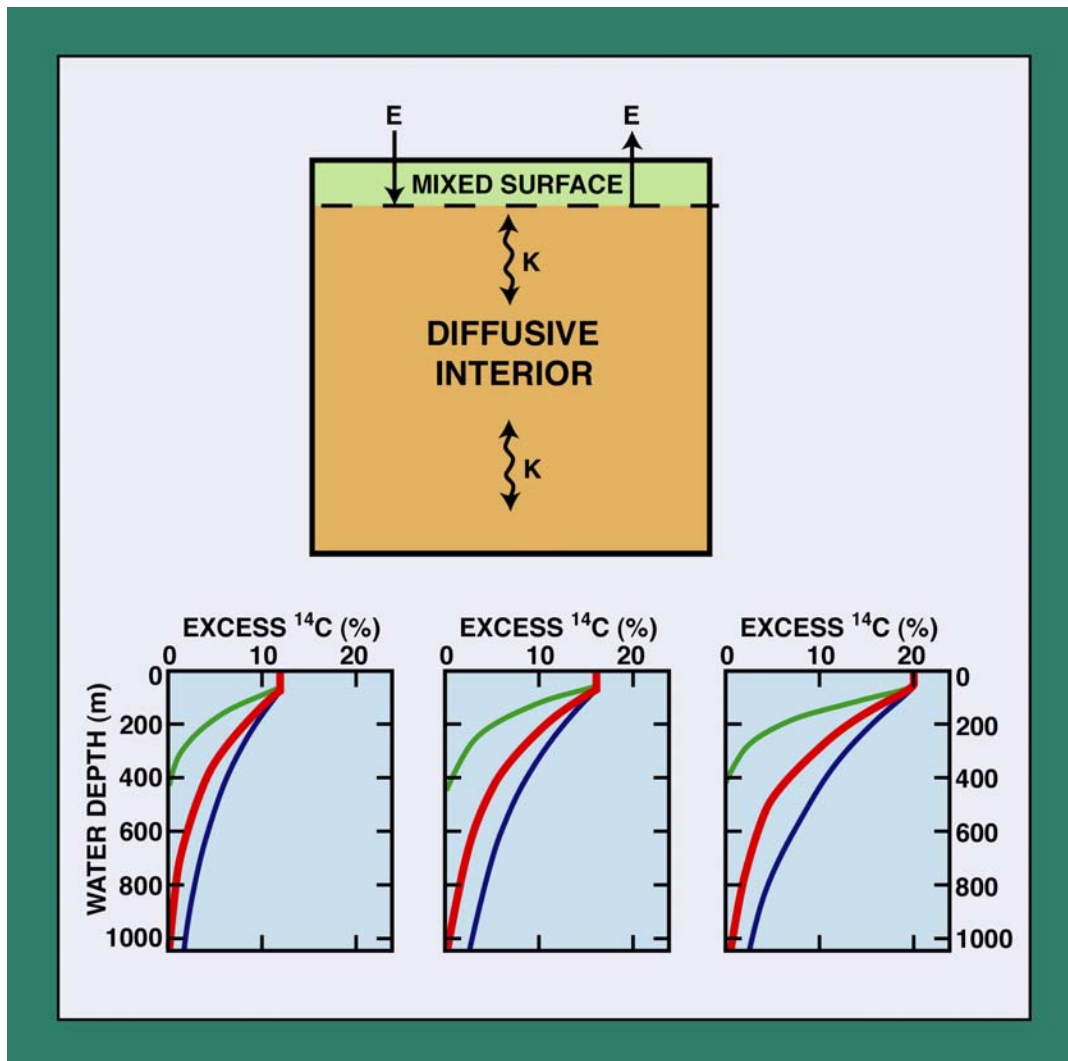
In the upper panels are shown the evolution of the atmosphere's CO_2 content and of its ^{14}C to C ratio. The small pre-1950 decline in ^{14}C reflects the addition of fossil fuel CO_2 . The post 1950 rise is the result of nuclear tests conducted in the atmosphere. The middle panels show the ^{14}C to C ratio in surface ocean as of the time of the GEOSECS survey (red lines) and prior to nuclear testing (green lines). The lows reflect upwelling of bomb ^{14}C free water. In the lower panel is shown the water column inventories of bomb ^{14}C atoms at each station occupied during the GEOSECS survey.¹¹⁴ The low values in the unshaded areas are the result of the upwelling of bomb ^{14}C free water.

per million matched 90 percent of the atmosphere's rise. Hence, although the surface ocean is not quite able to achieve equilibrium with the atmosphere, transfer from the atmosphere to the surface ocean constitutes a minor resistance to ocean uptake.

What Takahashi's measurements don't tell us is what fraction of the 8 parts per million deficiency in surface waters is the result of a steadily rising atmospheric CO₂ content and what fraction is the result of mixing with fossil fuel CO₂ deficient underlying water. For example, were this deficiency entirely the result of the increase in atmospheric CO₂ content, it would translate into a five-year lag time (i.e., 5 years x 1.6 ppm/yr. = 8 ppm).

However, measurements of the rate of CO₂ exchange between the ocean and atmosphere demonstrate most of the lag is, instead, the result of sluggish mixing between surface and subsurface water. The most reliable estimate of the atmosphere-ocean CO₂ exchange rate is that based on the invasion into the ocean of CO₂ molecules tagged with radiocarbon atoms produced as the result of the testing of hydrogen bombs. The neutrons released during such explosions find their way into the nuclei of atmospheric nitrogen atoms in the same way as do the neutrons produced by the bombarding cosmic rays. As of January 1, 1963 when the internationally agreed upon ban on atmospheric weapons testing went into force, the ¹⁴C inventory in the atmospheric CO₂ had very nearly doubled. With time, most of this extra ¹⁴C has been taken up in the ocean and in the terrestrial biosphere. Forty-two years later, as this book was being completed, the atmospheric ¹⁴C to C ratio had dropped back to about 7 percent above its pre-industrial value.

During the 1970s, a survey of the distribution of total radiocarbon (i.e.. bomb + natural) was conducted throughout the world ocean. This survey was part of a larger program which went by the acronym GEOSECS (Geochemical Ocean Sections Study). Included were measurements of tritium, PO₄, NO₃, SiO₂, ΣCO₂, and NCD. The CO₂ stripped from 200-liter water samples was sent to two laboratories for ¹⁴C analyses. One

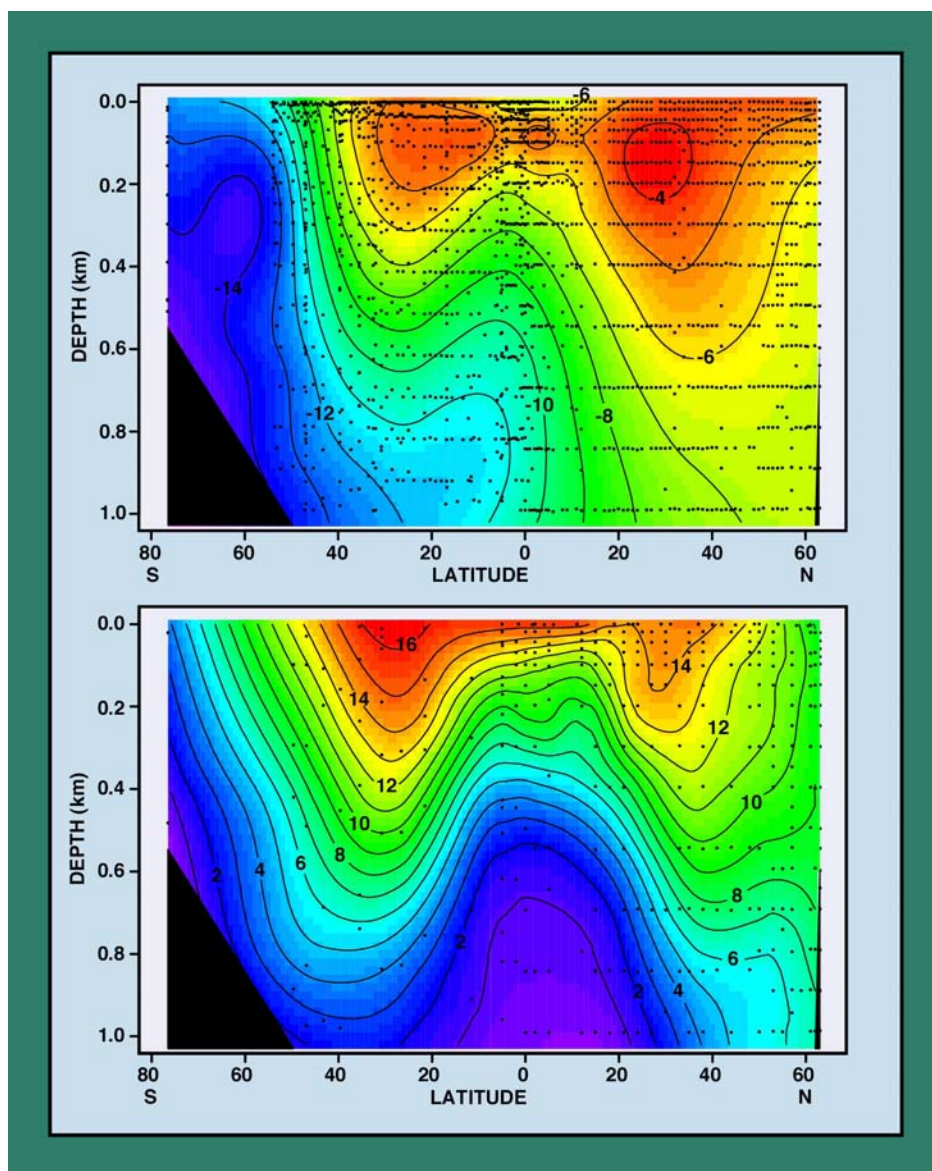


The late Uli Siegenthaler's one dimensional ocean model.¹¹⁵ A well-mixed surface layer is underlain by a "diffusive" interior. The model has only two adjustable parameters: the rate of CO₂ exchange between the atmosphere and surface ocean (E) and the rate of diffusive mixing (K). The values of these two parameters are adjusted until a match is achieved with both the horizontally averaged bomb-test radiocarbon in surface water and the horizontally averaged inventories of bomb-test radiocarbon as determined from measurements on samples collected as part of the GEOSECS survey (1972 to 1978). Shown in the lower panel are examples of depth profiles obtained using different combinations of diffusivities and CO₂ exchange rates. Only the red curve in the middle panel matches the measurements.

was operated by Minze Stuiver at the University of Washington and the other by Gote Ostlund at the University of Miami.

My own contribution involved figuring out how to separate the contributions of bomb ^{14}C and natural ^{14}C .¹¹⁶ To do this I made use of the distribution of tritium in the sea. As the tritium released during H-bomb tests totally swamped that produced by cosmic rays, its distribution as documented by the GEOSECS survey allowed waters in the ocean's interior into which bomb produced ^3H had yet to penetrate to be identified. The ^{14}C in these samples is all natural. Fortunately, enough ^{14}C measurements had been made on surface water samples collected prior to the onset of H-bomb testing that, when they were combined with ^{14}C measurements made on pre-nuclear growth layers in coral heads, the natural ^{14}C to C ratio in surface ocean waters could be reconstructed with reasonable accuracy. By subtracting this natural contribution from the total, the ^{14}C resulting from nuclear tests could be estimated for each of the stations occupied as part of the GEOSECS survey. Having the bomb ^{14}C to C ratio for surface waters and the depth at which the bomb ^{14}C to C ratio went to zero, only one more piece of information was required, namely, the shape of the decline with water depth of the excess bomb ^{14}C . This fell into place when I discovered that, in those portions of the ocean's thermocline into which tritium had yet to penetrate, the ^{14}C to C ratio correlated very nicely with the silica content of the water. Hence, using the silica versus depth profiles measured as part of the GEOSECS survey, I was able to complete the depiction of the distribution in the sea of bomb radiocarbon as of the mid 1970s.

A model of the ocean was necessary in order to recreate the evolution with time of the oceanic bomb ^{14}C distribution. For this purpose, I adopted the one-dimensional model created by the late Uli Siegenthaler of Bern University.¹¹⁵ It involved a thin surface mixed layer underlain by the bulk of the ocean. The radiocarbon tagged inorganic carbon in the surface ocean layer was assumed to be carried into the interior by what Siegenthaler referred to as "eddy diffusion". The advantage of this simple model was that

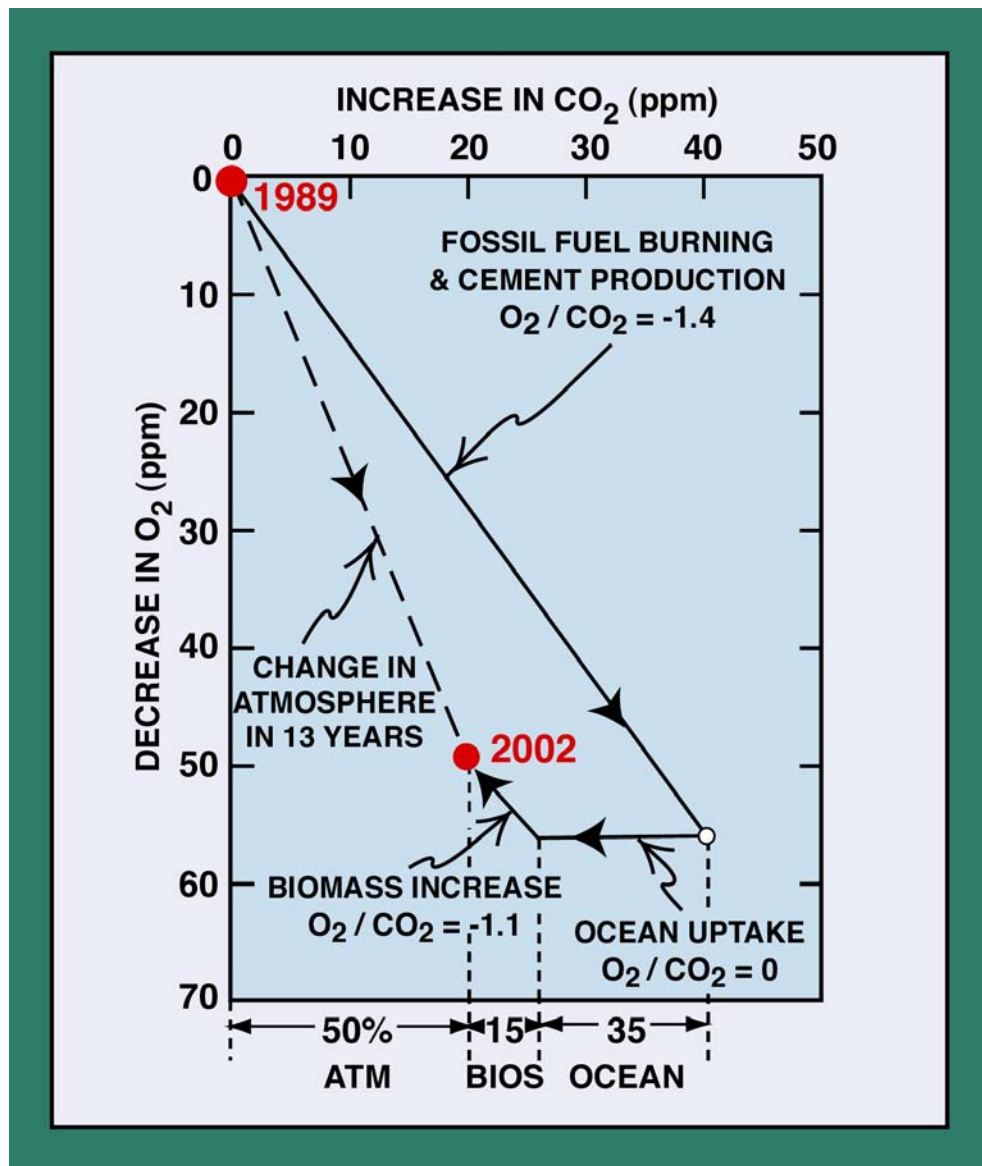


North-south sections of the radiocarbon content of the dissolved inorganic carbon in the upper kilometer of the Atlantic Ocean. A separation has been made between the contributions of natural ^{14}C (upper panel) and bomb test ^{14}C (lower panel). The units are percent differences from the ^{14}C to C ratio in a hypothetical ocean water sample which had achieved equilibrium with the pre-industrial atmosphere. Prior to nuclear testing, the ratio ranged from 5 to 14 percent below the atmosphere equilibrium value. Radiocarbon from nuclear tests has penetrated throughout the upper kilometer producing increases of up to 16 percent in surface waters. Both the distributions of natural and of bomb-test ^{14}C reflect the existence of deep water formation in the northern Atlantic. The sections were provided by Robert Key of Princeton University.¹¹⁷ The measurements were made by accelerator mass spectrometry at Woods Hole Oceanographic Institution. The samples (dots) were collected between 1986 and 1993.

it had only two unknown parameters: the CO_2 exchange rate between air and sea and the rate of eddy diffusion within the body of the ocean. By iteration these two parameters were set to reproduce two observations. One of these observations is the difference between the average bomb $^{14}\text{C}/\text{C}$ ratio in surface ocean waters (as of 1975, i.e., the midpoint of the GEOSECS survey) and that in the atmosphere at that time. The other observation to be fitted was the total number of bomb ^{14}C atoms present in the ocean (as of 1975). While a number of combinations of the model's two adjustable parameters yielded a match to either one of these two observations, only one set yielded a simultaneous match to both. Having determined these two parameters, the model could then be used to calculate the uptake of fossil fuel CO_2 by the sea.

One important difference between the uptake of bomb-radiocarbon tagged CO_2 and that of fossil fuel CO_2 must be mentioned. While, as of 1975, the surface ocean had taken up about 90 percent of its capacity of excess fossil-fuel-derived CO_2 , it had only taken up about 40 percent of its capacity for bomb-radiocarbon tagged CO_2 . The reason for this difference is that isotopic equilibration with the atmosphere requires that all three of the inorganic carbon pools (i.e., CO_2 , $\text{CO}_3^{=}$ and HCO_3^{-}) in sea water achieve ^{14}C to C ratios equal to that in atmospheric CO_2 . By contrast, for surface sea water to achieve chemical equilibrium with the atmosphere, only the $\text{CO}_3^{=}$ concentration need adjust. This relates to the requirement that the product of CO_2 and $\text{CO}_3^{=}$ concentration remain nearly constant. The bottom line is that, while it takes about ten years for a 40-meter thick surface ocean mixed layer to come to isotopic equilibrium with the atmosphere's $^{14}\text{CO}_2$, it takes only about one year for it to achieve chemical equilibrium with the atmosphere's CO_2 . The factor of ten relates to the ratio of the ΣCO_2 concentration (~ 2000 micromoles/liter) to the $\text{CO}_3^{=}$ concentration (~ 200 micromoles/liter) in surface sea water.

Having shown that entry into the sea poses only a minor resistance to uptake by the sea of fossil fuel CO_2 , let us turn our attention to the vertical mixing which constitutes the major resistance. The distribution of bomb radiocarbon in the body of the ocean as of



The red dots indicate the observed change in the content of CO₂ and of O₂ in the atmosphere from 1989 to 2002. During this 13-year period, the atmosphere's CO₂ content increased by 19 parts per million and its O₂ content decreased by 49 parts per million. Had there been no interaction with ocean or with the terrestrial biosphere, based on the amount of fossil fuel burned, the atmosphere should have increased by 40 parts per million in CO₂ and decreased by 56 parts per million in O₂ (see white dot). In order to explain the difference between the expected and observed changes, about 35 percent of the CO₂ emitted must have been taken up by the ocean and about 15 percent by the terrestrial biosphere.

the time of the GEOSECS survey provides a measure of the fraction of the volume made available for uptake of fossil fuel CO₂ on the time scale of about 12 years (1963 to 1975). Expressed as the mean penetration depth, the result is 350 meters. As the mean depth of the ocean is 3800 meters, this represents about 9 percent of the sea's volume. This number can't, however, be applied directly to fossil fuel CO₂ molecules because as of 1975, their average age (i.e., time elapsed since birth by fossil fuel burning) was close to 30 years. Hence, fossil fuel CO₂ molecules must on the average have penetrated deeper into the sea than bomb ¹⁴C atoms. If Siegenthaler's one-dimensional model is used to calculate the mean penetration depth (z) of fossil fuel CO₂, it turns out to be:

$$z = 350 \sqrt{\frac{30}{12}} = 550 \text{ meters}$$

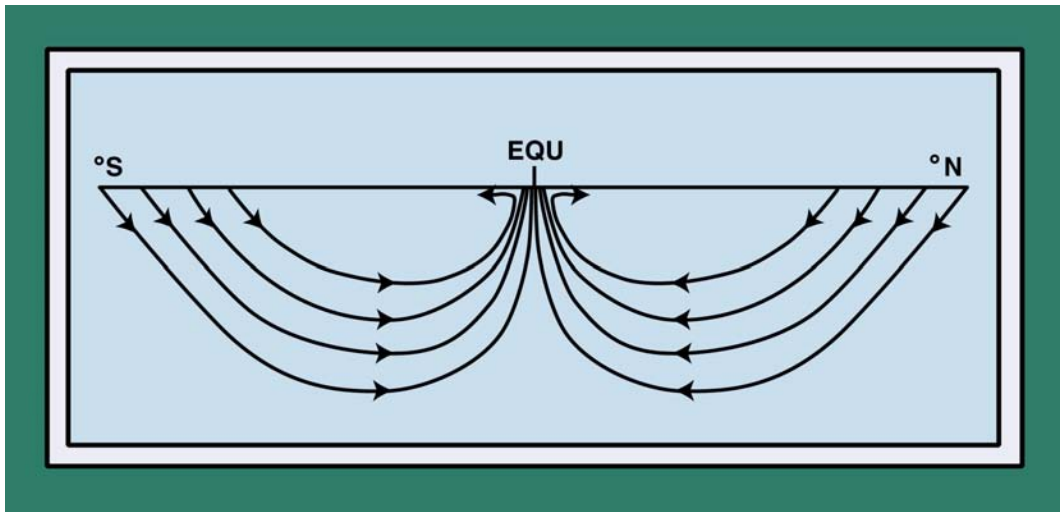
or 15 percent of the ocean's volume. As the average age of fossil fuel CO₂ molecules has remained close to 30 years, this fraction has also remained nearly the same.

But is there any justification for the assumption that the penetration into the ocean's interior increases as the square root of the time. After all, one might guess that Siegenthaler's reason for opting for an eddy-diffusive ocean interior had more to do with the simplicity of its mathematical expression than with how mixing actually takes place. In his defense, it turns out that the diffusion function yields a ventilation time for the deep sea comparable to that obtained from natural radiocarbon measurements. In Siegenthaler's diffusive ocean, the time (t) to mix to a depth of 3800 meters would be:

$$t = 12 \left[\frac{3800}{350} \right]^2 = 1120 \text{ years}$$

While a bit larger than the 900-year ventilation time of the deep sea established by radiocarbon measurements, it certainly is in the right ball park.

A cross-check on the result obtained using the simple Siegenthaler model was provided by Ralph Keeling (son of Charles David). While a graduate student at Harvard, Ralph developed a means of measuring the ratio of O₂ to N₂ in air samples with the ultra high accuracy necessary to detect the tiny decrease in O₂ resulting from its consumption

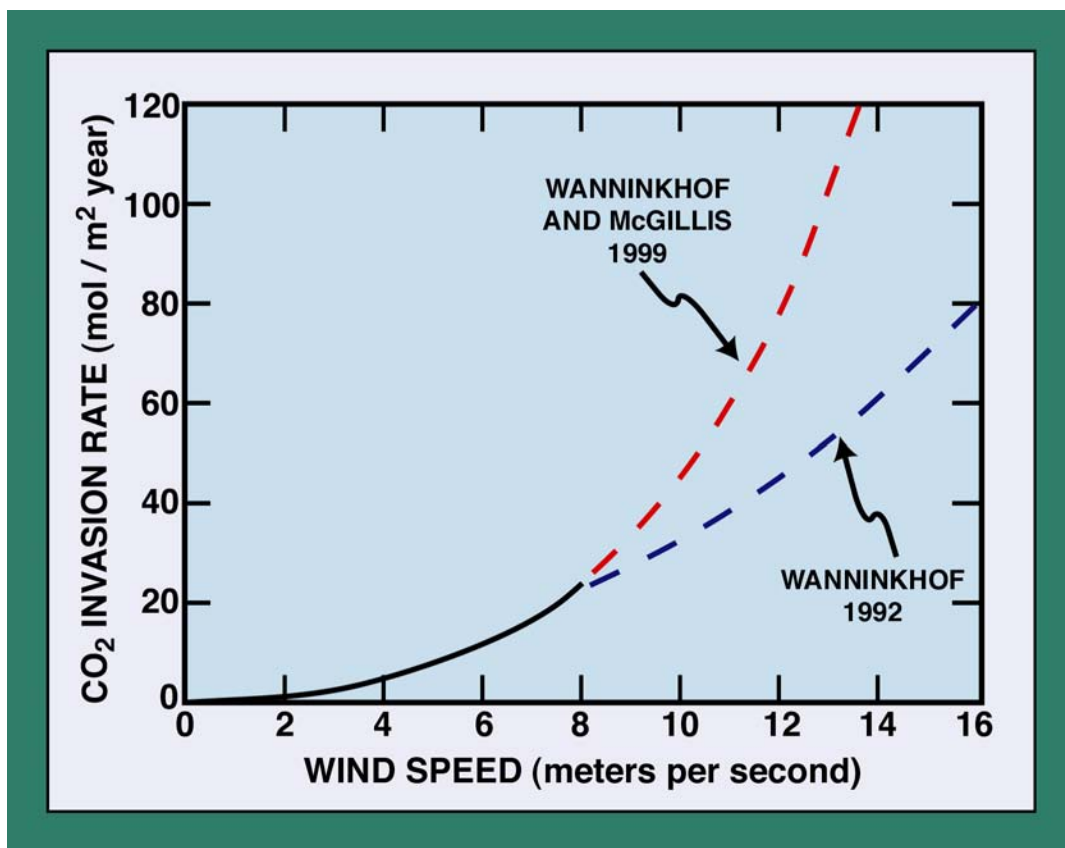


Idealized diagram showing how the thermocline of the Pacific Ocean is “ventilated.” In the late winter, surface waters dense enough to sink and flow along a series of isopycnals (i.e., horizons of constant density) are formed. These horizons deepen and then rise toward the surface at the equator. Upon reaching the surface, the upwelled water diverges: part moving to the north and part moving to the south.

as the result of the burning of fossil fuels. Since 1989, he has monitored both the decline in O_2 and the rise in CO_2 in the air blowing in from the Pacific Ocean to the pier at Scripps Oceanographic in La Jolla, California. He compared the measured changes with those predicted if the atmospheres were a “closed” reservoir (i.e., it did not communicate with the ocean or terrestrial biosphere) and found that the O_2 had not dropped as much and the CO_2 not risen as much as would be expected.¹¹⁸ Based on a simple graphical analysis, he was able to not only confirm that roughly half of the excess CO_2 was being removed to the ocean and terrestrial biosphere, but also the relative contributions of these two reservoirs to the uptake of CO_2 .

The real ocean operates in a totally different manner than Siegenthaler’s one-dimensional ocean. As we have seen, deep water descends from two high latitude locations and spreads laterally displacing upward the pre-existing deep water. The situation in the thermocline is much the same. Waters cooled during winter months slide down into the ocean’s interior along horizons of constant density displacing the resident water. As we discussed in the first chapter, this renewal is driven by the downward mixing of heat from the warm surface. Hence eddy diffusion plays a role in the real ocean. But, it occurs at an order of magnitude slower rate than that calculated from the distribution of bomb ^{14}C using Siegenthaler’s one-dimensional model. One might say that the real ocean is far more “advective” and far less “diffusive” than Siegenthaler’s ocean.

Because of the complexity of mixing in the real ocean, the only way to adequately represent the transport of fossil fuel CO_2 into its interior is through the use of simulations carried out using state-of-the-art computers. In these simulations the ocean is divided, in egg-crate fashion, into thousands of boxes. Movement of water through this three-dimensional matrix is driven by density gradients generated by differing surface water temperatures and salt contents and perturbed by winds and tides. However, not all the processes involved in transporting water from one place to another in these simulations can be based on the laws physics. For example, parameterized eddy diffusivities both in



The rate of invasion of CO₂ into the ocean depends strongly on wind speed. The surface drag induced as air passes over the sea surface works to reduce the resistance to the transfer of gases through the upper few tens of microns of water. While for low wind speeds the dependence has been reasonably well established, that for wind speeds higher than the ocean's average (i.e., 8 meters per second) remains highly uncertain. The problem is that the oceanic conditions associated with these high winds cannot be reproduced in the laboratory. Further, only very few reliable measurements have been made at sea. In 1999,¹¹⁹ Rik Wanninkhof of NOAA, an expert in this area, revised his 1992¹²⁰ estimate that the invasion rate followed the square of the wind velocity and concluded that it more likely followed the cube of wind velocity. The invasion rate scale is for a CO₂ content of 370 ppm.

the horizontal and vertical must be employed. Theory backed by purposeful injections of an SF₆ tracer suggests that the rate of mixing across horizons of constant density is inversely proportional to the gradient in density. However, in situ tracer experiments also show that interactions with topographic features exert a strong influence on mixing.

The dependence of air-sea CO₂ exchange on wind speed must also be introduced into these models. Unlike the situation for Siegenthaler's one-dimensional model where only a single CO₂ exchange rate is required, in 3-D models the large range in wind speed from region to region and season to season must be taken into account. Although information on the wind speed dependence of CO₂ exchange rates has been obtained based on experiments conducted in wind tunnels and on tracer SF₆ injections conducted in lakes and estuaries, uncertainties in the shape of this dependence remain. The biggest of these is that associated with high wind speeds. Spray and bubbles associated with white caps cannot be duplicated in the lab. Further, reliable observations at sea under stormy conditions prove to be extremely difficult to conduct.¹¹⁹ The challenge of obtaining reliable measurements at high wind speeds has yet to be fully met.

Thus, although 3-D simulations constitute an absolutely essential step forward, at their present state of development, the answers they yield regarding uptake of fossil fuel CO₂ are perhaps no more reliable than that obtained using Siegenthaler's ¹⁴C-calibrated 1-D model. That this is the case becomes apparent when the distributions of bomb radiocarbon generated by various of these ocean models are compared one with another and with observation. The differences remain unsatisfactorily large. It is encouraging, however, that the 3-D simulations yield CO₂ uptakes ranging around that given by Siegenthaler's 1-D model.

Fortunately, this situation is rapidly improving. Modelers are now attempting to adjust their simulations so that they achieve a better match with the observed distributions of both bomb-produced and cosmic ray-produced radiocarbon as mapped by the GEOSECS survey (1970s) and as mapped by the more recent WOCE survey (1990s).

P _{CO₂} 10 ⁻⁶ atm	NCD 10 ⁻⁶ mol/kg	CO ₂ 10 ⁻⁶ mol/kg	HCO ₃ ⁻ 10 ⁻⁶ mol/kg	CO ₃ ⁼ 10 ⁻⁶ mol/kg	Σ CO ₂ 10 ⁻⁶ mol/kg	B(OH) ₄ ⁻ 10 ⁻⁶ mol/kg	B(OH) ₃ 10 ⁻⁶ mol/kg	OH ⁻ 10 ⁻⁶ mol/kg	ΔΣ CO ₂ [*] 10 ⁻⁶ mol/kg	ΔΣ CO ₂ ^{**} 10 ⁻⁶ mol/kg
280	2216.0	9.6	1704.8	205.9	1920.3	95.0	315.6	4.4	0.0	—
360	2216.0	12.3	1781.8	175.0	1969.1	80.7	329.9	3.6	48.8	48.8
440	2216.0	15.1	1838.1	152.3	2005.5	70.2	340.4	3.0	85.2	36.4
520	2216.0	17.8	1881.1	135.0	2033.9	62.3	348.3	2.6	113.6	28.4
600	2216.0	20.6	1915.2	121.3	2057.0	55.9	354.7	2.3	136.7	23.1
680	2216.0	23.3	1942.9	110.1	2076.3	50.8	359.8	2.1	156.0	19.3
760	2216.0	26.1	1965.8	100.9	2092.8	46.5	364.1	1.9	172.5	16.5
840	2216.0	28.8	1985.2	93.1	2107.1	42.9	367.7	1.7	186.8	14.3

* Change in dissolved inorganic carbon concentration from that at equilibrium with 280 x 10⁻⁶atm atmospheric CO₂ partial pressure

** Change in equilibrium dissolved inorganic carbon concentration resulting from an 80 x 10⁻⁶atm rise in atmospheric CO₂ partial pressure

Change in the fossil fuel CO₂ uptake capacity by surface ocean water with increasing atmospheric CO₂ content. The uptake capacity for the 80x10⁻⁶atm rise from 280 to 360x10⁻⁶atm is 3.4 times larger than that for the 80x10⁻⁶atm rise from 760 to 840x10⁻⁶atm. This drop reflects the fact that the CO₃⁼ and B(OH)₄⁻ ion concentrations at 840x10⁻⁶atm are only about 45 percent those at 280x10⁻⁶atm.

They also strive to replicate the even more detailed surveys of the manmade CFCs in the upper ocean. But even when these adjustments have been satisfactorily accomplished, an act of faith will be required. While the man-made tracers tell us what goes on on the time scale of decades, our interest extends to time scales of a century or more.

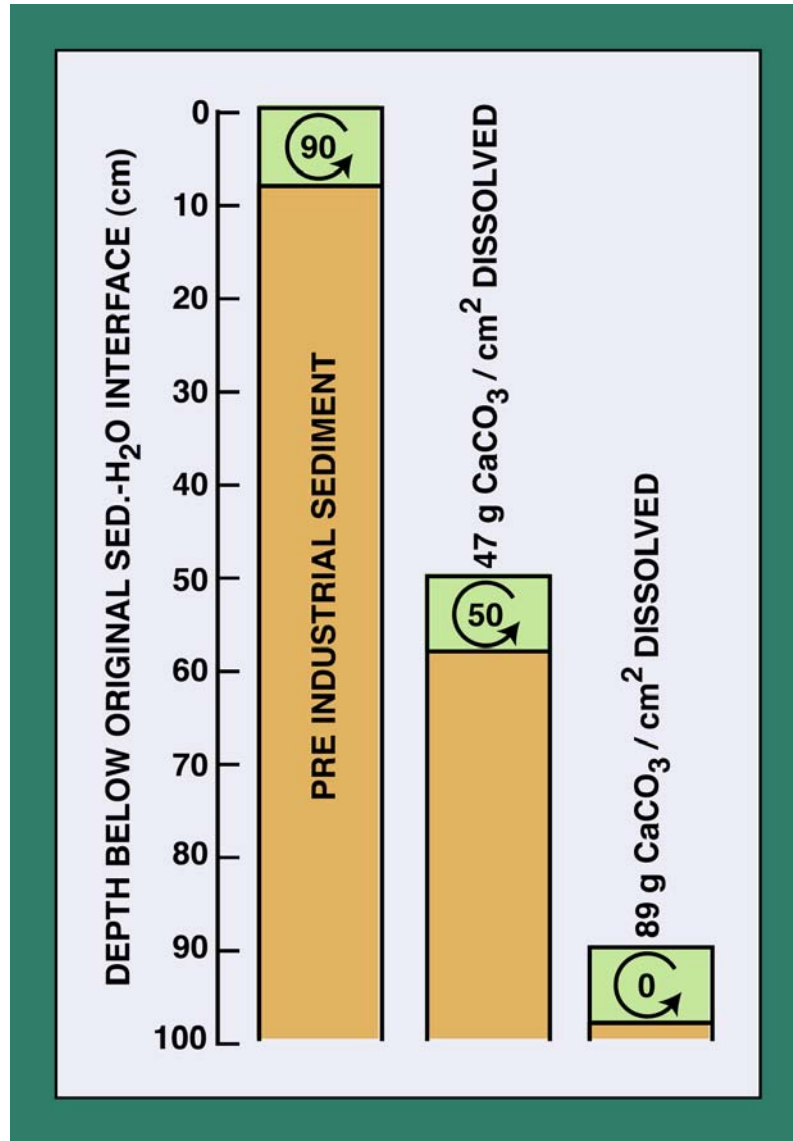
Clearly, it is important to project how the split of fossil fuel CO₂ between atmosphere and ocean will evolve. In this regard, there are two important considerations. First, were the annual percent age increase in emissions to decline, the mean age of CO₂ molecules generated by fossil fuel burning would slowly increase. This will allow the excess CO₂ to penetrate into a greater fraction of the sea's interior. Second, because the CO₃⁼ and B(OH)₄⁻ ions, which are primarily responsible for the uptake of fossil fuel CO₂, are being consumed, uptake by surface waters will decline.

If, for example, CO₂ emissions were stopped, then the mean age of fossil fuel-derived CO₂ molecules would increase by one year for each passing year. After 50 years, their mean age would be 80 years instead of 30 years. If the mean penetration depth (z) is assumed to increase in proportion to the square root of time, then it would become:

$$z = 550 \sqrt{\frac{80}{30}} = 900 \text{ meters}$$

Thus, the fraction of the ocean volume taking up its share of CO₂ would increase from about 15 to about 25 percent. As CO₂ emissions to the atmosphere will certainly continue over the next 50 years, the 25 percent figure surely represents an upper limit.

Assessment of the impact of the decrease of CO₃⁼ and B(OH)₄⁻ ion concentrations requires the use of models, for the result depends on details of the mixing scheme adopted. An upper bound on the magnitude of the decrease would be obtained using the simple Siegenthaler model. In such a model the water diffusing upward into the surface mixed layer is depleted in CO₃⁼ and B(OH)₄⁻ by nearly as much as surface water. A lower bound would be obtained using the simple two box ocean we employed to explore the Harvardton Bear scenario. In such a model, the water which replaces that in the surface



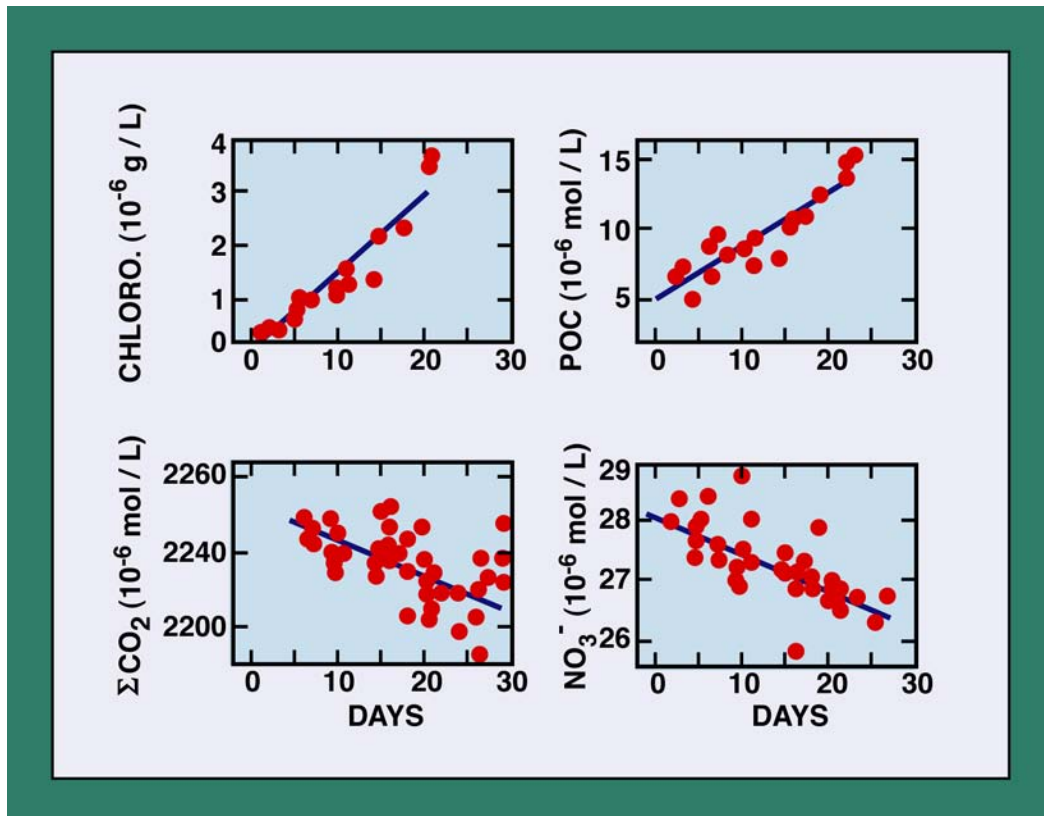
As the carbonate ion concentration in the deep ocean decreases with the addition of fossil fuel CO₂, calcite-rich sediments currently above the saturation horizon will begin to dissolve. Shown here is an example of a sediment originally 90 percent CaCO₃ (dry density 1 g/cm³). As the calcite in the 8 cm-thick bioturbated zone dissolves, the worms will exhume underlying sediment. The clay-contained in the exhumed material is left behind and thereby gradually lowers the calcite content of the bioturbated zone. This continues until its calcite content is reduced to zero. At that point, calcite dissolution will cease. The capacity for CO₂ neutralization provided by dissolution of sea floor CaCO₃ is comparable to that provided by all the CO₃⁼ and B(OH)₄⁻ dissolved in the deep sea.¹²¹ The difference is that while neutralization by CO₃⁼ and B(OH)₄⁻ will take place over centuries, dissolution of sediment CaCO₃ will take place over millennia.

layer comes from a well-mixed reservoir constituting 95 or so percent of the ocean's volume. Hence the replacement water would have as yet experienced only a small depletion in $\text{CO}_3^{=}$ and B(OH)_4^- ion concentrations.

The real ocean lies somewhere in between these two extremes. Surface waters are carried to the winter regions of the ocean where they are cooled and sent down into the body of the ocean along a series of vertically stacked density horizons. The water residing in the thermocline portion of this layer cake structure upwells in the equatorial zone. While early-on the upwelling water would be relatively free of fossil-fuel CO_2 , as time went on and the waters had been round the upper ocean circuit several times, their $\text{CO}_3^{=}$ and B(OH)_4^- ion concentrations would have been depleted. The extent of uptake depends strongly on the $\text{CO}_3^{=}$ and B(OH)_4^- concentrations in the replacement water. Were, for example, the atmosphere to achieve a CO_2 concentration of 840 ppm, it would make a very large difference whether the surface renewal was by water largely free of fossil fuel CO_2 or by water that had already largely equilibrated with atmospheric CO_2 .

In all models, the implicit assumption is made that the physical operation of the ocean will remain unchanged. But, clearly, as the surface ocean warms as the result of the ongoing buildup of greenhouse gases in the atmosphere, the gradient of density with depth will steepen. As a consequence, rate of mixing between surface and subsurface waters will be reduced. Currently, there is no reliable way to assess the magnitude of this reduction.

One thing that is needed in this connection is some measurement scheme that will constrain the ongoing rate of this slowdown. Bern University's Fortunat Joos suggested one possibility.¹²² It involves measurements of the secular decline in the O_2 gas content of thermocline waters. At steady state, the O_2 content of any subsurface water reflects a balance between O_2 supply by descending winter water and O_2 loss as the result of respiration. Were the ventilation rate to slow, but the supply of organic matter raining down from the surface to remain the same, then the O_2 content of the resident



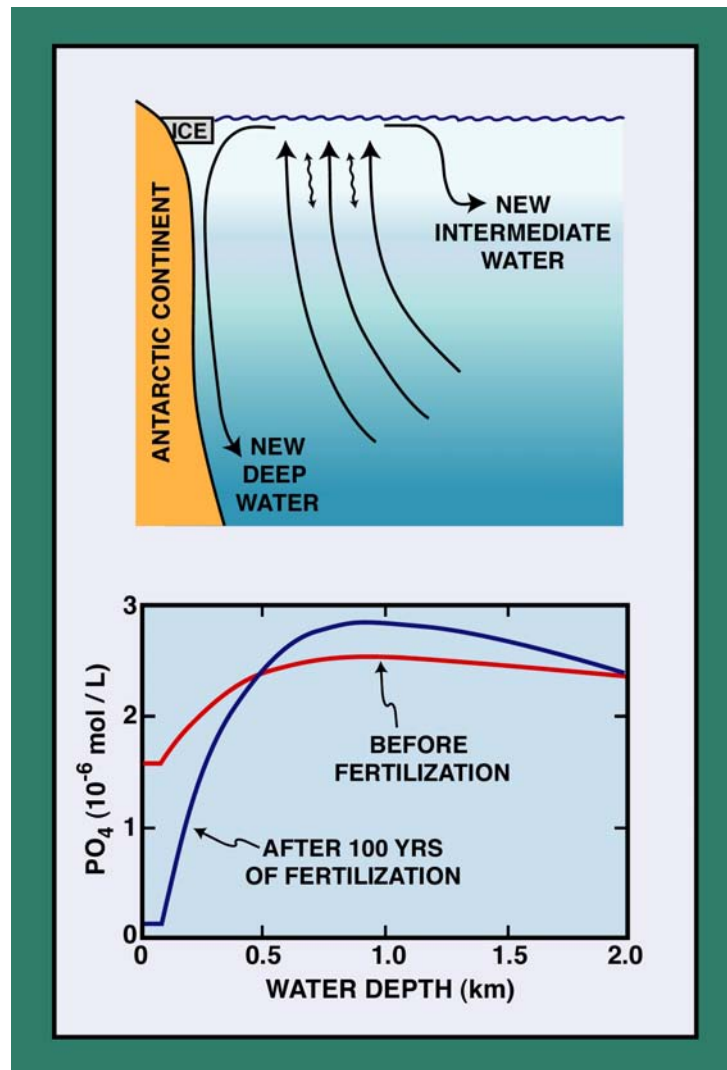
Response of a patch of Southern Ocean surface water (66°S , 172°E) to the addition of iron. As can be seen during the 30-day period following the onset of “fertilization,” the chlorophyll and particulate organic carbon concentrations steadily increased and the dissolved inorganic carbon and nitrate contents steadily decreased.

thermocline water would decline. Repeat surveys carried out in various parts of the ocean's thermocline over the past few decades suggest that such a decline is already underway. If so, then the 0.8°C or so warming of the surface ocean which has taken place over the last century has already impacted ocean mixing. Clearly, a high priority will be continued monitoring the thermocline's O₂ inventory.

Summarizing: of the three factors influencing the split of fossil fuel CO₂ between the atmosphere and ocean, the decrease in CO₃⁼ and B(OH)₄⁻ and the global warming-induced slowdown in ventilation will lead to a decrease in the ocean's contribution. While the increase in the average age of fossil fuel CO₂ molecules will tend to counter this decrease, it is likely to be much less important. Hence, as time passes, fraction of CO₂ emissions remaining in the atmosphere is likely to increase.

On very long timescales, dissolution of CaCO₃ stored in deep sea sediments will supplement the neutralization of fossil fuel CO₂ in the sea. The gradual buildup of CO₂ in deep sea will reduce the carbonate ion concentration and hence cause the saturation horizon to become ever shallower. This will lead to the dissolution of CaCO₃ stored in the uppermost sediment. The amount of CaCO₃ available for dissolution is comparable to combined inventory of CO₃⁼ and B(OH)₄⁻ in the deep sea. However, as dissolution will proceed only very slowly, utilization of this reservoir will require at least a millennium.¹²¹

A variety of proposals have been put forth to hasten the uptake of CO₂ by the ocean. One approach involves strengthening the ocean's biological pump. As it would be prohibitively expensive (and wasteful) to add phosphorous to the ocean, attention has been focused on those regions of the surface ocean where phosphate (and nitrate) go unused. In particular, because of its large areal extent, the focus is on the Southern Ocean. In situ experiments demonstrate that by adding iron the CO₂ partial pressure can be drawn down.¹²³ Would it be feasible to iron fertilize the surface waters of the entire Southern Ocean in such a way that their CO₂ partial pressure would be maintained at a



Simple box model designed to assess the response of the atmosphere's CO_2 content to continuous iron fertilization.¹²⁴ In the model, deep waters upwell to the surface. Superimposed on this upwelling is vertical mixing. These rates are set to yield a match to the GEOSECS radiocarbon results. The upwelled water splits: part flows northward and serves as the source for new intermediate water and part flows southward and sinks to the abyss as new bottom water. The fertilization is assumed to reduce the phosphate content from 1.6×10^{-6} moles per liter to a near zero value. The distribution of phosphate with water depth in the upwelling plume is shown in the lower panel both prior to fertilization and after 100 years of fertilization. The model suggests that were the atmosphere's CO_2 content to rise to 800 ppm during the next 100 years without iron fertilization, with full Southern Ocean fertilization, it would rise to 725 ppm. Further, if fertilization were to be suspended, the CO_2 reduction would largely be lost.

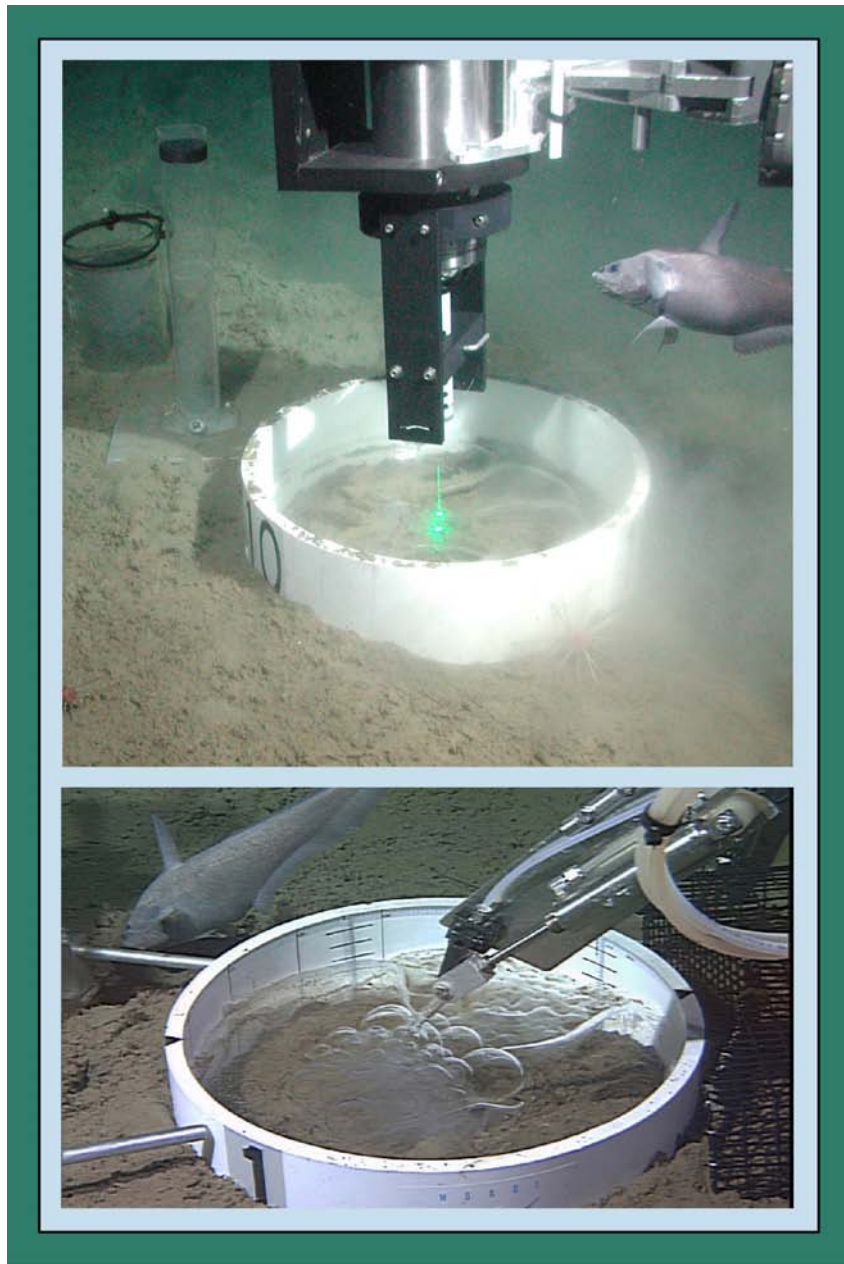
substantially lower value than today's? If so, by how much would the climb in atmospheric CO₂ content be reduced? Although at present these questions cannot be adequately answered, model simulations suggest that the reduction would be modest and were fertilization to be stopped, whatever CO₂ reduction had been gained would subsequently be largely lost.¹²⁴ Also, there is a fear that the increased rate of rain of organic matter generated by fertilization would cause parts of the thermocline to go anoxic with serious repercussions to the Southern Ocean ecosystems.

Another means by which the CO₂ buildup in the atmosphere might be reduced involves purposeful capture and burial of the CO₂ released by the burning of fossil fuels.¹²⁵ Some of the capture would be done at the sites of electrical power plants. However, as two thirds of the current release of CO₂ is from small sources (i.e., autos, homes...), recapture of CO₂ from the atmosphere would have to be carried out as well. At first thought, it might seem that removal of CO₂ from the atmosphere is impractical. Not only is it feasible, but the facilities required to do this would be 25 to 50 times smaller than the rotors required to produce an equivalent amount of wind power!

Once captured, the CO₂ would be liquefied and stored. Currently a number of storage options are being explored. These include the deep sea, lakes beneath the Antarctic ice cap, salty continental aquifers and mineralization by reaction with magnesium extracted from ultrabasic rock ($\text{CO}_2 + \text{MgO} \rightarrow \text{MgCO}_3$).

Of these storage options, only that involving the deep sea will be discussed here. The idea would be to short circuit access to those parts of the ocean which currently lie beyond the reach of mixing. As we have seen, 85 or so percent of the ocean currently falls into this category. In the absence of short-circuiting, many centuries will pass before these regions take up their share of fossil-fuel CO₂.

In the upper ocean liquid CO₂ is less dense than sea water. Hence, in order to insure that the CO₂ would not bubble back to the surface, disposal in these waters would require elaborate networks of dispersers. However, as liquid CO₂ is more compressible



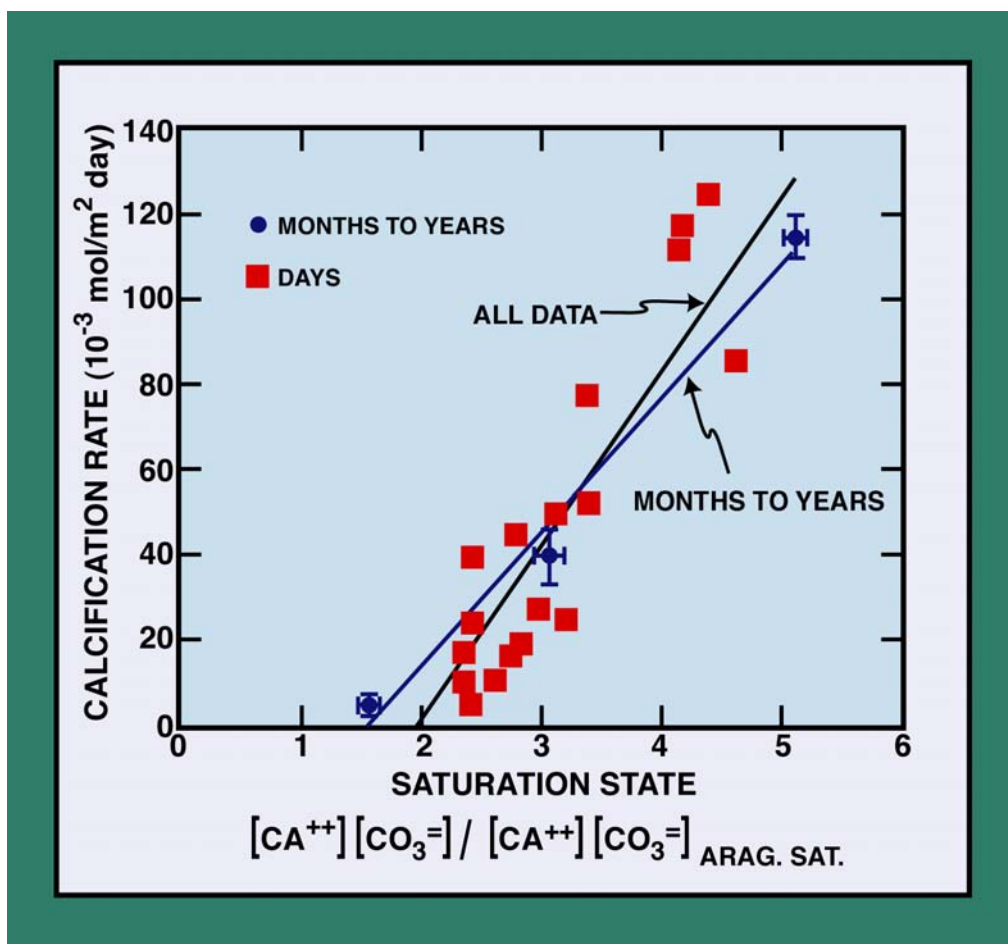
Liquid CO₂ injections into containers on the sea floor carried out by a robotic vehicle designed and operated by the Monterey Bay Aquarium Research Institute (MBARI) in Moss Landing, California. These experiments were conceived by MBARI's Peter Brewer. As can be seen, the local inhabitants keep a close eye on the intruders.

that sea water, at depths greater than 3500 meters the situation reverses.¹²⁶ Below this depth, liquid CO₂ is more dense than sea water and therefore if injected into the abyss, it would sink to the sea floor.

Experiments conducted by Peter Brewer of the Monterey Bay Research Institute reveal a further twist. Under the conditions where liquid CO₂ is more dense than sea water, a solid made of carbon dioxide and water spontaneously forms (7H₂O + CO₂). Chemists refer to this solid as a clathrate. Employing a robotic submersible, Brewer conducted a series of experiments at a depth of 3500 meters off Monterey, California. Liquid CO₂ injected into a clear glass cylinder sank to its bottom displacing the resident sea water. Initially the liquid CO₂ occupied about one third of the cylinder's volume. Once in place, the liquid CO₂ rapidly reacted with the overlying sea water forming a clathrate. The clathrate sank to the bottom of the cylinder, clearly demonstrating that it was more dense than liquid CO₂. As there are 7 water molecules for every CO₂ molecule in the clathrate, it soon filled the entire cylinder and began to overflow and sink beyond the camera's view.

In this way, Brewer showed that CO₂ injected from a long pipe into the deep sea would form a clathrate which would sink to the sea floor. During the formation of the clathrate, heat and salt would be released to the surrounding water. The heat would be generated as the result of the reaction of liquid carbon dioxide with sea water. The salt would be excluded when the water was taken up by the clathrate. It is important to evaluate the change in the buoyancy of the surrounding water resulting from the gain of heat and salt. Would the density increase associated with the addition of salt be larger than the density decrease associated with the addition of heat? At this writing, the magnitude of the heat release remains too uncertain to conclude whether the water surrounding the clathrate would tend to rise or to hug the bottom.

Of course, as will be the case for any CO₂ disposal option, the environmental consequences of ocean disposal will have to be evaluated. There is no free lunch. No



Calcification rate in Biosphere 2's tropical lagoon as a function of the degree of super-saturation of its water with respect to the mineral aragonite.¹²⁷ By chemical additions the concentrations of Ca^{++} and $CO_3^{=}$ ions were adjusted to produce degrees of super-saturation ranging from the high values which characterized glacial time to the low values which will be achieved if CO_2 emissions continue along a business-as-usual track. Although corals are present in this lagoon, aragonite production is mainly by calcareous algae. These experiments were conducted by Columbia University's Chris Langdon. The conclusion is that rising atmospheric CO_2 will reduce the growth rate of corals, adding yet another element of stress in their battle for survival.

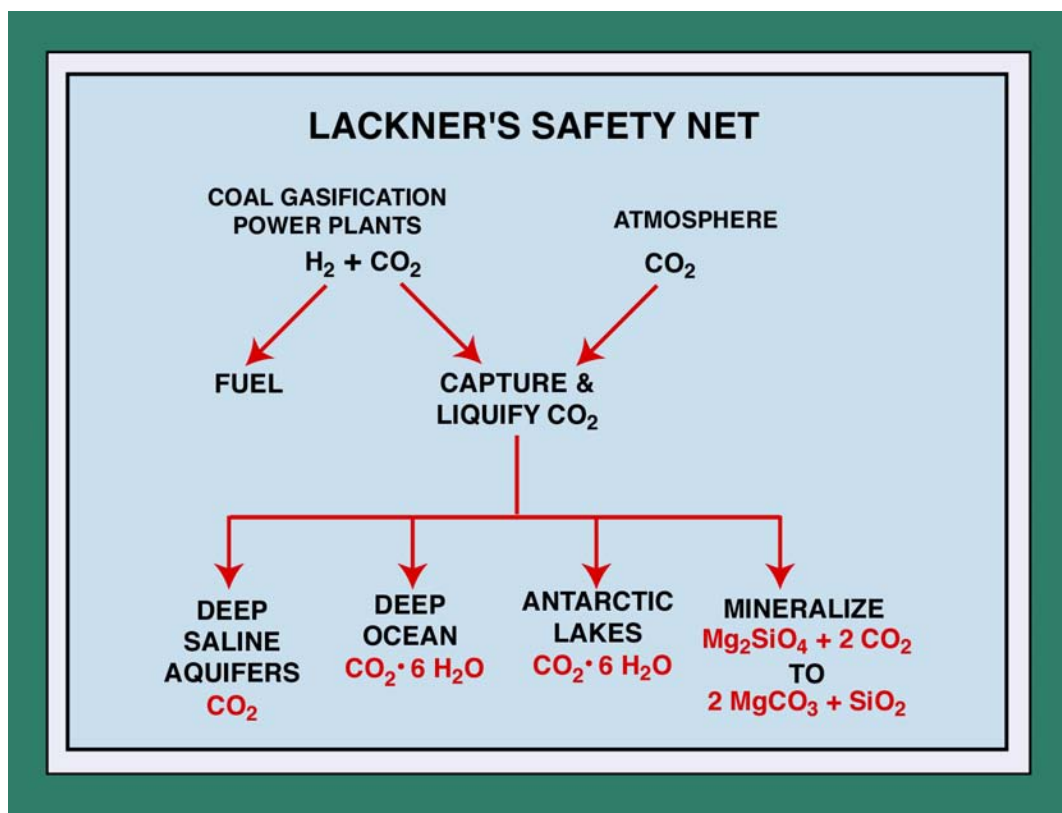
matter how the disposal of the captured CO₂ is carried out, there are bound to be negative environmental impacts. In the case of ocean disposal, the concern will be focused on the ecosystems of the abyss. Once the CO₂ injected into the deep sea had mixed into the bulk of the abyssal water, it would be largely neutralized by reaction with the resident carbonate and borate ions. As is the case for surface waters and the pH drop would be modest. Hence once dispersed, it would produce little environmental damage.

But, the CO₂ would not be immediately dispersed. Rather, it would initially pile up on the sea floor in solid form.¹²⁶ These clathrates would slowly dissolve and the CO₂ would be carried away from the dump site by bottom currents. As the rates at which the clathrates would dissolve and the rates of dispersal of the waters into which the CO₂ was added will depend on the details of the local situation, pilot injections would have to be conducted at each prospective dump site and the dispersal of the released CO₂ monitored.

Clearly, the worms and other critters which inhabit the sea floor at the disposal sites would be destroyed. But as the areas so impacted would constitute only a tiny fraction of the sea floor, the result would be equivalent to what happens when we build roads, buildings and parking lots. Rather, the concern will be with the fish which inhabit the abyssal ocean. How will they react when they encounter the CO₂-rich halos surrounding the clathrate piles or even the clathrates themselves? Again, these are questions which can only be answered by photographic monitoring of pilot disposal experiments.

It is my hope that these pilot experiments will be conducted despite the existing strong opposition to ocean disposal. As global warming eclipses all other environmental problems, we must put aside our prejudices and objectively explore all available options. Only after each has been carefully studied should decisions be made regarding the mode of disposal of the CO₂ we capture.

When considering ocean disposal, it is appropriate to consider the consequences to biota were the CO₂ to be released to the atmosphere instead of being short-circuited to



Klaus Lackner has the vision that the CO₂ produced by fossil fuel burning be captured and stored. In the case of large electrical power facilities, the CO₂ would be captured on site. However, such facilities currently account for only about one third of the CO₂ produced. The other two thirds of the CO₂ comes from small units (automobiles, airplanes, home-heating units...) for which CO₂ capture at its source is impractical. Lackner proposes that it be recaptured from the atmosphere. In either case, the captured CO₂ would be liquefied (at 14 atmosphere's pressure) and piped to a storage site. Four storage possibilities exist: 1) as liquid CO₂ in the pores of deep continental aquifers, 2) in the deep sea initially as a solid CO₂ clathrate, 3) in lakes beneath the Antarctic ice cap as CO₂ clathrates and 4) as the mineral, MgCO₃, using MgO dissolved olivine-bearing rocks.

the deep sea. Although no “hot” spots would be created by the entry of this CO₂ into the surface sea, its buildup would impact organisms which precipitate CaCO₃. Experiments conducted in aquaria and in the Biosphere 2 mesocosm clearly demonstrate that reductions in carbonate ion concentration associated with the rise in atmospheric CO₂ reduce the rate of calcification by these organisms. Experiments conducted in Biosphere 2’s indoor coral lagoon show the rate of CaCO₃ production by the lagoon community (dominated by coralline algae) undergoes an order of magnitude decrease when the CO₂ partial pressure of its waters is raised from 200 μ atm to 750 μ atm.¹²⁷ Interestingly, this change in CO₂ does not lead to a significant change in the aggregate rate of lagoon photosynthesis. In order to demonstrate the impact of carbonate ion concentration on the growth rate of individual corals, Langdon placed corallites mounted on clear plastic plates in aquaria filled with Biosphere 2’s sea water. He manipulated the CO₂ content of the aquaria water (and hence its carbonate ion concentration) and using a laser device capable of ± 3 micrometer precision, he was able to measure the corallite’s weekly growth. Langdon found that, as is the case for the lagoon assemblage, the growth rate of corallites slowed as carbonate ion concentration was reduced.

Coral reefs are the ocean’s equivalent of tropical forests in that they house a major fraction of ocean’s biodiversity. Most of the world’s coral reefs are being degraded. Over-fishing, algal proliferation due to the release of nitrate and phosphate from adjacent lands and reductions in water clarity are chief among man’s insults. These stresses appear to have made coral reefs more sensitive to temperature extremes. During hot periods, zooxanthellae which inhabit the coral’s polyps flee carrying with them not only the coral’s color but also its food source. The resulting “bleaching” events have become the battle cry of environmentalists intent on preserving the world’s reef communities.

It is in this context that the CO₂-driven decrease of carbonate ion in the surface ocean must be viewed. Because of it a deteriorating situation is being worsened. Hence, were our only options to add CO₂ to the atmosphere on the one hand or to the abyssal sea on the other, to me at least, the deep sea option would be far less objectionable. Of course, as other options are available, we may never be faced with a choice between these two.

Supplementary Readings

- 1) Stommel, H., “The Gulf Stream: A Physical and Dynamical Description”, 1965, University of California Press, 248 pp. The Gulf Stream transports warm and salty water to the northern Atlantic. Hence it constitutes the upper limb of the Atlantic’s conveyor circulation. The late Henry Stommel, widely recognized as dean among physical oceanographers, deals not only with the characteristics of this stream but also the development of ideas and explorations extending back to 1700 AD. An excellent read in connection with Chapter 1.
- 2) Imbrie J. and Imbrie, K.P., “Ice Ages: Solving the Mystery”, 1979 (reissued in soft cover in 1986), Harvard Press, 224 pp. This book deals with pacing of glaciation by cycles in the Earth’s orbit. Each chapter deals with a step in the evolution of observation and thought with regard to this pacing. It brings the reader up to the time just preceding the discovery of CO₂ changes and of abrupt reorganizations of the climate system. It’s very well written. No one has done a better job of explaining the Milankovich hypothesis.
- 3) Broecker, W.S., “The Glacial World According to Wally”, 2002 (third revised edition), 346 pp. A self-published book which deals with the proxies used to reconstruct the key aspects of the glacial environment, with methods employed to establish an absolute chronology for events which transpired during the Late Quaternary and with the record itself. In a sense, it covers in much greater depth the material in Chapter 2.
- 4) Alley, R., “The Two Mile Time Machine,” 2000, Oxford Press, 229 pp. A discussion as to how long cores in polar ice are obtained and processed and of the record they preserve. Emphasis is on the abrupt climate changes which punctuated the last glacial period. A very readable book which portrays Alley’s excitement about his subject. This book will prove helpful to those who wish to gain greater insight into the material in Chapter 2.
- 5) Broecker, W.S. and Peng, T.-H., “Tracers in the Sea,” 1982, Eldigio Press, 688 pp. This book was written just after the completion of the GEOSECS expeditions. It covers all aspects of marine inorganic chemistry with emphasis on stable isotopes and radio tracers. In addition, it has chapters on glacial CO₂ and anthropogenic CO₂. For 20 years, it was the standard guide to these subjects. Now out-of-print, it is rapidly becoming a historical document.

- 6) Zeebe, R.E. and Wolf-Gladrow, D., “CO₂ in Seawater: Equilibrium, Kinetics, Isotopes”, 2001, Elsevier, 346 pp. As the title suggests, this book deals with all aspects of the inorganic chemistry of carbon and boron dissolved in ocean water including the isotopes of carbon, boron and oxygen. For the reader interested in going beyond the material in Chapter 4, this book is an excellent resource.
- 7) Broecker, W.S., “Greenhouse Puzzles”, 1998 (revised edition), Eldigio Press, 277 pp. A self-published book in three parts. Part 1 deals with the geochemical aspects of the ongoing rise of atmospheric CO₂. Part 2 deals with scenarios put forth to explain the lowered CO₂ content of the glacial atmosphere. Part 3 deals with the control systems which regulate the atmosphere’s CO₂ content and the ocean’s chemical composition. The first two parts provide a more detailed discussion of the material in Chapters 5 and 6 of this book.
- 8) Sarmiento, J.L. and Gruber, N., “Ocean Biogeochemical Dynamics”, Princeton, NJ: Princeton University Press, in press (To be out around January of 2006). This book provides a broad theoretical framework for the study of the processes that control the mean concentration and distribution of biologically utilized elements and compounds in the ocean. It is written as a textbook for graduate students and upper level undergraduates. The first two chapters of the book provide an introductory overview of biogeochemical and physical oceanography. The next four chapters concentrate on processes at the air-sea interface, the production of organic matter in the upper ocean, the remineralization of organic matter in the water column, and the processing of organic matter in the sediments. The focus of these chapters is on analyzing the cycles of organic carbon, oxygen, and nutrients. The next three chapters round out the coverage of ocean biogeochemical cycles with discussions of silica, dissolved inorganic carbon and alkalinity, and CaCO₃. The final chapter discusses applications of ocean biogeochemistry to understanding the role of the ocean carbon cycle in interannual to decadal variability, in paleoclimate, and in the anthropogenic carbon budget.

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