THE ROLE OF VERTICAL CHEMICAL FRACTIONATION IN CONTROLLING LATE QUATERNARY ATMOSPHERIC CARBON DIOXIDE

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Abstract. The 30% decrease in atmospheric carbon dioxide during glacial maxima must be driven by some change in the chemical circulation of the ocean. Here, a new model for late Quaternary CO_2 variability is presented which resolves some problems occurring in previous models (including the timing of carbon dioxide response and changes in the oxygen content of the deep ocean). The primary driving factor in this model is a rearrangement of chemical distributions in the ocean whereby labile nutrients and metabolic CO_2 are concentrated in deep waters rather than in intermediate waters as observed in the modern ocean. This new "bottom-heavy" chemical structure does not affect atmospheric carbon dioxide directly. Instead, CO_2-induced acidity lowers the deep ocean carbonate ion concentration and temporarily increases carbonate dissolution rates. Oceanic alkalinity then rises until the deep ocean carbonate ion is restored to its steady state value. The resulting increase in oceanic alkalinity draws CO_2 out of the atmosphere into the ocean. Alkalinity and atmospheric CO_2 lag several thousand years behind the change in oceanic chemical structure; this delayed response is determined by the limited rate of continental weathering and deep ocean carbonate dissolution relative to the oceanic alkalinity inventory. It is proposed that characteristic deglacial and preglacial states of the ocean are leading factors driving glacial-interglacial climate changes. This concept reinterprets the carbon isotope contrast between surface water and deep waters [$\Delta\delta^{13}C(P-B)$] as due to a shift of light metabolic carbon from intermediate waters into deep waters. The process is illustrated here by a simple equilibrium five box ocean model. The observed intermediate-depth nutrient depletion is not sufficient in itself to determine which of several possible mechanisms are operating, and some mechanisms are not as effective in changing atmospheric CO_2 as others. The largest response is seen from deepening the regeneration cycle of organic carbon; the least response is seen from converting North Atlantic Deep Water into intermediate water.

Introduction

Polar ice core studies have shown that atmospheric carbon dioxide was 90 parts per million by volume (ppmV) lower during glacial maxima (190 ppmV) than during warmer periods (280 ppmV) [Barnola et al., 1983, 1987; Neftel et al., 1982, 1985, 1988; Oeschger et al. 1984, 1985]. Lower CO_2 significantly contributes to glacial cooling [Hansen et al., 1984] and provides an inter-hemispheric climate link. Considerable controversy has arisen regarding the causes of decreased glacial CO_2, although it is agreed that some alteration of the oceanic chemical, biological, and physical circulations must be reponsible. Broecker [1982a,b] examined numerous aspects of the glacial ocean and proposed

that an increase in the phosphorus content of the ocean (due to oxidation of organic matter on the continental shelves) resulted in more efficient operation of the "biological pump" which drives carbon dioxide into the deep ocean. His model was consistent with many observations available at the time. The most striking success of his analysis was the prediction that the carbon isotope contrast between surface waters and deep waters would be greater during glacial times. Shackleton et al. [1983] verified this effect through the analysis of fossil planktonic and benthic foraminifera ($\Delta\delta^{13}C(P-B)$). But Broecker's model has since fallen from favor because (1) it appears that the carbon isotope contrast changes before sea level change (as recorded by fossil carbonate $\delta^{18}O$) [Shackleton and Pisias, 1985] which argues against a link to shelf sediments; (2) the oceanic inventory of the nutrient analogue cadmium (Cd) does not record the large glacial increase required by Broecker's model [Boyle and Keigwin, 1985]; and (3) the continental shelves may not contain enough organic matter in any event [Broecker and Peng, 1986].

More recent models account for changes in the surface/deep CO_2 contrast by increasing nutrient depletion in high-latitude surface waters. These models call on improved efficiency of the "biological pump" by reducing the polar "leak" created by upwelling deep ocean waters [Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984]. A more efficient high-latitude pump can be attained by altered ocean circulation patterns or enhanced levels of high-latitude biological activity. These new models do not envision a direct link to sea level, nor do they call upon whole-ocean increases in nutrients. Some evidence appears to contradict the prime assumption of these models. The nutrient-related properties $\delta^{13}C$ and Cd/Ca in Antarctic planktonic foraminifera do not indicate any such glacial polar nutrient decrease (Table 1, Figure 1, [Labeyrie and Duplessy, 1985]). These new models (as well as Broecker's original model) also predict that parts of the deep ocean should become anoxic during glacial times. This prediction is contradicted by the presence of glacial age fossil benthic organisms in sediments and continuously high sedimentary iodine/carbon ratios from these regions [Pedersen et al., 1988]. Possibly, the evidence is misleading (e.g., perhaps Antarctic planktonic foraminifera did not grow during times of bottom water formation). But this failure to confirm glacial polar nutrient depletion and anoxia leaves these models without verification of key premises.

Another discrepancy between the theories and models has emerged recently. Further detailed work on planktonic and benthic foraminifera suggest that $\Delta\delta^{13}C(P-B)$ was at its minimum about 10,000 years ago and that it has since risen to levels not much less than those observed in glacial maximum sediments [Mix and Shackleton, 1986; Curry and Crowley, 1987; D. Oppo and R.G. Fairbanks, personal communication, 1988]. Recent work on polar ice cores does not support this scenario for atmospheric carbon dioxide; it appears instead that CO_2 has been consistently high during

Table 1.   Cd Data From the Top 4 m
of Core MD80304

Depth, cm	Cd/Ca, μmol/mol	s.d.	n	r	$\delta^{18}O$, ‰	$\delta^{13}C$, ‰
5	0.089	0.013	3		2.91	1.40
10	0.084	0.012	3		2.93	1.38
20	0.064	0.001	2		2.66	1.30
30	0.062	0.005	3		2.96	1.43
40	0.072	0.001	2		2.85	1.22
50	0.063	0.003	3		2.90	1.28
60	0.064	0.006	3		2.81	1.11
70	0.068	0.002	3		2.95	1.07
80	0.120		1	2	2.72	0.89
90	0.099	0.030	3		2.88	1.17
100	0.112	0.018	3		2.53	1.13
110	0.081	0.007	3		2.84	0.92
120	0.060	0.004	2		2.85	1.07
130	0.068	0.003	3		2.90	0.93
140	0.074	0.003	3			
150	0.048	0.011	3		3.26	0.83
160	0.056	0.019	3		3.29	0.84
170	0.058	0.001	3		3.73	0.84
180	0.051	0.009	3		3.62	0.97
190	0.045	0.001	2		3.63	0.53
200	0.080	0.019	5		3.47	0.29
210	0.073	0.014	3		3.45	0.19
220	0.038		1		3.67	0.22
230	0.096		1	1	4.46	0.53
240	0.064		1		4.75	0.45
250	0.065	0.008	2		4.25	0.38
260	0.054	0.003	2		4.26	0.64
270	0.055	0.006	3		4.23	0.56
280	0.059	0.014	2	1	4.09	0.57
290	0.056	0.004	2		4.14	0.52
300	0.057	0.007	3		3.32	0.39
310	0.105	0.029	3		4.09	0.55
320	0.096	0.009	3		4.10	0.51
330	0.095	0.017	2	1	3.82	0.58
340	0.091	0.012	3		4.20	0.45
350	0.087	0.027	3		3.79	0.43
360	0.043	0.010	3		3.75	0.43
370	0.096	0.009	3		3.58	0.43
380	0.082	0.016	2	1	4.01	0.33
390	0.067	0.002	2		3.94	0.84
400	0.049		1		3.56	0.91

Oxygen and carbon isotope data are
from Labeyrie and Duplessy [1985]. n is the
number of analyses in mean; r is the number
of samples rejected from the mean.

the last several thousand years [Barnola et al., 1987; Neftel et al., 1988]. As with the polar nutrient evidence, it is tempting to blame this discrepancy on the data: perhaps the ice core time scale is wrong, or perhaps foraminifera (especially planktonic foraminifera) do not record $\Delta\delta^{13}C(P-B)$ reliably. While it is possible that the observations are flawed by some as yet unappreciated problem, we should first examine whether it is possible to devise a model that can accommodate the observations.

This paper will describe a new model for glacial CO_2 which builds upon insights achieved in previous work but can account for a significant proportion of changes in glacial atmospheric CO_2 without discounting observations. This model relies heavily on the "carbonate ion response" noted by Broecker [1982a,b] and discussed in more detail by Broecker and Peng [1987]. The origin of the carbonate response in this

new model is novel, however, in that it does not assume shelf phosphorus transports nor does it assume altered polar preformed nutrient levels. Instead, the carbonate response in this new model arises from a shift of metabolic CO_2 from intermediate depths of the ocean into the deeper waters of the ocean. The model accounts for some observations which previously have been considered problematical or irrelevant, and it makes some predictions which can be tested by new observations.

Evidence for Reorganization of Intermediate/Deep CO_2 Fractionation

The model is based on the assumption that the oceanic distribution of dissolved carbon dioxide was shifted into a configuration where CO_2 was concentrated in the deep waters relative to intermediate waters. Several lines of evidence support this premise. Boyle and Keigwin [1986, 1987] analyzed Cd and $\delta^{13}C$ in glacial benthic foraminifera from cores representing the depth range 1700-4200 m in the western North Atlantic. These results show that glacial intermediate-depth North Atlantic was nutrient-depleted relative to today, and deeper waters were more nutrient-enriched (Figure 2). The intermediate-depth nutrient depletion is equivalent to a decrease of about 0.6 μmol/kg in phosphorus. One of the shallow cores was from the open North Atlantic, but the smoking gun confirming Atlantic intermediate water nutrient depletion comes from cores in the Caribbean Sea. Because the Caribbean is rapidly flushed by intermediate-depth Atlantic water flowing over its sill, the nutrient content of deep waters from this basin reflects the nutrient content of Atlantic intermediate water. So the Caribbean has lower Cd and more positive $\delta^{13}C$ during glacial times than during interglacial periods. Surprisingly, this observation languished unremarked in the literature for some time; the data appendix of the CLIMAP Project Members' [1984] "5e" study of the last interglacial included Caribbean $\delta^{13}C$ data from glacial stage 6 and interglacial stage 5e showing the same result as for Boyle and Keigwin's stage 2/1 comparison. Also, Cofer-Shabica and Peterson [1986] have obtained a long Caribbean benthic $\delta^{13}C$ record which showed that this pattern occurred repeatedly over the late Quaternary. Zahn et al. [1987] observe similar nutrient depletions from $\delta^{13}C$ data from intermediate-depth cores in the Eastern Atlantic near Gibraltar. Some time after the aforementioned work, Oppo and Fairbanks [1987] obtained benthic $\delta^{13}C$ from a high accumulation rate core which confirmed the results from the lower sedimentation rate cores of Cofer-Shabica and Peterson [1986)] and Boyle and Keigwin [1986, 1987]. More recently, N.A. Slowey and W.B. Curry (personal communication, 1988) have also documented the shallow nutrient depletion from $\delta^{13}C$ data from two shallow (<1000 m) cores near the Bahamas. There can be little doubt that the glacial intermediate-depth North Atlantic was nutrient-depleted relative to modern waters at this depth and relative to deeper waters during glacial times.

The vertical nutrient profile in the Pacific is not yet as well known. The available results suggest that the intermediate-depth Pacific was also nutrient-depleted during glacial times. Shackleton [1985] first reported that Uvigerina in continental margin cores near the Sea of Okhotsk had higher $\delta^{13}C$ values during glaciation. He suggested that this observation could be accounted for by hypothesizing bottom water formation in the North Pacific during glacial times. Nutrient depletion in these cores is confirmed by new Cd analyses from the same
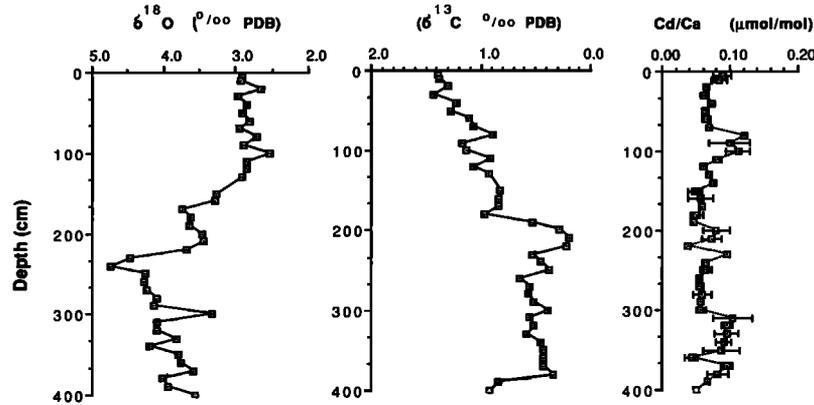
Fig. 1. Data from core MD80304 (51°04'S,67°44'E,1930 m). Oxygen and carbon isotope data are from Labeyrie and Duplessy [1985]. Picked samples of Neogloboquadrina pachyderma (left coiling) were kindly provided by L. D. Labeyrie. While there is some evidence for fluctuations in Cd, there is no systematic difference in the mean glacial and mean interglacial values (the preformed nutrient models predict a change of more than 0.05 in Cd/Ca). The glacial carbon isotope values are shifted from the Holocene values by more than the estimated change in mean $\delta^{13}C$; i.e., it would appear from the surface $\delta^{13}C$ that Antarctic nutrients were higher during glacial times (the opposite of the pre-formed nutrient model predictions).

core (Table 2, Figure 3). Evidence against the proposed bottom-water formation was provided by Keigwin [1987], who found a deep (2980 m) core from the North Pacific (with the reliable species Cibicidoides wuellerstorfi) that did not indicate any nutrient depletion during glacial times. Subsequently, Duplessy et al. [1988] obtained more extensive glacial Pacific core data (again, from Cibicidoides) which they interpreted to provide evidence that it was Pacific intermediate waters (above 2500 m) which became more nutrient-depleted during glaciation. The glacial-interglacial carbon isotope shift suggested by their work is about +0.4‰. More recently, Kallel et al. [1988] obtained data showing that intermediate waters in the northern Indian Ocean also were depleted in nutrients during glacial times. While the documentation in the Pacific is not as good as that in the North Atlantic and Indian oceans, and while there is little evidence as yet from the southern hemisphere, it is now plausible to hypothesize that metabolic chemicals are generally transferred from intermediate waters into deeper waters during glacial times.

Why are Nutrients and CO_2 Transferred from Intermediate into Deep Waters During Glacial Times?

The new glacial CO_2 distribution may have arisen in several ways. While these different mechanisms may be assigned different degrees of plausibility, there is no way at present to ascribe assign dominance to any of these mechanisms. It is possible that all contribute to some extent.

1. Boyle and Keigwin [1987] argued that nutrient-depleted North Atlantic winter surface waters formed less dense intermediate waters rather than deep waters during glacial times. This process would fill the upper Atlantic with nutrient-depleted waters, and some of this might extend into other ocean basins.

2. Oppo and Fairbanks [1987] used the evidence of Zahn et al. [1987] to argue that Mediterranean Water outflow increased substantially during glacial times. As with mechanism 1, this process would make the upper North Atlantic more nutrient depleted.

3. Boyle [1986] presented a model which demonstrated that increased low-latitude upwelling rates during glacial times

would be expected to transfer nutrients from intermediate waters into greater depths. Each time nutrients are cycled into surface waters by low-latitude upwelling, there is a fixed chance (about 10%) that organic debris will escape degradation during descent through the upper water column. Each time a phosphorus atom is cycled into the surface ocean, it has one more change to leak into the deep ocean. When the upper ocean cycles more frequently, metabolic chemicals concentrate themselves into the deep ocean.

4. It is possible that source waters for intermediate depth waters had a lower nutrient content than they do at present. Knox and McElroy [1984] suggested that higher light levels during summers could accomplish such an effect (although they actually were thinking of higher-latitude waters that form
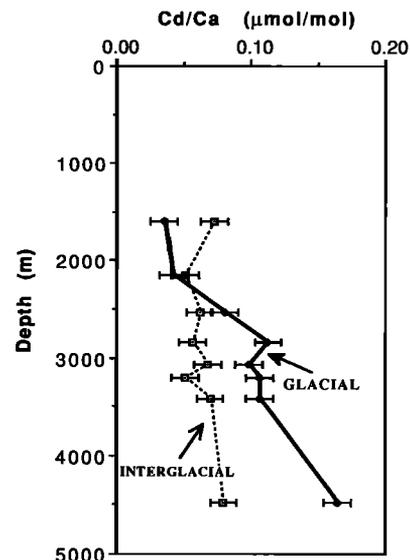

Fig. 2. Intermediate water nutrient depletion in the glacial Atlantic. Open squares are core top data; solid diamonds are from 18kyr core samples. Error bars are arbitrarily set at ±0.01, which is a subjective estimate of the minimum reliability of the data based on numerous replicate analyses.

Table 2. Data from Core V32-161

Depth, cm	Cd/Ca, μmol/mol	s.d.	n	r	$\delta^{18}O$, $^o/_{oo}$
11					3.66
16	0.169		1		
21					3.50
31					3.49
41					3.55
45	0.167		1		
51					3.45
61					3.55
66	0.206		1		
71					3.68
76	0.189		1		
81					3.86
87	0.127		1		
101					3.89
110					3.72
116					
121					3.95
124					
131					4.53
136					
141					4.77
145	0.143	0.008	2		
150					5.01
155	0.164	0.014	3		
160					5.06
165	0.143	0.004	3		
170					5.07
175	0.143	0.014	3		
181					4.85
185	0.140	0.017	3		
190					4.92
196	0.104	0.024	3		
196	0.108		1		
206	0.105	0.004	2		
210					4.81
220	0.169		1		
237				1	
243					4.45

Oxygen and carbon isotope data from N.J. Shackleton (personal communication, 1987). n is the number of analyses in the mean; r is the number of samples rejected from the mean. Although most analyses were of Uvigerina spp., the sample at 196 cm includes a C. wuellerstofi analysis which agrees with the Uvigerina analysis (.104 average of 3 Uvigerina; .108 for C. wuellerstofi).

bottom water). More recently, Martin and Gordon [1988] and Martin and Fitzwater [1988] suggested that iron is a limiting nutrient in the subpolar ocean and that increased dust fluxes during glacial times may have stimulated more biological activity. If this process occurred in the higher-nutrient water masses which form Pacific intermediate waters, it could account for nutrient depletion in the Pacific.

5. Some biologists and chemists who have studied the effect of productivity levels on particle fluxes (in daily- or weekly- variant upper-water-column regimes) argue that recycling of carbon is more efficient in times of low productivity than during those of high-productivity [Bishop et al., 1980]. If so, then an increase in the frequency of these high-productivity events would drive carbon more efficiently into the deep ocean; e.g. perhaps recycling only 80% of the

organic matter in the upper 2500 m, compared to about 90% at present. This change would transfer nutrients and metabolic CO_2 into the deep ocean at the expense of the intermediate ocean.

Until we have more evidence, it will be difficult to assign any one of these mechanisms the dominant role. As will be seen, the effect on atmospheric CO_2 of several of these mechanisms is similar, so it is possible to examine the consequences of this empirically observed phenomenom without understanding the primary cause. Nonetheless, if we are ultimately to acquire a predictive understanding of the process lowering glacial CO_2, we will have to understand which specific mechanisms are operating.

A Scenario for Glacial CO_2

This model for the transition from an interglacial high CO_2 world to a low-CO_2 glacial world assumes that there are two extreme states of ocean chemical distributions (see Figure 4). For reasons that will become apparent, these states are not considered "Interglacial" and "Glacial", but rather "Deglacial" and "Preglacial":

1. A new ocean circulation and biology regime emerges which alters the nutrient structure of the ocean, from a deglacial mode in which intermediate waters are nutrient-rich to a preglacial mode in which intermediate waters (above 2500 m) are nutrient-depleted. CO_2 and nutrients are transferred from intermediate waters into the deep waters; the total nutrient content of the ocean is constant.

2. As a result of this redistribution of light metabolic carbon from intermediate waters into deep waters, the carbon isotope contrast between surface and deep waters [$\Delta\delta^{13}C$(P-B)] increases. The oxygen content of intermediate waters increases at the expense of lowered oxygen content of deep waters. Atmospheric CO_2 is not affected directly by this change in chemical distributions.

3. Higher deep CO_2 decreases the carbonate ion concentration [$CO_3^=$] of the deep ocean. Decreased [$CO_3^=$] results in higher carbonate dissolution rates in the deep sea and thereby creates an imbalance between carbonate input from continental weathering and output by deep sea sedimentation. The alkalinity of the ocean rises at a rate determined by the excess of continental supply relative to sedimentation and dissolution of carbonate sediments. The response time for this restoration is at least 2500 years and perhaps as long as 6000 years [Broecker and Peng, 1987; Boyle, 1983]. Hence the deep carbonate ion concentration is restored to its steady state value several thousand years after the initial change.

4. This increase in oceanic alkalinity lowers the CO_2 partial pressure over the surface ocean. The CO_2 content of the atmosphere approaches the new lower equilibrium value at the same rate as the alkalinity changes, i.e., several thousand years.

Similar reasoning applies to the transition from glacial to interglacial conditions. In this case, nutrients move from the deep ocean into the intermediate ocean, deep [$CO_3^=$] increases, and there is there is an excess of carbonate sedimentation over input. The balance is restored with a response time of several thousand years, and the carbon dioxide content of the atmosphere increases.

Qualitatively, this scenario eliminates a number of discrepancies between observations and previous models for glacial CO_2:

1. $\Delta\delta^{13}C$(P-B) changes several thousand years before atmospheric CO_2 does, in accord with the observations. In
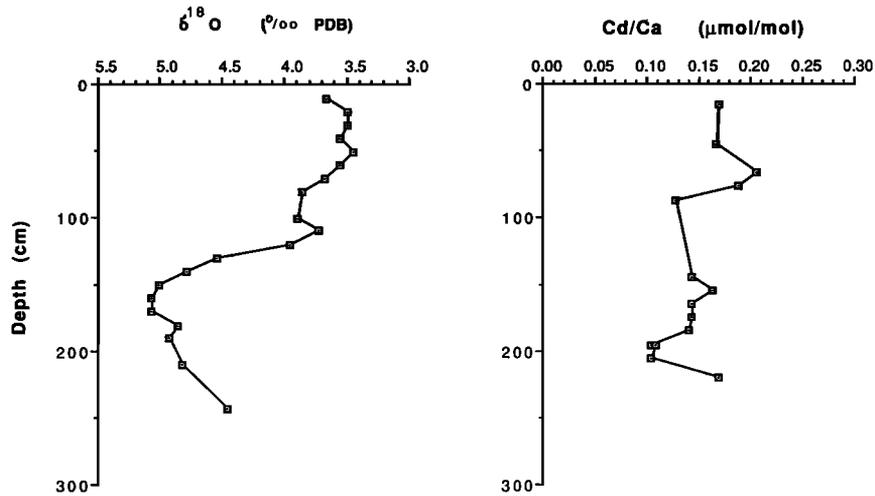
V32-161   48°17′ N   149°04′E   1600m

Fig. 3. Data from core V32-161, located on the continental margin of the Sea of Okhotsk, northeast Pacific ocean. Most samples were run in duplicate (see table 2). Note that the lowest values occur in the glacial section, particularly about 40 cm below the $\delta^{18}O$ maximum. Highest values occur in the Holocene, particularly about 70 cm below the core top.
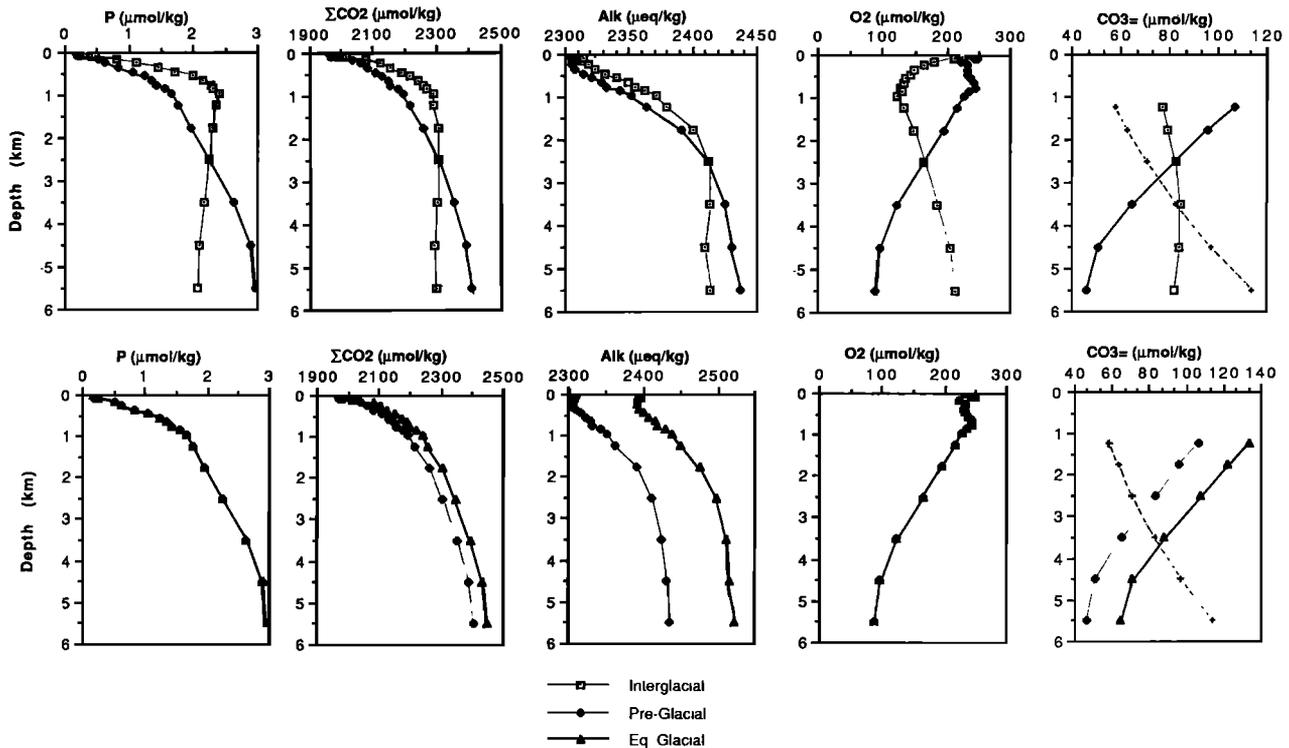

Interglacial
Pre-Glacial
Eq Glacial

Fig. 4. Profiles illustrating the proposed changes occuring in the preglacial and equilibrium glacial ocean. (Top) comparison of modern (interglacial) ocean data from the Geochemical Ocean Sections Study (GEOSECS) (open squares) with proposed preglacial state of the ocean (solid diamonds), with a transfer of organic metabolites (P, CO₂) from the intermediate depth ocean into the deep ocean. "Critical" (saturation) carbonate ion concentration indicated by crosses (dashed line). Note that the chemical rearrangement makes the deep ocean more undersaturated, so that the lysocline (the crossover point of the new [CO₃⁼] with critical [CO₃⁼]) moves upward. This movement leads to higher rates of carbonate dissolution. (Bottom) comparison of proposed preglacial state of the ocean to the state attained when carbonate dissolution has restored the carbonate system to its steady state value. P and O₂ are unchanged; CO₂, Alk, and [CO₃⁼] respond to carbonate dissolution. Note that the lysocline moves back to its original interglacial position. This movement restores carbonate dissolution rates back to the steady state level.
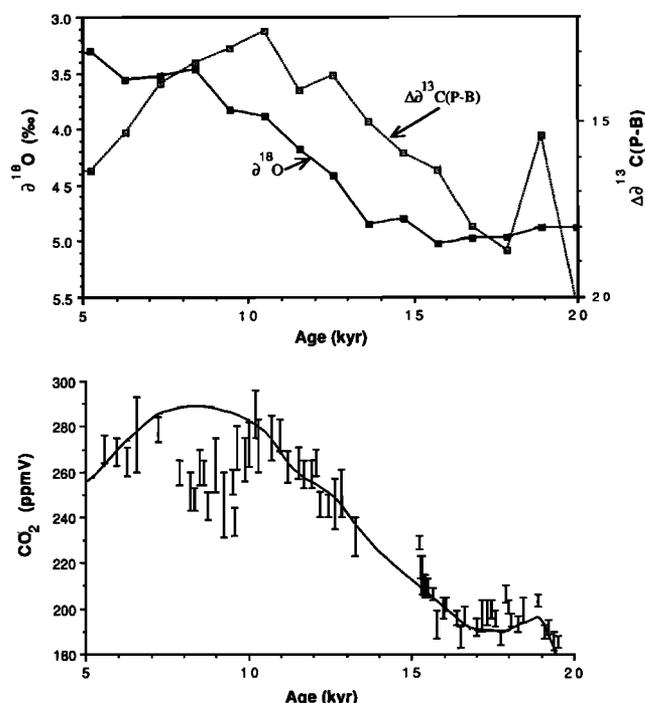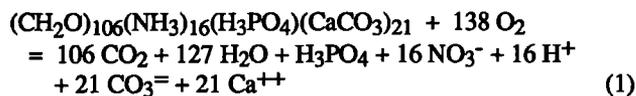
Fig. 5. Comparison of Byrd station CO_2 data [Neftel et al., 1988] with V19-30 $\Delta\delta^{13}C$(P-B) data. Raw $\Delta\delta^{13}C$ data is shown at top, in juxtaposition with the $\delta^{18}O$ data, showing the "lead" of $\Delta\delta^{13}C$(P-B) relative to the $\delta^{18}O$ response. At the bottom, the line shows arbitrarily-scaled output from using the V19-30 $\Delta\delta^{13}C$(P-B) data as input into a linear equation with a 3 kyr time constant. While the match is not perfect, the overall glacial to interglacial CO_2 change occurs on a timescale that is consistent with the V19-30 $\Delta\delta^{13}C$(P-B) data input when put through the carbonate response model described in the text.

fact, the lag of CO_2 relative to $\Delta\delta^{13}C$(P-B) is consistent with a time constant of several thousand years (Figure 5).

2. Antarctic nutrient concentrations need not change, hence there is no conflict with the planktonic $\delta^{13}C$ and Cd data.

3. More oxygen remains in intermediate waters because of the depleted nutrient content. The oxygen minimum zone (which was thought to be most in danger of approaching anoxia) would have higher oxygen concentrations during glacial times, and aerobic benthic organisms would continue to deposit their shells.

As has been shown elsewhere [Boyle, 1988], the magnitude of the glacial-interglacial atmospheric CO_2 change can be estimated if we assume that the deep box is homogeneous and that all sinking particulate biogenic matter degrades in "Redfield" proportions 106 CH_2O:21 $CaCO_3$: 16 N:1 P.

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)(CaCO_3)_{21} + 138 \, O_2$$
$$= 106 \, CO_2 + 127 \, H_2O + H_3PO_4 + 16 \, NO_3^- + 16 \, H^+$$
$$+ 21 \, CO_3^= + 21 \, Ca^{++} \qquad (1)$$

(This stoichiometry is not entirely appropriate, since the mean regeneration depth of calcium carbonate is deeper than that of organic carbon. This issue will be dealt with in a following section). For a given change in the deep phosphorus content

(ΔP), the deep total dissolved carbon dioxide (ΣCO_2) and alkalinity (ΔAlk) will initially change by

$$\Delta\Sigma CO_2 = 127 \, \Delta P \qquad (2)$$

$$\Delta Alk = (42-16) \, \Delta P = 26 \, \Delta P \qquad (3)$$

and [$CO_3^=$] will drop. To restore [$CO_3^=$] to its initial value, ΔAlk - ΔCO_2 must be returned to zero by the addition of 2 equivalents of alkalinity for every mole of $CaCO_3$ dissolved:

$$\Delta Alk = 26 \, \Delta P + 2 \, \Delta(CaCO_3) = 26 \, \Delta P + 2 \, (101 \, \Delta P)$$
$$= 227 \, \Delta P \qquad (4)$$

$$\Delta CO_2 = 127 \, \Delta P + \Delta(CaCO_3) = 127 \, \Delta P + 101 \, \Delta P$$
$$= 228 \, \Delta P \qquad (5)$$

When this deep ocean water upwells to the surface, Alk and CO_2 are decreased by removal of biogenic debris:

$$\Delta Alk(surface) = \Delta Alk(deep) - 26 \, \Delta P$$
$$= 227 \, \Delta P - 26 \, \Delta P = 201 \, \Delta P \qquad (6)$$

$$\Delta CO_2(surface) = \Delta CO_2(deep) - 127 \, \Delta P$$
$$= 228 \, \Delta P - 127 \, \Delta P = 101 \, \Delta P \qquad (7)$$

The expected new atmospheric CO_2 content can be calculated by substituting these values into the thermodynamic equations for pCO_2 of surface waters as a function of ΣCO_2 and Alk (in this work the calculation was done according to the constants summarized by Millero [1979]).

The average change in intermediate water nutrient content appears to be about 0.6 $\mu mol/kg$. The volume of the ocean above 2500 m is nearly equal to the volume below that depth [Menard and Smith, 1966], so deep ocean phosphorus must have increased by the same amount. According to (3), at steady state this change would increase the alkalinity of the ocean by 61 $\mu eq/kg$; this alkalinity change is equivalent to a 54-ppmV drop in atmospheric CO_2. Thus the magnitude of the CO_2 change calculated in this fashion is about half of that observed in polar ice cores (about 90 ppmV). The residual might be due to underestimation of intermediate water nutrient depletion or perhaps due to contributions from other mechanisms.

One aspect of the ocean hydrography-CO_2 system that bears noting is that the alkalinity response of the CO_2 system integrates and minimizes short-term variability in ocean circulation. Since the circulation time of the ocean is under 1000 years, it is possible for the ocean to change its state in a relatively short time. Even if the ocean can change its state in less than a thousand years, the alkalinity lag smooths out these variations and acts as a stabilizing force on climate.

Equilibrium Five-Box Model Illustration

A simple 5-box model was constructed to illustrate the concept quantitatively. The goal of this model is to include the most relevant processes without introducing excessive complications. The following requirements dictated the structure of the model: (1) high-nutrient and low-nutrient polar surface boxes were included so that the preformed
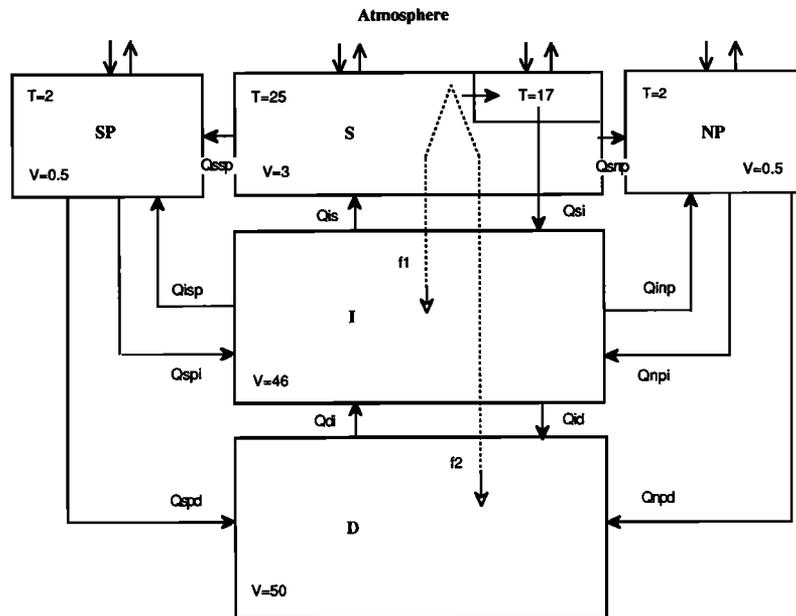
Fig. 6. Equilibrium box models for atmospheric CO_2. Flows of water are indicated by solid arrows; equilibration between atmosphere and surface ocean is indicated by arrows and transfer of sinking particles is indicated by dotted line and open arrows. Relative volumes of boxes are indicated at in the bottom corner; temperature of gas equilibration is indicated in the top corner. SP, nutrient-enriched "south polar" box; NP, nutrient-depleted "north polar" box; S, warm surface box; I, intermediate box; D, deep box.

nutrient effects on CO_2 could be controlled and so that advective sources of cold low- and high-nutrient water would be available, (2) separate intermediate and deep boxes were required to allow for variations in vertical nutrient fractionation, and (3) the warm surface ocean covers the largest portion of the surface area of the ocean, and hence must be included to account for gas exchange between the ocean and atmosphere. Model details are described in Appendix A and illustrated in Figure 6. The model is intended to serve as a simple illustration of the above scenario, and there is no reason to defend the realism of the model as a complete and definitive description of the late Quaternary ocean. Some processes which are likely to be significant (such as the effect of forest/soil regrowth on carbon isotopes) are neglected deliberately to keep the model simple.

Inter-box fluxes in the equilibrium-interglacial models IG-1 and IG-2 (see Tables 3 and 4 and Figure 6) were adjusted to approximate modern oceanic distributions [Takahashi et al., 1981] and set to fill the ocean with new bottom water in 1000 years. There are many other possible solutions to the modern distributions, even given the restricted structure of this model. A particularly interesting case is discussed in Appendix B. There is a tradeoff between the deep carbonate regeneration parameter (i.e., the fraction of carbonate assumed to dissolve in the deep ocean) and the mixing rate between intermediate and deep ocean. These two cases are henceforward refered to as low-mixing and high-mixing parameters. This tradeoff is illustrated in models IG-1 and IG-2, which have similar chemical distributions but assume quite different carbonate regeneration parameters and intermediate-deep mixing rate. It appears that the vertical distribution of alkalinity does not mandate a unique value for the percentage of carbonate that dissolves in the deep ocean, contrary to most current opinion [Edmond, 1974; Dymond and Lyle, 1985].

Equilibrium-glacial models (Tables 3 and 4) were modified from the equilibrium-interglacial glacial model to produce a specified vertical transfer of nutrients from the intermediate ocean into the deep ocean while keeping polar surface nutrient concentrations constant. This transfer was achieved in several ways:

G-1 and G-2: The vertical regeneration of organic matter was altered for more remineralization in the deep box. This change is the most effective way to alter atmospheric CO_2, since it puts "pure" CO_2 into the deep box and maximizes the alkalinity response. In this version, reduction of mean intermediate water phosphorus by 0.4 μmol/kg elicits a pCO_2 reduction of 46 ppmV (low mixing) and 41 ppmV (high mixing). The response here does not depend much on assumed alkalinity regeneration parameters.

G-3 and G-4: The rate of intermediate water/warm surface water overturn (i.e., wind-driven upwelling) was increased in these trials. G-3 used "low mixing, low deep carbonate regeneration" parameters and G-4 used "high mixing, high deep carbonate regeneration" parameters. The same intermediate water nutrient depletion seen in the other glacial models was obtained in both trials, although a larger upwelling rate increased was needed in the "high-mixing" case G-4. In low-mixing G-3, pCO_2 was reduced by 27 ppmV, whereas in high-mixing G-4, pCO_2 only went down by 13 ppmV. If all carbonate regeneration occurs in the deep box, the pCO_2 will actually increase. The enhanced upwelling mechanism cannot be as effective in reducing pCO_2 as G-3 because of the additional deep alkalinity regeneration that accompanies the increase in surface carbonate productivity.

G-5: Here, the intermediate water nutrient reduction is achieved by changing most North Atlantic Deep Water (NADW) into North Atlantic Intermediate Water (NAIW) (low-mixing case only). This change reduces intermediate water phosphorus by 0.4 μmol/kg, but pCO_2 decreases by only 8 ppmV. Hence simple changes in the NADW

Table 3. Variable Parameters Input to Box Model

	IG-1	IG-2	G-1	G-2	G-3	G-4	G-5
$f_d(Org)$	0.13	0.14	0.26	0.40	0.13	0.14	0.13
$f_d(CaCO_3)$	0.27	0.42	0.27	0.42	0.27	0.42	0.27
Q_{s-i}	126	126	126	126	270	400	126
Q_{i-s}	159	159	152	152	296	426	152
Q_{i-sp}	28	28	38	38	28	28	29
Q_{sp-i}	16	16	19	19	9	9	10
Q_{i-np}	11	11	16	16	16	16	15
Q_{np-i}	16	16	21	21	21	21	36
Q_{sp-d}	20	20	20	20	20	20	20
Q_{np-d}	20	20	20	20	20	20	4
Q_{s-np}	25	25	25	25	25	25	25
Q_{s-sp}	8	8	1	1	1	1	1
Q_{i-d}	10	60	10	100	10	60	10
Q_{d-i}	50	100	50	60	50	100	34

Water fluxes (Q) in sverdrups (1 Sv = $10^6 m^3/sec$). For explanation of model code, see footnote to table 4.

ventilation are not an effective means to change atmospheric CO_2. A decrease in intermediate water phosphorus is not in itself sufficient to elicit an atmospheric CO_2 response.

These calculations show that it is possible for a transfer of CO_2 from intermediate waters into deep waters to significantly affect atmospheric carbon dioxide by eliciting an alkalinity response. The most effective way to do this is to remineralize more organic matter in the deep ocean. It is also possible to obtain a response by altering wind-driven upwelling, but the magnitude (and even the direction) of the response to this mechanism depends strongly on the assumed regeneration function.

While the calculations show that it is possible to maintain polar preformed phosphorus constant despite a fall in intermediate phosphorus concentrations, it is not obvious why the ocean should adopt the configuration required to achieve this stability. In the model, the effect is achieved by altering the mix of zero-P warm surface water and higher-P intermediate water flowing into the polar boxes. Intermediate-depth nutrient depletion could serve as a mechanism to deplete Antarctic preformed nutrients, and it offers a potential mechanism for the preformed phosphorus response to amplify the CO_2 change due to the alkalinity response.

Deep Sea Oxygen

The consequences of the vertical chemical reorganization on the oxygen content of intermediate and deep waters are predicted by the equilibrium models. In the absence of major changes in ocean temperatures, the nutrient redistribution proposed above will change oxygen levels by about 80-100 $\mu mol/kg$. Hence, in the preglacial ocean, intermediate oxygen levels would rise to 190-210 $\mu mol/kg$, and deep ocean concentrations would fall to 90-100 $\mu mol/kg$. The oxygen crisis that occurs in previous models is averted. Only in the most oxygen depleted deepwaters of the ocean would near-anoxia occur. The oxygen content of the Panama Basin is 115 $\mu mol/kg$, so these waters would approach oxygen depletion. If the deep waters of the ocean were about 2°C cooler [Shackleton and Chappell, 1986], then the deepwater oxygen concentration of the Panama Basin during glacial times would have been 20-40 $\mu mol/kg$. It may also help that the Panama Basin is rapidly (~50 yr) ventilated over a relatively shallow sill depth (2920 m) in the Ecuador Trench and may be influenced somewhat by higher intermediate water oxygen levels [Lonsdale, 1977].

While average deep ocean oxygen is not in danger of depletion during glacial times, this model predicts that the oxygen content of the deep ocean decreases significantly, and any sedimentary process which depends on the bottom water oxygen content should record this event. Using the model developed by Emerson [1985] the predicted decrease in deep water oxygen could account for the increased organic carbon content of Panama Basin sediments [Pedersen, 1983]. The predicted decrease in oxygen with depth might also account for the increase in organic carbon content with depth observed for glacial age sediments in the eastern equatorial Atlantic [Curry and Lohmann, 1983]. Another consequence of this model is that the oxygen content of the middepth ocean would have increased, so we would expect to find lower organic carbon contents in glacial-age sediments from intermediate-depth ocean cores (in regions where surface productivity did not increase). These changes also have implications for the sedimentary cycle of redox-sensitive elements such as manganese, which may explain the occurrence of correlations between sedimentary manganese and climate [Bostrom, 1970; Berger et al., 1983].

Table 4. Results of Box Model Study

	P	CO$_2$	Alk	δ^{13}C	O$_2$	pCO$_2$
		IG-1				
Warm surface	0.00	1925	2319	2.41	265	281
South polar surface	1.63	2149	2348	0.44	340	281
North polar surface	0.64	2118	2331	1.68	340	257
Intermediate	2.09	2255	2357	0.02	65	
Deep	2.19	2280	2390	-0.06	168	
$\Delta\delta^{13}$C(P-B)				2.47		
		IG-2				
Warm surface	0.00	1925	2319	2.42	265	281
South polar surface	1.63	2149	2348	0.44	340	281
North polar surface	0.64	2117	2331	1.68	340	255
Intermediate	2.10	2255	2357	0.01	65	
Deep	2.18	2279	2390	-0.05	112	
$\Delta\delta^{13}$C(P-B)				2.46		
		G-1				
Warm surface	0.00	1974	2440	2.35	265	235
South polar surface	1.64	2219	2469	0.45	340	234
North polar surface	0.66	2188	2452	1.63	340	216
Intermediate	1.68	2258	2470	0.44	127	
Deep	2.58	2378	2488	-0.43	118	
$\Delta\delta^{13}$C(P-B)				2.78		
		G-2				
warm surface	0.00	1971	2427	2.37	265	241
South polar surface	1.67	2214	2457	0.41	340	240
North polar surface	0.67	2183	2439	1.62	340	222
Intermedi	1.72	2257	2457	0.41	123	
Deep	2.54	2363	2474	-0.40	69	
$\Delta\delta^{13}$C(P-B)				2.76		
		G-3				
Warm surface	0.00	1955	2389	2.37	265	254
South polar surface	1.63	2192	2418	0.43	340	255
North polar surface	0.66	2160	2401	1.63	340	233
Intermediate	1.69	2236	2419	0.42	82	
Deep	2.56	2372	2482	-0.40	113	
$\Delta\delta^{13}$C(P-B)				2.77		
		G-4				
warm surface	0.00	1940	2353	2.39	265	268
South polar surface	1.66	2171	2383	0.39	340	268
North polar surface	0.67	2141	2365	1.62	340	248
Intermedi	1.72	2225	2384	0.39	65	
Deep	2.53	2358	2468	-0.38	37	
$\Delta\delta^{13}$C(P-B)				2.76		
		G-5				
Warm surface	0.00	1958	2371	2.39	265	273
South polar surface	1.65	2189	2401	0.42	340	272
North polar surface	.64	2157	2382	1.67	340	250
Intermediate	1.71	2243	2402	0.43	113	
Deep	2.54	2341	2453	-0.42	139	
$\Delta\delta^{13}$C(P-B)				2.80		

Models are as follows: IG-1, interglacial model with low intermediate-deep (I-D) mixing and low deep CaCO$_3$ diss.; IG-2, interglacial model with high I-D mixing and higher deep CaCO$_3$ diss.; G-1, glacial model with higher deep organic regeneration only; low I-D mixing, low deep CaCO$_3$ regeneration; G-2, glacial model with higher deep organic regeneration only; high I-D mixing, high deep CaCO$_3$ regeneration; G-3, glacial model with increased upwelling only; low I-D mixing, low deep CaCO$_3$ regeneration; G-4, glacial model with increased upwelling only; high I-D mixing, high deep CaCO$_3$ regeneration; G-5, glacial model with NADW transformed into NAIW only; low I-D mixing, low deep CaCO$_3$ regeneration.
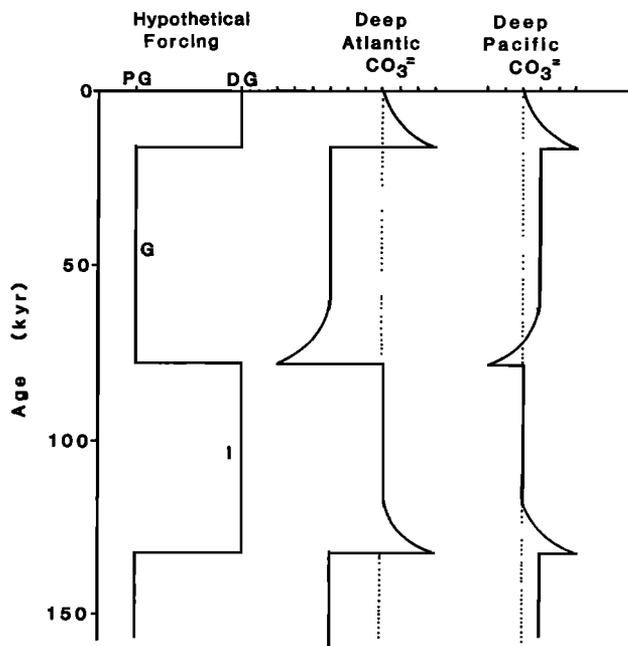
Fig. 7 Schematic drawing illustrating the carbonate ion response to hypothetical "100 kyr" square wave forcing. The dashed line indicates the "equilibrium interglacial" [$CO_3^=$] position for both oceans. The responses are (1) an equilibrium response due to basin-basin transfers caused by reduction of North Atlantic Deep Water flow, (2) a transient response due to the intermediate-deep chemical transfers, and (3) the restoring equilibrium forcing which drives carbonate sedimentation back into balance.

Late Quaternary Carbonate Dissolution Cycles

Alkalinity and circulation changes predicted by this model have major implications for calcium carbonate sedimentation. In the modern ocean, carbonate preservation is enhanced in shallow sediments relative to deeper ones, because solubility increases with increasing pressure. Carbonate preservation is better in the Atlantic relative to the Pacific, because low-CO_2 North Atlantic Deep Water is less corrosive to carbonate than high-CO_2 Pacific Deep Water. Carbonate deposition in the Atlantic equals that deposited in the rest of the ocean [Turekian, 1965] even while containing only 25% of the total seafloor area [Menard and Smith, 1966]. In the steady state preglacial ocean, carbonate preservation is enhanced in the deep Pacific, and more dissolution occurs in the deep North Atlantic, because less CO_2 is pushed into the deep North Pacific by North Atlantic Deep Water [Boyle and Keigwin, 1982, 1985]. In shallower cores, steady-state preservation is enhanced in both ocean basins, because of lower dissolved CO_2 levels.

The carbonate preservation record is complicated by the alkalinity lag relative to the nutrient structure. Ignoring other factors that influence carbonate sedimentation, the following sequence of events is expected (Figure 7):

1. Immediately following the preglacial nutrient rearrangement, carbonate dissolution increases in the deep North Pacific and increases dramatically in the deep North Atlantic.

2. As the alkalinity of the ocean moves toward the new higher steady-state value, carbonate saturation increases everywhere in the ocean. After the rapid response to ocean circulation in the first step of this sequence, Pacific carbonate preservation becomes better than it was during late interglacial

times. In the Atlantic, however, the initial dissolution pulse is followed by only slightly improved preservation, that is still worse than preservation during late interglacial times.

3. Immediately upon restoration of ocean circulation patterns to the deglacial mode, there is a preservation spike throughout the deep ocean, as acidic CO_2 is moved out of the deep ocean into intermediate waters [Diester-Haas et al., 1973].

4. As oceanic alkalinity approaches the steady state deglacial level, dissolution increases throughout the ocean. In the deep Pacific, this extra dissolution results in poorer preservation than during late glacial times. But in the Atlantic, while preservation is poorer than it was immediately following the change in ocean circulation, it is better than it is during "glacial" periods, however.

The "lag" of Pacific carbonate sedimentation relative to climate change has been commented on previously [Moore et al., 1974] and attributed to the response time of the calcium carbonate system [Boyle, 1983], so the above scenario only belatedly provides a particular mechanism for this observation. The sequence of events is consistent with the evidence on deep Pacific dissolution provided by Keir and Berger [1985] (Figure 8). This new model provides more insight into Atlantic carbonate records. As Crowley [1983] has pointed out, over the last 140,000 years the most intense dissolution (in many parts of the Atlantic) occurred during oxygen isotope stage 4; this effect is expected when glaciation follows a long period of warm climate such as isotope stage 5. Furthermore, dissolution became quite a bit less severe during stage 3; this observation is in accord with Atlantic dissolution relaxation following alkalinity response combined with a return to oceanic conditions closer to the deglacial mode.

Conclusion and Speculations

Vertical rearrangement of oceanic chemical distributions is a potentially important mechanism for driving late Quaternary
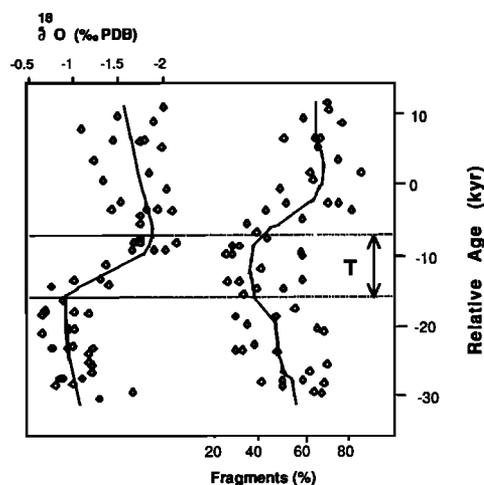

Fig. 8. Stacked $\delta^{18}O$ and %fragments records from terminations in core V28-238, redrawn from Keir and Berger [1985]. Note that best preservation (fewer fragments, higher [$CO_3^=$]) occurs on the termination, followed by the most intense dissolution (greater fragmentation, lower [$CO_3^=$]) several thousand years after peak interglacial climate. This should be compared with the Pacific diagram from Fig. 7 but note that sense of direction is reversed in the two figures.

glacial-interglacial CO_2 fluctuations. Increasing oceanic alkalinity follows upon establishment of the deep-CO_2-rich preglacial mode of the ocean. Since the alkalinity of the ocean takes several thousand years to respond to the change in oceanic nutrient structure, atmospheric CO_2 lags significantly behind the oceanographic forcing. This alkalinity lag accounts for the phase lead of $\Delta\delta^{13}C(P-B)$ and Cd relative to CO_2 and $\delta^{18}O$. However, this mechanism can only account for changes in CO_2 on the 10^3 year time scale; more rapid variations would require some other mechanism.

What this model does not explain is why the ocean alternates between preglacial and deglacial modes. Since it has been established that there are strong statistical relationships between climate and Milankovitch-style orbital insolation variation, it seems likely that these insolation variations may somehow drive the ocean between modes. Exactly how orbital insolation would drive the ocean in this way is still a mystery. Future observations on the timing and geographic extent of intermediate and deep water nutrient contents should settle these questions.

Appendix A: Five-Box Ocean Model

The compositions of the warm surface box and the two cold polar boxes control atmospheric CO_2. Two cold polar boxes are needed to represent polar waters similar to those of the modern North Atlantic (which are nutrient-impoverished), and those similar to the modern Antarctic (which are nutrient-enriched). Although it is convenient to think of these two polar boxes as "Atlantic" (north polar surface) and "Antarctic" (south polar surface), there is no necessity for these water sources to be geographically restricted. In order to represent the transfer of nutrients from intermediate depths into the deep ocean, intermediate and deep ocean boxes are needed. In this model, the two ocean basins are not separated.This additional complication would be necessary for a full description of variability in the system along with some additional vertical resolution. The simplification was made deliberately to limit the number of free parameters.

Water fluxes between boxes are restricted in a few cases, partly based on oceanographic information and partly based on the desire to minimize the number of variables. It is assumed that water flows only from warm surface waters into cold polar waters, and not vice-versa; this a reasonable representation of the thermohaline character of high-latitude circulation. In view of data indicating that Antarctic polar surface nutrients did not change much, exchanges between intermediate and nutrient-enriched polar surface waters are adjusted to keep polar surface phosphorus constant. It is also assumed that deep water formation in polar regions is a one-way process; while there is an upwelling flux from intermediate waters into the polar oceans, there is no direct upwelling from the deep ocean into any of the surface boxes.

These simplifications and assumptions are not really necessary for functioning of the proposed mechanisms. The aim has been to keep the model as simple and determinate as possible, and to minimize arbitrary adjustments of variable parameters. The solutions adopted for the equilibrium extrema were arrived at by trial and error, seeking to maximize the resemblance of the equilibrium deglacial model to the modern ocean (GEOSECS data), and to produce the intermediate-to-deep chemical fractionation in the equilibrium preglacial model. The solutions adopted here are not the only ones which can produce the intermediate-deep chemical fractionations, even given the structural constraints outlined here. Models

IG-1 and IG-2 illustrate this point. While the interbox fluctuations were chosen to be qualitatively defensible, they are not meant to be definitive descriptions of the ocean at any time. This uncertaintly should not be considered a deficiency, since the goal of this model is not to describe exactly how modern and glacial oceans function, but rather to illustrate the functioning and response times of processes that were of importance in controlling atmospheric CO_2 fluctuations.

A feature of this box model which differs significantly from previous models lies in its treatment of the upwelling and downwelling into/from the warm surface box. Because the upper ocean is ventilated more by late winter convection than vertical physical mixing [Jenkins, 1980], the "warm surface water" that returns into the intermediate box is actually colder, and its gas content reflects that cooler temperature. In this model, it is assumed that the downwelling water is $17°C$ and has higher CO_2 and $O2$ concentrations consistent with equilibration with the atmosphere at this temperature. Computationally, this is achieved for CO_2 by withdrawing some CO_2 from the upwelling intermediate water and placing it directly into the downwelling flux; for oxygen, it is achieved by specifying that oxygen in the the downwelling water is 265 $\mu mol/kg$. The waters in the cold surface box are assumed to have 340 $\mu mol/kg$ of oxygen.

In addition to physical water circulation, chemical transfer processes were as follows:

1. All of the phosphorus upwelling into warm surface waters is removed through the formation of "Redfield" particulate matter whose composition is

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)(CaCO_3)_{21}$$
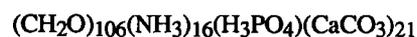
However, it is assumed that 20% of the $CaCO_3$ formed "comes from" river input of dissolved $CaCO_3$ and this fraction is sedimented onto the seafloor without dissolution.

2. This particulate matter is regenerated into intermediate and deep boxes with appropriate regeneration efficiencies (f_1 for the intermediate box; f_2 for the deep box; f values differ for organic matter [f(org)] and calcium carbonate [f(inorg)]). The f efficiencies for organic matter are constrain by estimates for the vertical regeneration efficiencies of organic matter [Jenkins, 1980; Suess, 1980], and the f efficiency for $CaCO_3$ is selected to give the correct modern intermediate-deep alkalinity distribution (as based on GEOSECS data [Takahashi et al., 1981]).

3. A correction for the effect of nitrate regeneration on alkalinity is made in the fashion outlined by Broecker [1982a,b].

4. No biological activity is included in the polar surface boxes, in part because the rate of biological production relative to physical turnover is low and in part because the effects of this process have been already discussed in published models and there is no need to investigate it here. The goal of this model is to illustrate a few processes which go on in the real world, not to exhaustively mimic the real world.

5. Gas exchange through the atmosphere is allowed to equilibrate the pCO_2 between the surface boxes. Computationally, this is accomplished by shifting CO_2 between the warm surface box and the cold polar boxes by the amount required to balance their pCO_2. (Note: after this work was finished, a flaw was found in the algorithm used for pCO_2. As a result, the north polar box always has pCO_2 about 20 ppmV lower than the other two surface boxes. Since this degree of disequilibrium is common in the modern ocean and since the revision would not change the solution

significantly, it was not deemed worthwhile to redo the model).

6. Carbon isotopes are incorporated into the model assuming that organic carbon has $\delta^{13}C = -22^0/oo$, that inorganic carbonate has $\delta^{13}C$ equal to that of warm surface water, and that the CO_2 which is transfered into the cold polar boxes is $1^0/oo$ heavier than that of the warm surface box from which it comes. The latter assumption is chosen because the equilibrium carbon isotope composition at 2^0C is $1^0/oo$ heavier than at 25^0C. The additional shift in the carbon isotope system due to this assumption is relatively minor.

7. Oxygen is incorporated into the model assuming that 138 oxygen molecules are consumed for every 106 organic carbon molecules regenerated. Takahashi et al. [1985] have recommended a higher value (170) for this ratio. The lower value was chosen, not because it necessarily is considered better than the newer estimate, but rather because a model of the structure given here results in too little oxygen in the "modern" ocean when the higher value is used. This problem could be due just as likely to deficiencies in the realism of this model as it is due to problems with the O_2:C Redfield ratio; this problem needs to be considered in more detail elsewhere. Cold surface waters are assumed to start with 340 µmol/kg.

Given these assumptions and the structure of the model shown in Figure 5, the equations are determined, and it should not be necessary to list all of them here except for the example of the intermediate box (P = phosphorus concentration; C = CO_2 concentration, A = alkalinity, $\delta = \delta^{13}C$, X = oxygen).

The phosphorus balance for the intermediate box is

$$0 = -(Q_{i-s} +Q_{i-np} +Q_{i-sp} +Q_{i-d})P_i +Q_{d-i}Pd$$
$$+Q_{sp-i}P_{sp} +Q_{np-i}P_{np} \qquad + f_1(org)Q_{i-s}P_i$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (A1)$$

..............water fluxes..............   ...regeneration...

The carbon balance for the intermediate box is

$$0 = -(Q_{i-s} +Q_{i-np} +Q_{i-sp} +Q_{i-d})C_i +Q_{d-i}C_d +Q_{sp-i}C_{sp}$$
$$+ Q_{np-i}C_{np} +Q_{s-i}C_s +\Delta C_s$$
$$+ [106f_1(org) +17f_1(inorg)] Q_{i-s}P_i \quad (A2)$$

where $Q_{i-s}P_i$ is the net organic phosphorus flux from the surface, 106 is the C:P Redfield ratio, 17 is the "dissolvable" $CaCO_3$:P ratio, and ΔC_s is the amount of carbon which must be added to maintain pCO_2 when the 25^0C warm surface water is cooled to 17^0C before downwelling into the intermediate box. The alkalinity balance for the intermediate box is

$$0 = -(Q_{i-s} +Q_{i-np} +Q_{i-sp} +Q_{i-d})A_i + Q_{d-i}A_d + Q_{sp-i}A_{sp}$$
$$+ Q_{np-i}A_{np} + Q_{s-i}A_s +[34f_1(inorg) - 16f_1(org)]Q_{i-s}P_i$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (A3)$$

where 34is 2 equiv. Alk per 17 moles of "dissolvable" $CaCO_3$ and 16 is the number of acid equivalents released from the oxidation of 16 moles of NH_3 (from the N:P Redfield Ratio). The carbon isotope balance for the intermediate box is

$$0 = -(Q_{i-s} +Q_{i-np} +Q_{i-sp} +Q_{i-d})C_i\delta_i +Q_{d-i}C_d\delta_d +Q_{sp-i}C_{sp}\delta_{sp}$$
$$+Q_{np-i}C_{np}\delta_{np} +Q_{s-i}C_s\delta_s -(106)(22)f_1(org))Q_{i-s}P_i$$
$$+17f_1(inorg)\delta_s +\Delta C_s\delta_s \qquad\qquad (A4)$$

where the 22 is the assumed carbon isotope composition of organic carbon. The oxygen balance for the intermediate box is

$$0 = -(Q_{i-s} +Q_{i-np} +Q_{i-sp} +Q_{i-d})X_i +Q_{d-i}X_d$$
$$+340(Q_{sp-i} +Q_{np-i}) +265Q_{s-i} -138f_1(org)Q_{i-s}P_i \qquad (A5)$$

where 340 is the oxygen content of cold surface water, 265 is the oxygen content of 17^0C surface water, and 138 is the assumed O_2:P Redfield ratio.

The model was solved first by using the matrix inversion function of a microcomputer spreadsheet and then by an iterative finite difference approach (to verify the accuracy of the spreadsheet inversion routine).

Appendix B: The Vertical Regeneration Cycle of $CaCO_3$

The vertical distribution of alkalinity and dissolved carbon dioxide is determined by a balance between (1) the vertical regeneration functions of sinking organic debris and $CaCO_3$ and (2) the intensity of mixing between intermediate and deep waters. It is believed that most organic matter sinking out of the euphotic zone decomposes in the upper ocean (about 85%). This belief is based on models of oxygen consumption in the upper ocean [Jenkins, 1980] and fluxes estimated by sediment traps [Suess, 1980]. It is generally assumed that $CaCO_3$ is returned into solution deep in the water, perhaps dominantly by dissolution on the seafloor. The flux of organic carbon out of the euphotic zone is higher than that of inorganic carbonate, but sediment traps deployed in the deep ocean generally show C_{org}: $CaCO_3$ ratios close to 1:1 (see data summarized by Dymond and Lyle, [1985], due to the preferential degradation of organic carbon relative to carbonate. The vertical profile of alkalinity shows a deep maximum than phosphorus and is consistent with a deeper regeneration cycle [Edmond, 1974]. Neither line of evidence concerning the relative efficiency of organic and inorganic regeneration rules out significant calcium carbonate dissolution during descent through the water column. Because the collection efficiency of shallow traps is uncertain (because of artifacts created by hydrodynamic effects and "swimmers"), changes in the vertical flux of $CaCO_3$ are not easily established.

The observed alkalinity and dissolved carbon dioxide profiles could be generated with quite different vertical regeneration functionalities. The simplest illustration of this point can be made with a two-box model. Fluxes of water (Q) between the intermediate and deep boxes must be equal. In the euphotic zone of the upper box, organisms transform dissolved elements into a flux of particulate phosphorus (Fp), organic carbon (106Fp) (denoted by "O" subscript), and inorganic calcium carbonate (21Fp) (denoted by "I" subscript). Some of this sinking particle flux dissolves in the upper box $(1-f_{O-d}, 1-f_{I-d})$, some dissolves in the deep box (f_{O-d}, f_{I-d}), and some of the carbonate is permanently removed from the system into sediments (5Fp, which is taken as equal to the influx of calcium carbonate from rivers into the upper box). The mass balance equations for dissolved carbon dioxide (C) and alkalinity (A) determine two linearly independent equations for this system (written here for the deep box; the equations for the upper box are dependent and differ only by sign inversion):

$$16 F_P f_{I-d} + 106 F_P f_{O-d} + Q (C_u - C_d) = -116 F_P \qquad (B1)$$

$$32 F_P f_{I-u} + Q (A_u - A_d) = -32 F_P \qquad (B2)$$

Taking the observed concentrations (C and A) and the new

production (Fp) as constraints to be fulfilled, there are three unknowns in two equations. If we presume to know the fraction of organic matter regenerated in the deep box (f$_{O-d}$), then the possible set of solutions to the system trades off changes in the interbox fluxes (Q) against the changes in the fraction of inorganic carbonate redissolved in the deep box (f$_{I-d}$). In this system, there are many possible solutions consistent with given vertical distributions of dissolved carbon dioxide and alkalinity. One extreme of this set invokes rapid interbox fluxes and a higher fraction of calcium carbonate dissolution in the deep box, and the other extreme invokes slow interbox fluxes and a lower fraction of calcium carbonate dissolution in the deep box.

This simple model illustrates a principle applicable to more complex models: one cannot tell the difference between calcium carbonate and carbon dioxide molecules that have been regenerated within a box and those that have been mixed into the box. This point is illustrated with scenarios from the more complex model in the main body of this paper (IG-1 and IG-2). Independent lines of evidence can overcome this uncertainty (e.g. sediment traps, measurements of carbonate dissolution on the seafloor, or physical evidence on intermediate-deep mixing rates), but the present state of knowledge allows one to presume a range of regeneration functions. Other authors have chosen to assume that all calcium carbonate regeneration occurs on the seafloor [Dymond and Lyle, 1985; Sarmiento et al., 1988].

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