PRESENT OCEAN

ICE AGE OCEAN

Fig. 3 Atmospheric P_{CO_2} (in p.p.m.) as predicted by our model for various values of the parameters f_{hd}, p_h and T. $f_{hd}^0 = 38.1 \times 10^6 \, m^3 \, s^{-1}$, $p_h^0 = 2.31 \times 10^6 \, mol \, C \, s^{-1}$, and $T^0 = 24.5 \times 10^6 \, m^3 \, s^{-1}$. (See text for a description of the various scenarios.) The ice age ocean has an ocean volume that has been decreased by 3.5% and a total carbon and alkalinity content increased by 6%.

signal, and the precipitation of $CaCO_3$ which would have to accompany it, poses a dilemma. A time-dependent model is needed to study the problem in more detail.

Changes in the tilt of the Earth's axis, which would affect particularly the high latitude winter insolation, may actually drive the climate through the CO_2 response we have discussed here. The extremes within which the P_{CO_2} could conceivably vary with the present ocean volume, total carbon and alkalinity, and value of T, are ~190 p.p.m. to 300 p.p.m. If T were to approach zero the P_{CO_2} could vary between ~163 and 425 p.p.m. The climatic effect of P_{CO_2} changes within this range would be considerable. Manabe and Stouffer[12] as well as many others have shown that a halving or doubling of P_{CO_2} should lead to a decrease or increase of ~2 °C in global mean temperature.

Changes in the oceanic carbon distribution by the processes represented by T, f_{hd} and P_h, may also have an impact on fossil fuel uptake. It is difficult to tell what the effect would be. A decrease in T and/or f_{hd} might be expected as high latitude surface waters warm up. A decrease in T and f_{hd} would affect the CO_2 uptake in opposite directions (see Fig. 3). We have not studied this problem, but suspect the effect of variations in T, f_{hd} and p_h on CO_2 uptake would be relatively small because of a tendency for the effects of T and f_{hd} to cancel each other out and because of the short time scales of the fossil fuel CO_2 transient relative to large-scale oceanic overturning.

Evidence of the types of changes we have suggested here for the ice ages should be available in sediment records. An increase in high latitude productivity should lead locally to fairly dramatic increases in sedimentation rates. The palaeo-PO_4, which Boyle estimates by Cd measurements in foraminifera[10], should be lower near deep water formation regions. Table 1 shows that the deep ocean oxygen levels would have decreased enormously in the extreme conditions of the ice age. One would expect anoxia to have been widespread at the depth of the oxygen minimum with possible effects on the sediments and trace metal distributions. We are presently seeking confirmation of our hypothesis in data of this sort, as well as working on the development of a three-dimensional ocean circulation model of the carbon cycle that will more realistically simulate the effect of high latitude productivity and thermohaline overturning rate on atmospheric P_{CO_2}.

1. Neftel, A. H., Oeschger, H., Schwander, J., Stauffer, B. & Zumbrunn, R. Nature 295, 220–223 (1982).
2. Broecker, W. S. in The Sea Vol. 2 (ed. Hill, M. N.) 88–108 (Interscience, New York, 1963).
3. Sarmiento, J. L. J. phys. Oceanogr. 13, 1269–1274 (1983).
4. Broecker, W. S. & Peng, T.-H. Tracers in the Sea (Eldigio, Palisades, 1982).
5. Broecker, W. S. Geochim. cosmochim. Acta 46, 1689–1705 (1982).
6. Broecker, W. S. & Takahashi, T. Ann. Glaciol. (submitted).
7. Siegenthaler, U. J. geophys. Res. 88, 3599–3608 (1983).
8. Redfield, A. C., Ketchum, B. H. & Richards, F. A. The Sea Vol. 2 (ed. Hill, M. N.) 26–75 (Interscience, New York, 1963).
9. Takahashi, T., Broecker, W. S., Bainbridge, A. E. & Weiss, R. F. Tech. Rep. No. 1, CU-1-80 (Lamont-Doherty Geol. Observatory, Palisades, New York, 1980).
10. Boyle, E. A. & Keigwin, L. D. Science 218, 784–787 (1982).
11. Streeter, S. S., Belanger, P. E., Kellogg, T. B. & Duplessey, J. C. Quat. Res. 18, 72–90 (1982).
12. Manabe, S. & Stouffer, R. J. J. geophys. Res. 85, 5529–5554 (1980).
13. Oeschger, H. et al. Maurie Ewing Symp. 1982 Vol. 4 (American Geophysical Union, Washington DC. in the press).
14. Levitus, S. Climatological Atlas of the World Ocean (NOAA Professional Pap. 13, US Dept. of Commerce, Washington DC, 1982).

Rapid atmospheric CO_2 variations and ocean circulation

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Studies on air trapped in old polar ice[1,2] have shown that during the last ice age, the atmospheric carbon dioxide concentration was probably significantly lower than during the Holocene— about 200 p.p.m. rather than 270 p.p.m. Also, Stauffer et al.[3] recently showed by detailed analyses of Greenland ice cores, that during the ice age, between about 30,000 and 40,000 yr BP, the atmospheric CO_2 level probably varied between 200 and 260 p.p.m. These variations occurred parallel to climatic variations as indicated by $\delta^{18}O$ of the ice; astonishingly, the changes took place within rather short times, no more than a few centuries or even less. Here we examine the hypothesis[4] that CO_2 variations arose from changes in ocean circulation that affected the distribution of chemical properties and thus of P_{CO_2} in the surface waters of the world ocean. Such changes can take place in a rather short time, in contrast to changes of whole ocean properties.

Table 1 Model parameters for the standard case

Properties	Warm surface	Cold surface	Whole ocean
Relative area	**0.89**	**0.11**	**1**
Depth (m)	**200**	**200**	**3,700**
Temperature (°C)	**23**	**3**	—
Salinity (‰)	**35**	**35**	**35**
ΣCO_2 (μmol kg^{-1})	1,952	2,158	**2,268**
Alkalinity (μequiv. kg^{-1})	2,315	2,360	**2,389**
Phosphate (μmol kg^{-1})	**0.30**	1.43	**2.15**

Fluxes: 1 sverdrup (sv) = 10^6 m^3 s^{-1}
Water: F_u = 15 sv; F_{cd} = 44 sv; F_{cw} = 10 sv
Particles: P_w = 0.64 mol C m^{-2} yr^{-1}; P_c = **0.93** mol C m^{-2} yr^{-1}
Gas exchange (for 300 p.p.m.): F_{aw} = **19.5** mol C m^{-2} yr^{-1}; F_{ac} = **33** mol C m^{-2} yr^{-1}

Values in bold type were kept constant, the others were varied in sensitivity tests.

Fig. 1 Four-box model consisting of warm surface ocean (W), cold surface ocean (C), deep-sea reservoir (D) and atmosphere (A). F_{cd}, F_{cw}, F_u (= upwelling flux) are water fluxes; F_{aw}, F_{ac}, air–sea gas exchange fluxes; P_w, P_c, particle fluxes.

The ocean is the greatest of the rapidly exchanging global carbon reservoirs and therefore effectively controls the atmospheric concentration of carbon dioxide over time scales of less than 10^5 years. P_{CO_2}, the equilibrium partial pressure of CO_2, of sea water is determined mainly by the temperature (via the solubility of CO_2 gas) and the carbonate chemistry of the water (ΣCO_2 and alkalinity), and to a lesser degree by salinity. During the glacial maximum at 18,000 yr BP, the average sea surface temperature was ~2 K lower[5] and the average salinity of the ocean ~1‰ higher than now. Temperature and salinity changes together would have caused a net decrease of the atmospheric CO_2 concentration of 10–20 p.p.m., compared with Holocene conditions[7]. This is much less than the observed difference of 50–70 p.p.m.; this difference must therefore have been caused by chemical changes in surface waters.

ΣCO_2 in average surface seawater is 10–20% lower than in deep-sea water, because biological activity provides a continuous carbon flux in the form of organic and carbonate particles from the surface to deeper layers. It is the interplay of biological activity and transport by water circulation which mainly regulates ΣCO_2, and therefore P_{CO_2}, in the surface waters. In large areas of the ocean, biological productivity is limited by the nutrients phosphate and nitrate, which are depleted there to near zero. In these areas the biological pump is closely linked to water circulation: a change in the vertical circulation rate, and therefore in supply of nutrients from depth, involves a proportional change in biological activity, so that the chemical concentrations in surface waters remain unaffected.

Broecker[6,7] suggested that during glacial times, the mean oceanic concentration of nutrients was considerably higher than in the Holocene, thus permitting, for the same water circulation pattern, a higher biological productivity and therefore a larger surface deficit of ΣCO_2, compared with deep-sea water which would lead to an overall lower ΣCO_2 and P_{CO_2} in surface water. The mechanism leading to the nutrient increase, as suggested by Broecker, was erosion of nutrient-rich organic sediments on the continental shelves, deposited there during the last interglacial high sea level period. This hypothesis could explain glacial–postglacial changes of atmospheric CO_2 as well as of marine $\delta^{13}C$. However, deposition and erosion of shelf sediments are slow processes and bound to major changes in sea level. Therefore, they cannot have been responsible for the recently detected rapid CO_2 variations during the Ice Age[3].

Significant surface concentrations of phosphates and nitrates are found in some oceanic regions where vertical mixing is rather fast, especially in the Antarctic Ocean where the phosphate concentration is about 70% of its deep-water value of 2.2 μmol kg^{-1}; in warm surface water, it is typically ~10%.Thus, the biological productivity in the Antarctic Ocean is not limited by availability of nutrients, therefore changes in either productivity or circulation may lead to changes in the carbonate chemistry and hence in the P_{CO_2} of Antarctic surface water. In the North Atlantic Ocean, where deep water formation also occurs, surface nutrient concentrations are generally low.
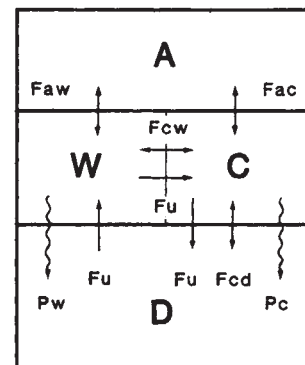
To estimate the effects of various changes in the ocean, we have used a simple 4-box model of ocean and atmosphere (Fig. 1). Box C represents the Antarctic Ocean south of 50° S. Temperatures and chemical concentrations (all normalized to a salinity of 35‰; see Table 1) have been chosen essentially in agreement with averaged GEOSECS results[8]. Phosphate is considered to be the limiting nutrient; taking nitrate instead would not affect our results. ΣCO_2, alkalinity and phosphate are transferred by means of water fluxes between the three boxes and by particle fluxes from surface to depth.

The ratios of carbon, alkalinity and phosphorus carried by biogenic particles are fixed as $\Delta \Sigma CO_2 : \Delta A : \Delta PO_4 = 155 : 35 : 1$. These generalized Redfield ratios were obtained by assuming (1) a ratio of 130:1 for $\Delta \Sigma CO_2 : \Delta PO_4$ in organic matter[9]; (2) an average ratio of inorganic ($CaCO_3$) to organic carbon in particles of ~0.2:1; (3) carbonate alkalinity accounts for 70% of the change in titration alkalinity, which is affected also by nitrate carried by organic particles. The water exchange fluxes to the deep sea for Holocene conditions can roughly be estimated from mean ^{14}C concentrations of 0.84 for the deep sea and ~0.91 for the cold surface (the pre-industrial atmospheric value is 1). This yields a mean ^{14}C age of deep-sea water of ~700 yr with respect to the cold surface from which it originates. Thus, the flux between the cold surface and the deep sea approximately corresponds to a transfer velocity of 3,500 m per 700 yr = 5 m per yr, referring to the whole ocean area, equivalent to about 60×10^6 m^3 s^{-1} (60 sverdrup). We have chosen a standard case believed to represent Holocene conditions (see Table 1). The particle fluxes are computed such that the imposed chemical properties are reproduced; their values of 0.93 and 0.64 mol C m^{-2} yr^{-1} from cold and warm surface are comparable with the values estimated from observation[10], that is, 0.34–0.83 mol C m^{-2} yr^{-1}. The surface boxes exchange CO_2 via the atmosphere by gas transfer. The gas transfer fluxes are proportional to P_{CO_2}; for P_{CO_2} = 300 p.p.m. they are 33 and 19.5 mol m^{-2} yr^{-1} for cold and warm surface water, respectively. The difference is due to the higher solubility and higher transfer velocities of CO_2 in cold water, as derived from radon measurements in the Antarctic Ocean[11]. P_{CO_2} values in surface water are calculated using a procedure described by Bacastow[12]. For the standard case an atmospheric concentration of 282 p.p.m. is obtained.

By using the model we can test the effect of different processes on atmospheric P_{CO_2} and its isotopic composition. For these tests, the phosphate concentration in warm surface water is considered constant, arguing that PO_4 is almost completely consumed by organisms. Also, the particle flux from the cold surface and the total oceanic inventories of all properties are assumed to be constant. First, the exchange C–D is reduced to 50% of its standard value (Table 2). This causes a decrease of ΣCO_2 and of P_{CO_2}, because the biological particle flux, while absolutely constant, becomes relatively more important. The atmospheric CO_2 concentration decreases by 52 p.p.m., a difference comparable to the CO_2 changes found in ice cores. An interesting result is that P_{CO_2} in W changes drastically from 283 to 233 p.p.m., although the circulation change does not directly influence W. This is a result of a net carbon transport from W to C via the atmosphere[13]. The importance effect of atmospheric

Table 2 Sensitivity tests; properties in the reservoirs for atmosphere (A), and warm (W) and cold (C) surface ocean

		Particle flux (mol C m^{-2}yr^{-1})	PO$_4$ (µmol kg^{-1})	Standard gas exchange			Gas exchange → O		
				ΣCO$_2$ (µmol kg^{-1})	P_{CO_2} (p.p.m.)	δ^{13}C (‰)	ΣCO$_2$ (µmol kg^{-1})	P_{CO_2} (p.p.m.)	δ^{13}C (‰)
Standard case	W	0.64	0.30	1,952	283	1.6	1,981	323	2.6
(F_u = 15 sv, F_{cd} = 44 sv)	C	0.93	1.43	2,158	276	1.4	2,156	274	1.3
	A	—	—	—	282	−6.9	—	315	−6.0
Reduced exchange C–D	W	0.58	0.30	1,910	233	2.0	1,981	323	2.6
(F_u = 15 sv, F_{cd} = 22 sv)	C	0.93	1.05	2,101	215	1.8	2,097	211	1.7
	A	—	—	—	230	−6.4	—	304	−5.8
Stronger upwelling	W	1.08	0.30	1,934	260	2.1	1,981	323	2.6
(F_u = 30 sv, F_{cd} = 44 sv)	C	0.93	1.23	2,127	241	1.5	2,125	238	1.5
	A	—	—	—	257	−6.4	—	308	−5.9

CO_2 transport is illustrated by reducing the air–sea exchange fluxes to nearly zero (10^{-4} of their standard values): now the same reduction of the water exchange C–D causes an atmospheric drop of only 11 p.p.m. and does not affect P_{CO_2} in W at all (see Table 2). ΣCO_2 and P_{CO_2} in C are less affected by the gas exchange than in W, because C is strongly coupled to the deep sea by a large water-exchange flux.

The model includes a deep-water formation—upwelling circulation, F_u. If F_u is increased from 15 to 30 sverdrup, the atmospheric CO_2 decreases by 25 p.p.m. Thus an increase in low-latitude upwelling, accompanied by higher biological productivity in low latitudes, leads to a smaller atmospheric CO_2 concentration. The reason is found again in the cold surface water, which is diluted by low-latitude water depleted in ΣCO_2. The enhanced upwelling of ΣCO_2 (and nutrients) to the warm surface is automatically compensated by a larger particle flux, since a constant PO_4 concentration is assumed in W.

A change of the surface exchange flux, F_{cw} has an effect comparable to that of varying the upwelling circulation. An increase of F_{cw} from 10 to 20 sverdrup results in an atmospheric concentration decrease of 19 p.p.m.

Data from the eastern equatorial Pacific indicate that the δ^{13}C difference between warm surface and deep water during the glacial maximum was about 0.5‰ greater than during the Holocene[25]. Our 4-box model yields changes of this magnitude for both scenarios, reduced C–D exchange and enhanced upwelling circulation. The sediment data[25], however, also point to significant long-term δ^{13}C changes in average deep water, which cannot be explained by circulation changes (δ^{13}C in the deep sea is constant within 0.03‰ in the different model scenarios considered here). These changes must be due to carbon shifts between the ocean and organic carbon pools of either terrestrial biomass[15] or shelf sediments[6,7]. Information on δ^{13}C changes in atmospheric CO_2 should soon be available from analyses of ice cores performed in this laboratory.

These examples demonstrate that changes of the oceanic circulation, especially those directly affecting the Antarctic Ocean, may potentially cause changes of atmospheric CO_2. Is there any evidence for such circulation changes during the glacial? Sediment studies in the Vema channel[16] indicate a stronger flow of Antarctic Bottom Water into the Atlantic Ocean at 18,000 BP. This may indicate a stronger upwelling—deep water formation circulation (see Table 2). The wind-induced circulation in the tropics was stronger at 18,000 BP in the Atlantic[14] and probably also in the eastern equatorial Pacific Ocean where productivity was increased[17]; it is not clear if this involved a stronger flux from low to high latitudes or whether it was restricted to shallow recirculation in low latitudes. A number of deep-sea sediment studies in the North Atlantic concerning temperature[18], δ^{13}C (ref. 19), oxygen[20] and cadmium concentrations[21] have demonstrated that the formation of North Atlantic deep water was significantly reduced during the last glacial. Ruddiman and MacIntyre[22] have shown that the surface circulation—and probably also deep water formation—in the North Atlantic Ocean underwent rapid and drastic changes during late glacial times, ~13,000 to 10,000 BP. However, these changes probably did not exert a major direct

effect on atmospheric CO_2, because nutrient concentrations are low in North Atlantic surface water. We know of no similar studies for the Antarctic Ocean. Thus, there is ample evidence for dramatic and rapid changes of the circulation in the North Atlantic, but it is not clear how this affected the Antarctic Ocean which is the most critical region for atmospheric CO_2 variations.

Thus, we propose that changes of the surface ocean circulation were responsible for rapid atmospheric CO_2 variations during and at the end of the last Ice Age. The variations predicted by the model are fast since the residence times of carbon in the surface reservoirs are of the order of a century only. The simple 4-box model used here cannot be expected to yield final or quantitatively reliable results, but it indicates that the Antarctic Ocean may have a major effect on the level of atmospheric CO_2.

Independently of this study, Knox and McElroy[23] and Sarmiento and Toggweiler[24] discuss the idea that the Antarctic Ocean, in which ΣCO_2 is not fixed by the availability of nutrients, may be responsible for atmospheric CO_2 variations. These authors assume that changes in light conditions led to changing biological productivity and thus affected P_{CO_2}. We rather think that ocean circulation changes were the essential cause. Besides this, there are differences between the results of these authors and of ours, due to differing assumptions on fluxes, concentrations and model geometry.

1. Neftel, A., Oeschger, H., Schwander, J., Stauffer, B. & Zumbrunn, R. Nature 295, 220–223 (1982).
2. Delmas, R. J., Ascencio, J. M. & Legrand, M. Nature 284, 155–159 (1980).
3. Stauffer, B., Hofer, H., Oeschger, H., Schwander, J. & Siegenthaler, U. Ann. Glaciol. 5, (in the press).
4. Oeschger, H. et al. Maurice Ewing Symp. 1982 Vol. 4 (American Geophysical Union, in the press).
5. CLIMAP Science 191, 1131–1137 (1976).
6. Broecker, W. S. in Climatic Variations and Variability: Facts and Theories (ed. Berger A.) 111–121 (Reidel, Dordrecht, 1981).
7. Broecker, W. S. Geochim. cosmochim. Acta 46, 1689–1705 (1982)
8. Takahashi, T., Broecker, W. S. & Bainbridge, A. E. in Carbon Cycle Modelling, SCOPE 16 (ed. Bolin, B.) 159–200, 271–286 (Wiley, New York, 1981).
9. Broecker, W. S., Takahashi, T. & Langer, J. mar. Res. (in the press).
10. Mopper, K. & Degens, E. T. in The Global Carbon Cycle, SCOPE 13 (eds Bolin, B., Degens, E. T., Kempe, S. & Ketner, P.) 293–316 (Wiley, New York 1979).
11. Peng, T.-H., Broecker, W. S., Mathieu, G. G. & Li, Y.-H. J. geophys. Res. 84, 2471–2496 (1979).
12. Bacastow, R. B. in Carbon Cycle Modelling, SCOPE 16 (ed. Bolin, B.) 95–101 (Wiley, New York, 1981).
13. Broecker, W. S. & Takahashi, T. Ann. Glaciol. 5, (in the press).
14. Gardner, J. V. & Hays, J. D. Mem. geol. Soc. Am. 145, 221–246 (1976).
15. Shackleton, N. J. in The Fate of Fossil CO₂ in the Oceans (eds Andersen, N. R. & Malahoff, A.) 401–427 (Plenum, New York, 1977).
16. Ledbetter, M. T. & Johnson, D. A. Science 194, 837–839 (1976).
17. Pedersen, T. F. Geology 11, 16–19 (1983).
18. Duplessy, J. C., Chenourad, L. & Vila, F. Science 188, 1208–1209 (1975).
19. Shackleton, N. J., Imbrie, J. & Hall, M. A. Earth planet. Sci. Lett. 65, 233–244 (1983).
20. Streeter, S. S. & Shackleton, N. J. Science 203, 168–171 (1979).
21. Boyle, E. A. & Keigwin, L. D. Science 218, 784–787 (1982).
22. Ruddiman, W. F. & MacIntyre, A. Palaeogeogr. Palaeoclimatol. Palaeoecol. 35, 145–214 (1981).
23. Knox, F. & McElroy, M. B. J. geophys. Res. (in the press).
24. Sarmiento, J. L. & Toggweiler, J. R. Nature (in the press).
25. Shackleton, N. J., Hall, M. A., Line, J. & Shuxi, C. Nature 306, 319–322 (1983).