

# CO<sub>2</sub> Increase and Climate Prediction: Clues from Deep-Sea Carbonates

by Wolfgang H. Berger

*The rising concentration of carbon dioxide in the atmosphere, from the burning of coal and hydrocarbons, is projected to produce substantial warming in the near future. How high will the CO<sub>2</sub> content rise? Will climate be more stable or less? How will the Antarctic ice and sea level respond? Our geological past, as recorded in deep-sea carbonates, offers clues to possible answers.*

## Introduction

The carbon dioxide content of the atmosphere has increased by some 25% within the past 100 years, due to the use of fossil fuels and the effects of deforestation. Though the reserves of coal and hydrocarbons are large - on the order of ten times the carbon mass of the atmosphere - it is expected that they will be burned within the next several hundred years. Figure 1 shows one such projection, made in 1969 by M. King Hubbert, who predicted the timing of the oil shortage 20 years ahead of the crisis. Recent developments indicate that the growth of energy use is unlikely to be as fast as he suggested: a more realistic curve would reach a lower peak and stretch over a larger time interval.

When the expected rise in atmospheric CO<sub>2</sub> is seen in geological perspective (Fig. 2), one gains an impression of the tremendous acceleration of geological processes that is the hallmark of our own time. The exact values for former CO<sub>2</sub> concentrations given by Budyko (1982) are open to discussion, but the trend is not in question. The background level of atmospheric CO<sub>2</sub> is ultimately set by the rate of weathering of igneous rocks, a process that consumes the acids supplied by volcanic activity. Mountain-building and uplift of continental crust during the late Tertiary greatly increased the opportunities for weathering and hence must have led to a draw-down of CO<sub>2</sub>. Thus, we are now witnessing, within centuries, the reversal of a trend that dominated the last 10 million years.

An increase in atmospheric CO<sub>2</sub> will lead to an increase in the global temperature (the "greenhouse effect"). Augmented by other greenhouse gases, CO<sub>2</sub> is thought to be driving global temperatures above natural background fluctuations within the present decade. For every doubling of CO<sub>2</sub> content a temperature increase of between 1° and 4° C is anticipated. The questions that emerge are familiar. How fast and how high will global temperatures rise? What will be the impact of the rise on regional climate patterns, especially with regard to agriculture? Will Antarctic ice melt and sea level rise?

Much has been written on these subjects (see Andersen and Malahoff, 1977, Hansen and Takahashi, 1984, and Sundquist and Broecker, 1985). The focus here is on the proposition that the calcareous sediments on the deep sea floor contain clues to at least partial answers to these questions. Their study suggests that a general rise in temperature may not be the most important problem in the offing. A much more alarming prospect is the possibility of increasing instability in ocean-atmosphere dynamics.

## Link Between Atmospheric CO<sub>2</sub> and Deep-Sea Carbonates

On a time-scale of decades to millennia, the carbon budget of the atmosphere is chiefly controlled by the carbon chemistry of the ocean. The ocean carbon reservoir (mostly bicarbonate ion) is about 60 times larger than that of the atmosphere, and since the atmosphere is in intimate contact with the

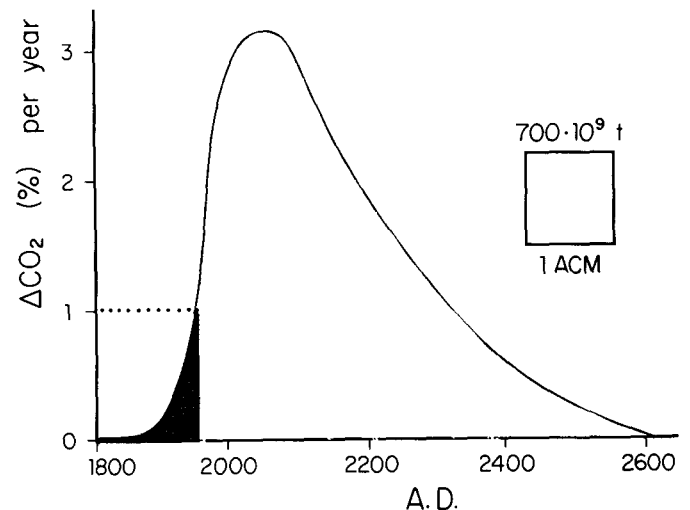


Figure 1: Projected release of CO<sub>2</sub> from the burning of fossil fuels, in percentage of present atmospheric content. From Berger (in Andersen and Malahoff, 1977). The square indicates the size of the present atmospheric carbon mass (ACM).

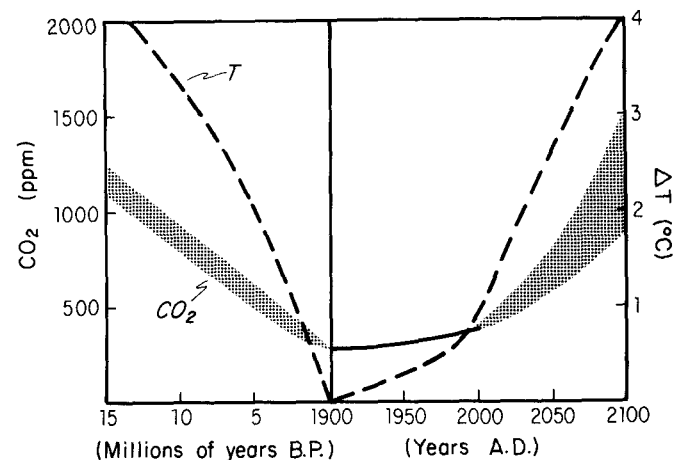
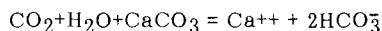


Figure 2: Reconstructed carbon dioxide content for the Tertiary (left) as given by Budyko (1982), compared with projections for the near future (right). Delta T based on  $3 \cdot \ln (CO_2(t)/CO_2(0))$ , where  $T$  = temperature and  $t$  = time since AD1900.

surface of the seas over 70% of the planet, the ocean acts as a major regulating device. Already roughly one half of the newly introduced CO<sub>2</sub> has gone into the ocean, thereby relieving the pressure on the atmosphere.

One might expect, given enough time, that the new CO<sub>2</sub> should almost all end up in the ocean, with only one part in 60 left over for the atmosphere. However, this is not so because of the limited supply of carbonate ion, which reacts with the invading CO<sub>2</sub>. As this supply is used up, the pH drops and back-pressure develops. As a rule of thumb, for a change of 1% in the dissolved carbon in the ocean, the atmospheric composition changes by 10%. This factor of ten is known as the "buffer factor," the importance of which was recognized by Revelle and Suess (1957).

Excess carbon dioxide is neutralized on the sea floor when it arrives there and dissolves carbonate:



This reaction decreases the buffer factor to about 27% of its original value, according to Bacastow and Keeling (1979). Thus, the main effect of carbonate dissolution is to increase the ability of the ocean to hold CO<sub>2</sub> and hence to accelerate CO<sub>2</sub> uptake (Fig. 3).

Projections of future CO<sub>2</sub> levels depend on many assumptions. Especially important is the expected CO<sub>2</sub> production from industrial activity, and for these studies an input curve much like that in Figure 1 was used. Another assumption concerns the rate at which the sea floor responds by carbonate dissolution to new CO<sub>2</sub>. The projection in Figure 3 is based on instantaneous equilibrium, that is on fast

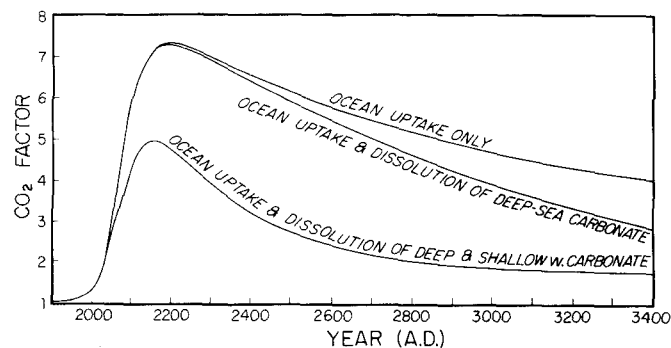


Figure 3: Projected increase in atmospheric CO<sub>2</sub> in three model scenarios. From Bacastow and Keeling (1979).

dissolution of carbonate in unlimited supply. A more realistic assessment of this rate-limited process can be obtained by comparing the carbonate preservation on the Atlantic and Pacific sea floors, as recorded by the condition of the shells of planktonic foraminifera.

On the whole, planktonic shells are in good to excellent shape above a certain depth level, called the lysocline. As shown in Figure 4, they deteriorate toward greater depths until they disappear at the carbonate compensation depth (CCD). The amount of total carbonate dissolved at the level of the lysocline, compared with sediments well above it, is about 20% (Berger, Bonneau and Parker 1982), increasing to 100% at the CCD.

The preservation profiles are quite different for Atlantic and Pacific: in the Atlantic the lysocline and CCD levels are typically about one kilometer deeper. The deep Atlantic is better ventilated than the deep Pacific, due to the geographic location of deep water sources. Thus, the Pacific deep waters have considerably more time in which to enrich themselves with CO<sub>2</sub> from the oxidation of organic matter

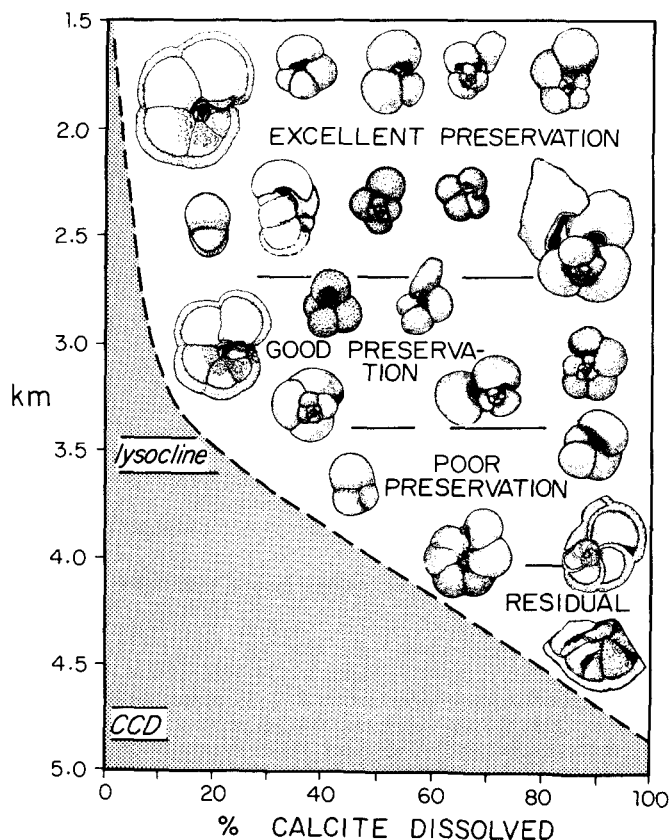


Figure 4: The state of preservation of foraminifera on the sea floor. Profile from Berger, Bonneau and Parker (1982) and drawings of foraminifera from Parker (1962).

settling from surface waters. The result is a higher content of unbalanced CO<sub>2</sub> in the deep Pacific, that is, a greater undersaturation. It is as though 5% of "new" CO<sub>2</sub> had been introduced into the deep Pacific, but not the Atlantic.

Using the Atlantic/Pacific analogy, we can estimate that for each percent of "new" CO<sub>2</sub> the lysocline and CCD will rise by 200 meters. The area of new seafloor thus subjected to increased dissolution is not all that large, and the increase in dissolution rate at any one depth is moderate. Calculations based on the difference in alkalinity and in age between Pacific and Atlantic deep water, suggest that to titrate one third of the new CO<sub>2</sub> would take a thousand years or so. As for shallower-water environments, the supply of carbonate required to titrate CO<sub>2</sub> simply does not exist.

#### Deglaciation: A Message from the Ice Record

In order to determine the characteristics of climate dynamics from the history of the Earth, detailed studies must be made of periods of deglaciation. During the transition from glacial to postglacial time, enormous masses of ice melted in North America and in northern Europe and sea level rose by more than 100 meters, converting shelf land to shelf sea. Sea ice disappeared over large regions, forests expanded, and the climate became warmer and wetter, encouraging the beginnings of agriculture. The CO<sub>2</sub> content of the atmosphere apparently also changed.

Exciting new information about the change of CO<sub>2</sub> comes from the study of ice cores from Greenland and Antarctica (see Oeschger et al., in Hansen and Takahashi, 1984). The CO<sub>2</sub> in the ice is measured as a ratio between it and nitrogen. Although problems of interpretation exist, associated with the exact mechanism whereby the gases are locked into

the ice, it is now tentatively accepted that the CO<sub>2</sub> concentration rose from a value near 200 ppm at the glacial maximum to an early Holocene value near 300 ppm (Fig. 5).

One way to produce the CO<sub>2</sub> increase is to lower the productivity of the ocean, as suggested by Broecker (1982). Ocean productivity controls the atmospheric CO<sub>2</sub> as shown in Figure 6. In the sunlit zone, photosynthesis precipitates organic matter, removing dissolved CO<sub>2</sub> from the surroundings. Some of the organic matter is removed by settling, and thus the surface waters on the whole are depleted in CO<sub>2</sub>. The atmosphere is in equilibrium with the surface waters, hence it is depleted in CO<sub>2</sub> also. The deep waters are correspondingly enriched in CO<sub>2</sub> because organic matter there is oxidized, releasing CO<sub>2</sub>. This "biological pump," a term coined by Roger Revelle, is responsible for roughly halving the atmospheric CO<sub>2</sub> content from an expected value

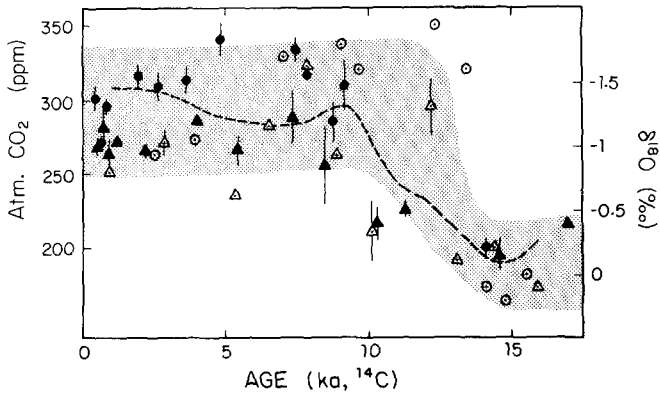


Figure 5: Glacial-to-Holocene change of atmospheric carbon dioxide as seen in ice cores (various symbols) from Greenland and Antarctica. Compiled in Berger and Keir (in Hansen and Takahashi, 1984). Oxygen isotope curve from the west-equatorial Pacific superimposed for time-scale (from Berger, 1982).

of between 600 and 700 ppm to the one actually observed. Carbonate precipitation in surface waters and the settling of shells oppose the effect, but a correction for this is already included in the estimate above.

There are various ways to measure changes in productivity within the deep-sea record, for example by noting the abundance of organic carbon or of siliceous fossils (e.g. Suess and

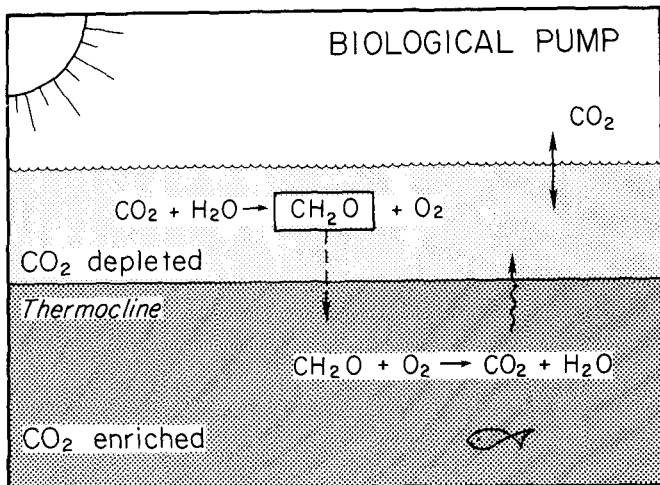


Figure 6: Sketch of the mechanism linking productivity to the carbon dioxide content of the atmosphere.

Thiede, 1983). Another approach is to analyze assemblages of planktonic organisms to determine paleofertility. For instance, low and high-fertility water masses have very different communities of planktonic foraminifera. *Neogloboquadrina dutertrei* prefers productive waters, while *Pullemmatina obliquiloculata* does quite well in waters of lower fertility. A changing ratio between these two species, therefore, may be taken as a change in productivity. In the equatorial Pacific this ratio does change in the expected direction from glacial to Holocene sediments.

Broecker (1982) has suggested direct measurement of the efficiency of the pump by comparing the <sup>13</sup>C/<sup>12</sup>C ratios of planktonic and benthic foraminifera. As photosynthesis removes organic matter from the sunlit zone, it also removes preferentially <sup>12</sup>C, which is enriched relative to <sup>13</sup>C within the organic matter. The harder the pump works, the more <sup>12</sup>C is removed and the higher the ratio of <sup>13</sup>C to <sup>12</sup>C in the water of the sunlit zone. This ratio is reflected in the calcareous shells of the planktonic foraminifera (PF). The shells of benthic foraminifera (BF), on the other hand, simply reflect the overall <sup>13</sup>C/<sup>12</sup>C ratio of the deep ocean. Thus, the productivity hypothesis of glacial-postglacial CO<sub>2</sub> change can be tested in the foram record.

Our data in the western equatorial Pacific only showed about one third of the calculated effect (Berger and Keir, in Hansen and Takahashi, 1984). However, in the eastern equatorial Pacific, Shackleton and others (1983a) did find a signal very much like the one predicted (Fig. 7). The background difference between planktonics and benthics in the observations is lower by 1‰ than in the calculations, because the planktonic species analyzed (*Neogloboquadrina dutertrei*) tends to reflect sub-surface waters and because the background difference assumed for the box model is somewhat too high.

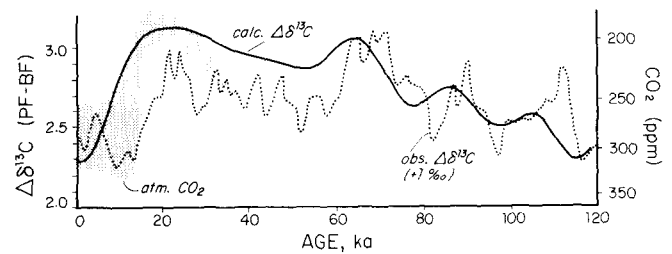


Figure 7: Difference between the <sup>13</sup>C values of planktonic (PF) and benthic foraminifera (BF) as an indicator of atmospheric CO<sub>2</sub>. Solid curve: expected values (Keir and Berger, 1983) if a global change in productivity parallel to a sea level change is the sole mechanism for the glacial-Holocene CO<sub>2</sub> change. Stippled curve: actual record from the east-equatorial Pacific (Shackleton et al., 1983a). Shaded area indicates the range of pCO<sub>2</sub> values from ice core measurements (based on data in Delmas et al. and Neftel et al., compiled in Keir and Berger, 1983).

The good qualitative agreement between model and observation does not, of course, mean that the process is understood. Other models might give an equally good fit, and cores from many more regions have to be looked at, because changes in the eastern equatorial Pacific (where upwelling is important) are not necessarily representative of those for the entire ocean. In charting the glacial to Holocene productivity fluctuations for different areas of the ocean, much will be learned about the dynamics of the carbon system, greatly improving our modelling of the response to CO<sub>2</sub> input.

#### The Mystery of the Younger Dryas

A period of severe cooling in the middle of the last deglaciation is well known from glacial readvances and other climate indicators in northern Europe, and also from the

Greenland ice record (Dansgaard et al., 1971). This so-called "Younger Dryas" lasted for only a few hundred years, between 11,000 and 10,000 years ago. It was preceded by a period of unusual warmth, the "Alleroed," and was followed by a period of very fast warming, the "Preboreal" (Mangerud et al., 1974). The effects of this major cooling episode are seen in many oceanic deep-sea cores from various regions (Fig. 8). Profound changes in precipitation patterns may be indicated, with tropical rivers running high during the warm periods and low during the Younger Dryas. The polar front, migrating north from its glacial position between New York and Lisbon, apparently turned and moved south again during the Younger Dryas (Ruddiman and McIntyre, 1973).

The Younger Dryas event may be regarded as the expression of a major instability in the ocean-atmosphere system, one worth studying in detail. In principle, instability can be introduced from two sources: positive feedback with a lack of damping, and transient reservoirs of water or carbon that can be activated quickly to disturb the system. One powerful source of positive feedback is albedo. When ice first melts,

land area increases, as does the vegetation and the area covered by the ocean. The net effect is a decrease in surface albedo, which can lead to further warming. A change in sea ice cover must also be considered, for ice is much more reflective than water, and it delivers less moisture (i.e. heat) to the atmosphere. Another feedback mechanism is tied to the carbon system: warming of surface waters makes CO<sub>2</sub> less soluble in seawater, so some of it will enter the atmosphere.

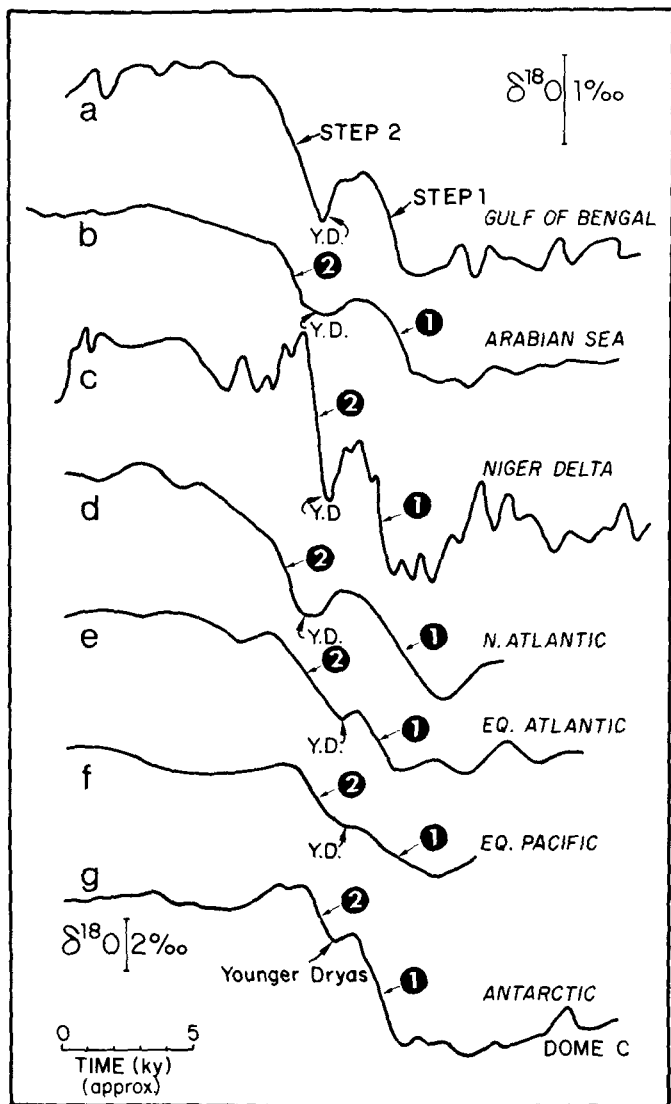


Figure 8: Correlation between six deep-sea oxygen isotope records and an ice-core record. Curves a and b from Duplessy et al. (1981a), c- Pastouret et al. (1978), d- Duplessy et al. (1981b), e- Berger (1978), f- Berger (1982), g- Lorius et al. (1981). Y.D. = Younger Dryas, centered on 10,500 yBP. Note different vertical scale for curve g.

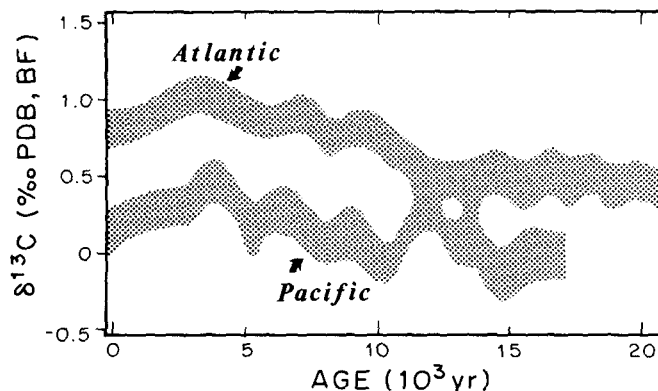


Figure 9: Evidence for intermittent production of deep water during deglaciation. For the central Atlantic  $\delta^{13}\text{C}$  values are shown for *Cibicides wuellerstorfi* near 3.5 km depths, and in the west-equatorial Pacific at depths of 2-3 km. (Berger and Vincent, in press).

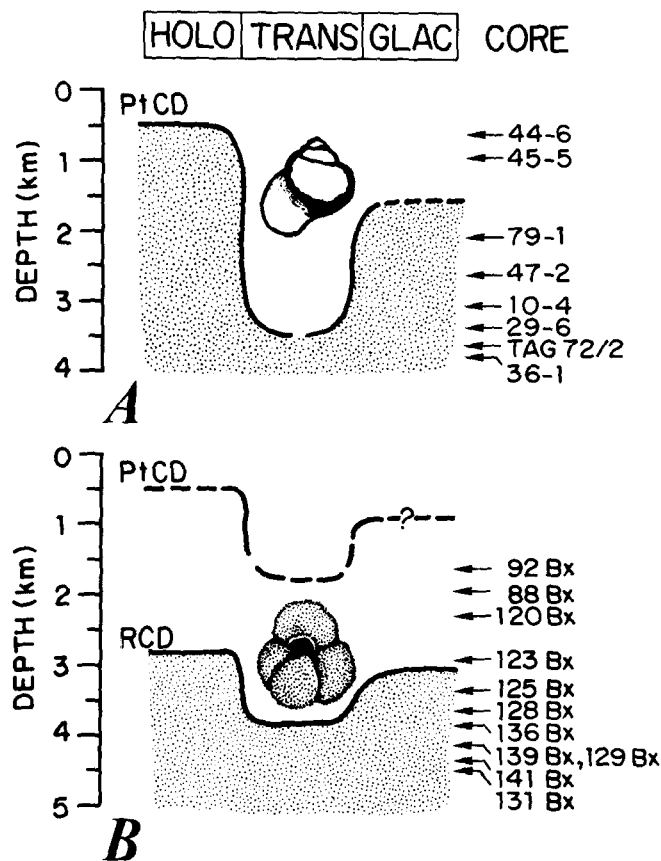


Figure 10: Increased preservation of calcareous fossils during deglaciation. A- pteropod compensation depth (PtCD) in glacial, transitional and Holocene time, off NW Africa. B- compensation depth for *Globigerina rubescens* (RCD) in the west-equatorial Pacific. Data from Berger (1977).

How then was the major warming trend interrupted and put into reverse? The duration of the Younger Dryas (about 500 years) may hold the clue, because it is close to deep ocean mixing times. If mixing was strongly reduced during the Allerød, CO<sub>2</sub> could have been trapped in deep waters even while warming of surface waters proceeded. With a lowered atmospheric CO<sub>2</sub> content, the stage would have then been set for a plunge into a brief ice-age, via positive albedo feedback. At some point the release of the trapped CO<sub>2</sub> would have reversed the trend again, allowing the resumption of rapid warming.

Ideas such as these are purely speculative at this point. However, it is very likely that vertical mixing did indeed decrease sporadically during the latest Pleistocene, due to a reduction in sinking of surface waters in the Norwegian Sea. Stable stratification from meltwater input during deglaciation in this region has been proposed by Ruddiman and collaborators (Ruddiman et al., 1980; Ruddiman and McIntyre, 1981), among others. As Broecker et al. (1985) have pointed out, a decrease in North Atlantic deep water (NADW) production would substantially decrease the amount of heat entering the Norwegian Sea (and northern Europe) from the south. During glacial time, the NADW source seems to have

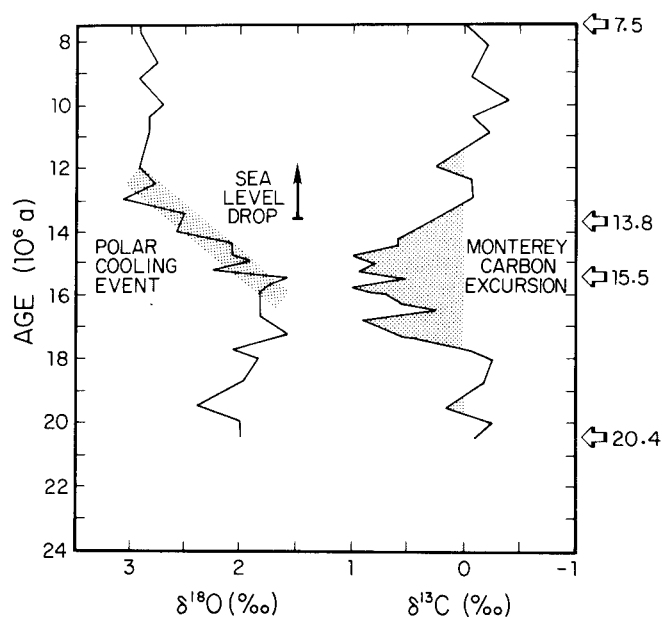


Figure 11: Stable isotope records, based on the analysis of benthic foraminifera from DSDP Site 216, tropical Indian Ocean. Data from Vincent et al. (in press).

been much reduced (Duplessy et al., 1975; Boyle and Keigwin, 1982; Shackleton et al., 1983b), in keeping with this hypothesis.

We have recently found evidence, as have others (Jansen and Erlenkeuser, 1985), that deep-water production in the North Atlantic was sporadically shut down during deglaciation (Fig. 9). When the deep water source in the North Atlantic is turned on fully, as it is now, the δ<sup>13</sup>C-values of Atlantic and Pacific deep-sea benthic foraminifera are clearly distinct. The reason is that the deep Atlantic is filled with "young" oxygen-rich water with a strong imprint of surface water properties. As mentioned, earlier the high δ<sup>13</sup>C values of this water result from the preferential removal of <sup>12</sup>C by the biological pump (Fig. 6); low δ<sup>13</sup>C values on the other hand indicate "old" waters enriched in CO<sub>2</sub> and depleted in oxygen. When the NADW source is turned down, the Atlantic

and Pacific deep-water δ<sup>13</sup>C-values become similar, as happened episodically between 14,000 and 11,000 years ago (Fig. 9).

That mixing rates of the deep ocean changed during deglaciation and affected the carbon balance is supported by the curious observation that deep-sea carbonate preservation is unusually good during deglaciation, with a peak near the level of the Younger Dryas (Fig. 10). Some of this effect may have to be ascribed to the buildup of the biosphere, as suggested by Shackleton (in Andersen and Malahoff, 1977). However, we know that ocean mixing and productivity are intimately tied to carbonate preservation, so that some message about these processes is probably hidden here. A change in mixing rates is also favoured by the unusually high <sup>14</sup>C content of the atmosphere in the earliest Holocene (Keir, 1983).

The processes of warming and of meltwater input are, to a large extent, dynamically equivalent as far as deep ocean mixing is concerned. In the future there may thus be a con-

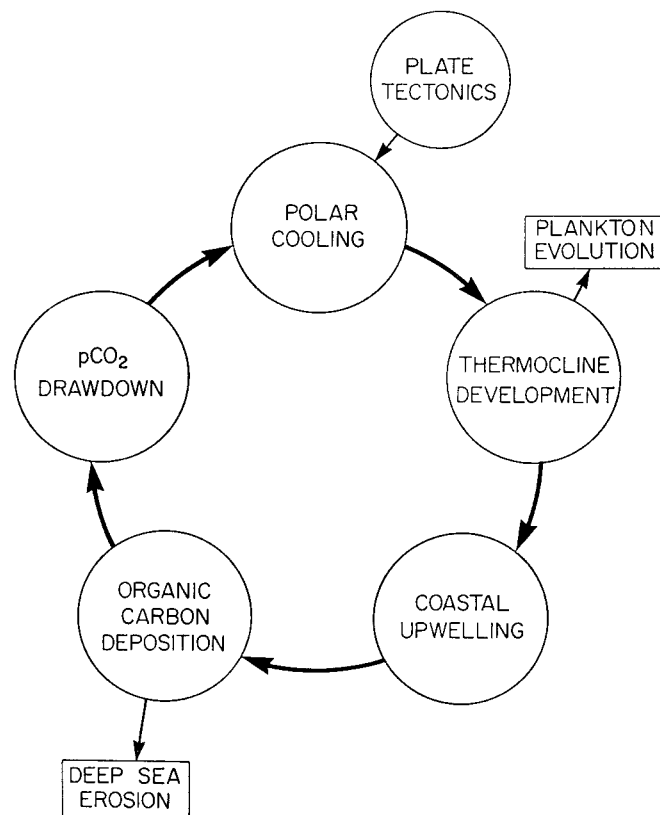


Figure 12: Conceptual model of positive feedback loop involving cooling, upwelling, organic carbon deposition and further cooling. From Vincent and Berger (in Sundquist and Broecker, 1985).

siderable reduction of deep mixing, starting with a decrease in the production of NADW. On the whole, this should decrease the stability of the global heat budget, increase the episodicity of ocean-atmosphere exchange, and hence produce more extreme climatic conditions.

#### Antarctic Ice-Buildup: the Monterey Connection

If the Antarctic ice were to melt, sea level would rise by more than 50 meters. There is little doubt that if the climate warms for long enough the ice will melt. The question is at what level of CO<sub>2</sub> would we expect the Antarctic ice sheet to be unstable.

It seems safe to assume that the sought-for levels of CO<sub>2</sub> and global temperature are close to those which existed when the Antarctic ice was forming. The most important episode of growth was apparently within the Middle Miocene, about 15 million years ago. At this time there was a major shift in the oxygen isotope composition of benthic foraminifera toward heavier values, which indicate cooling and ice buildup (Shackleton and Kennett, 1975). These two processes were probably not entirely synchronous (Fig. 11). We have suggested that cooling came first and that it represents about two-thirds of the oxygen shift, starting at 15.5 million years (Vincent et al., in press).

As shown in Figure 11, the cooling step is associated with a large excursion of carbon isotopes toward heavier (higher)  $\delta^{13}\text{C}$  values. This feature is called the "Monterey Excursion" because it is synchronous with the deposition of the phosphate- and carbon-rich portion of the Monterey Formation of California, well known as a source of hydrocarbons. The Monterey and equivalent deposits, all around the North Pacific and elsewhere, apparently provided a large sink for carbon at the time of their origin. The carbon isotope excursion seen between 17 million and 14 million years ago reflects the extraction of organic carbon (enriched in <sup>12</sup>C) in newly established upwelling regions (Vincent and Berger, in Sundquist and Broecker, 1985). This preferential extraction of <sup>12</sup>C, of course, left the ocean enriched in <sup>13</sup>C.

If the Monterey hypothesis is correct, then the sequestration of carbon can be interpreted as a precondition for the ice-buildup (Fig. 12). The time relationship between the two isotope signals clearly shows that a shift in carbon isotopes precedes one in oxygen isotopes by a million years or more (Fig. 11). During this period of "geochemical conditioning" of the climate, the carbon dioxide of the atmosphere would have been slowly reduced due to the extraction of organic carbon from the ocean. Prior to the start of cooling the mass of carbon involved was approximately 30 times larger than the present atmospheric carbon mass. Assuming equilibrium conditions before the mid-Miocene ice buildup, the CO<sub>2</sub> content of the atmosphere must have been reduced by more than one ACM in the process, making the pCO<sub>2</sub> more than twice that of the present atmosphere.

A level of four times the present pCO<sub>2</sub> has been suggested by Budyko (see Fig. 2), based on shallow-water carbonate abundances. However, more sophisticated geochemical models (Berner, Lasaga and Garrels, 1983) make it obvious that a large number of assumptions must be made in the calculation of past atmospheric CO<sub>2</sub>. The reason is that on time scales of millions of years we must consider several geochemical cycles simultaneously. Those of P, N, S, Ca and Mg are all closely intertwined with that of carbon. In addition, the history of volcanism and the rates of weathering of igneous and sedimentary rocks must be taken into account.

Fortunately, the sedimentary record of the deep-sea is quite detailed back into the Early Miocene, and the effects of diagenetic alteration are not too great. A substantial effort to reconstruct the atmospheric pCO<sub>2</sub> for the last 20 million years would add much to our understanding of the carbon dynamics of the ocean-atmosphere system.

#### Acknowledgments

The studies on deep-sea carbonates have been carried out in close collaboration with Drs. E. Vincent, J.S. Killingley, F.L. Parker, and R.S. Keir. The CO<sub>2</sub>-related studies were funded mainly by the U.S. National Science Foundation (Ocean Sciences), and recent modelling efforts (with Keir) by the Electric Power Research Institute. The present essay is adapted from the 1984 Huntsman lecture, given at the Bedford Institute of Oceanography, Nova Scotia, Canada.



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