

- pretation. The various isotopic records show remarkable similarities, at least for their long-term changes, both for Antarctica (33) and Greenland (27). This indicates that the derived climatic information is clearly regionally robust.
36. J. J. Pichon, L. D. Labeyrie, G. Bareille, M. Labracherie, J. Duprat, J. Jouzel, *Paleoceanography* 7, 289 (1992).
 37. T. Sowers, M. Bender, D. Raynaud, Y. S. Korotkevich, J. Orchado, *ibid.* 6, 679 (1991).
 38. D. Etheridge, G. I. Pearman, F. de Silva, *Ann. Glaciol.* 10, 28 (1988); M. A. K. Khalil and R. A. Rasmunssen, *ibid.* 10, 73 (1988); D. Zardini, D. Raynaud, D. Scharffe, W. Seiler, *J. Atmos. Chem.* 8, 189 (1989).
 39. M. Leuenberger and U. Siegenthaler, *Nature* 360, 449 (1992). In this article, Leuenberger and Siegenthaler derived a total glacial-interglacial greenhouse forcing of 3 W m^{-2} , 50% higher than that used by Lorius *et al.* (58) because of a different formulation of the CO_2 forcing.
 40. R. A. Houghton, in preparation; see also E. Sundquist, *Science* 259, 934 (1993).
 41. D. Raynaud and J. M. Barnola, *Nature* 315, 309 (1985); U. Siegenthaler *et al.*, *Ann. Glaciol.* 10, 151 (1988).
 42. M. A. K. Khalil and R. A. Rasmunssen, *Tellus* 41 B, 554 (1989).
 43. I. C. Prentice, M. T. Sykes, M. Lautenschlager, S. P. Harrison, O. Denissenko, P. J. Bartlein, in preparation.
 44. W. S. Broecker and T.-H. Peng, in preparation.
 45. W. S. Broecker and T.-H. Peng, *Radiocarbon* 28, 329 (1986).
 46. W. F. Budd, in *Carbon Dioxide and Climate: Australian Research*, G. I. Pearman, Ed. (Australian Academy of Sciences, Canberra, 1980), pp. 115–128; F. Faure, *C. R. Acad. Sci. Paris* 305, 523 (1987).
 47. M. Leuenberger, U. Siegenthaler, C. C. Langway, *Nature* 357, 488 (1992); B. D. Marino, M. D. McElroy, M. J. Salawitch, W. G. Spaulding, *ibid.*, p. 461; J. P. Jasper and J. M. Hayes, *ibid.* 347, 462 (1990).
 48. J. Jouzel *et al.*, in *The Last Deglaciation: Absolute and Radiocarbon Chronologie*, E. Bard and W. S. Broecker, Eds. (NATO ASI Ser. 12 (Springer, Berlin, 1992), pp. 229–266.
 49. According to the Vostok results, the regression between CH_4 concentration (C) and Vostok surface temperature T_s is: $C \text{ (ppbv)} = 23.7 T_s \text{ (}^\circ\text{C)} + 591.5$. Based on the temperature estimates for the glacial-interglacial transition, a 1°C change in global temperature corresponds to a 2°C change in the surface temperature at Vostok. Consequently, the corresponding CH_4 -temperature gradient is $47.4 \text{ ppbv}/^\circ\text{C}$.
 50. J. A. Chappellaz, I. Y. Fung, A. M. Thompson, *Tellus* 45B, in press; A. M. Thompson, J. A. Chappellaz, I. Y. Fung, T. L. Kuscera, *ibid.*, in press.
 51. E. G. Nisbet, *J. Geophys. Res.* 97, 12859 (1992).
 52. D. Raynaud and U. Siegenthaler, in *Global Changes in the Perspective of the Past*, J. A. Eddy and H. Oeschger, Eds. (Wiley, Chichester, in press).
 53. J. Imbrie, A. McIntyre, A. Mix, in *Climate and Geosciences*, A. Berger *et al.*, Eds. (Kluwer, Norwell, MA, 1989), pp. 121–164.
 54. N. J. Shackleton and N. G. Pisias, in *The Carbon Cycle and Atmospheric CO_2 : Natural Variations Archaean to Present*, E. T. Sundquist and W. S. Broecker, Eds. (American Geophysical Union, Washington, DC, 1985), pp. 303–317; W. B. Curry and T. J. Crowley, *Paleoceanography* 2, 489 (1987).
 55. T. Sowers, M. Bender, J. M. Barnola, *Eos* 73, 260 (1992).
 56. J. Jouzel *et al.*, *Nature* 329, 403 (1987); P. Yiou *et al.*, *J. Geophys. Res.* 96, 20365 (1991).
 57. J. D. Hays, J. Imbrie, N. J. Shackleton, *Science* 194, 1121 (1976).
 58. C. Lorius, J. Jouzel, D. Raynaud, J. Hansen, H. Le Treut, *Nature* 347, 139 (1990).
 59. A. J. Broccoli and S. Manabe, *Climate Dynam.* 1, 87 (1987); A. Berger, H. Gallée, C. Tricot, *J. Glaciol.*, in press.
 60. B. Saltzman, *Climate Dynam.* 5, 67 (1990); M. Ya. Verbitsky and R. J. Oglesby, *J. Geophys. Res.* 97, 5895 (1992).
 61. J. Imbrie *et al.*, *Paleoceanography*, in press. Two articles on the structure and origin of major glaciation cycles in two parts (i) linear response to Milankovitch forcing and (ii) the 100,000 year cycle.
 62. I. J. Winograd *et al.*, *Science* 258, 255 (1992); R. A. Kerr, *ibid.*, p. 220; W. S. Broecker, *Nature* 359, 779 (1992); K. Lambeck and M. Nakada, *ibid.* 357, 125 (1992).
 63. J. E. Hansen *et al.*, in *Climate Processes and Climate Sensitivity*, J. E. Hansen and T. Takahashi, Eds. (American Geophysical Union, Washington, DC, 1984), pp. 130–163.
 64. CLIMAP project members, *Geol. Soc. Am. Map Chart Ser. MC 36* (1981).
 65. S. Manabe and A. J. Broccoli, *J. Atm. Sci.* 42, 2643 (1985).
 66. L. D. D. Harvey, *J. Geophys. Res.* 94, 12783 (1989).
 67. M. I. Hoffert and C. Covey, *Nature* 360, 573 (1992); These authors derived climate sensitivity both from LGM and mid-Cretaceous data and obtained a ΔT_{2x} of $2^\circ \pm 0.5^\circ\text{C}$ for the LGM and $2.5^\circ \pm 0.2^\circ\text{C}$ for the mid-Cretaceous. However, as noted by E. Barron [*Nature* 360, 533 (1992)] the LGM estimate would yield a sensitivity closer from 3.0°C if a value of 5°C colder than the present (instead of 3.0°C) would have been taken as estimate of the glacial temperature.
 68. T. M. L. Wigley and S. C. B. Raper, *Nature* 357, 293 (1992).
 69. M. E. Schlesinger, X. Jiang, R. J. Charlson, in *Climate Change and Energy Policy*, L. Rosen and M. Glaser, Eds. (American Institute of Physics, New York, 1992), pp. 75–108.
 70. P. M. L. Kelly and T. M. L. Wigley, *Nature* 360, 328 (1992); M. E. Schlesinger and N. Ramankutty, *ibid.*, p. 330.
 71. T. Sowers, M. Bender, D. Raynaud, Y. S. Korotkevich, *J. Geophys. Res.* 97, 15683 (1992).
 72. S. J. Johnson, W. Dansgaard, H. B. Clausen, C. C. Langway, *Nature* 235, 429 (1992).
 73. T. Sowers *et al.*, in preparation.
 74. D. G. Martinson, N. G. Pisias, J. D. Hays, J. Imbrie, T. C. Moore, N. J. Shackleton, *Quat. Res.* 27, 1 (1987).
 75. We thank P. Duval for a review of the existing data on the brittle and clathrate zones, D. Etheridge for providing Fig. 3, and M. Bender, D. Etheridge, R. Francey, and M. Leuenberger for comments and discussions. Part of this review was prepared during a 3-month stay of D.R. at the Division of Atmospheric Research (CSIRO). The research on the ice core record of greenhouse gases is in France, supported by PNEDC (Programme National d'Etudes de la Dynamique du Climat) and by the Commission of the European Communities.

The Global Carbon Dioxide Budget

Eric T. Sundquist

The increase in atmospheric CO_2 levels during the last deglaciation was comparable in magnitude to the recent historical increase. However, global CO_2 budgets for these changes reflect fundamental differences in rates and in sources and sinks. The modern oceans are a rapid net CO_2 sink, whereas the oceans were a gradual source during the deglaciation. Unidentified terrestrial CO_2 sinks are important uncertainties in both the deglacial and recent CO_2 budgets. The deglacial CO_2 budget represents a complexity of long-term dynamic behavior that is not adequately addressed by current models used to forecast future atmospheric CO_2 levels.

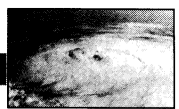
Biogeochemists are the budget experts of the earth sciences. They monitor the income and outgo of materials through intricate biological and geochemical transactions. Budgets of many elements—especially C, N, P, and S—are necessary to understand the factors that contribute to environmental problems such as acid rain, eutrophication, and the greenhouse effect. No biogeochemical problem has drawn more recent attention than the global budget of atmospheric CO_2 .

For more than 20 years, the principal problem in budgeting atmospheric CO_2 has been the excess of known sources over identified sinks. The amount of CO_2 produced by human activities (principally consumption of fossil fuels and destruction of forests) significantly exceeds our best estimates of the amount of CO_2 absorbed by

the oceans and atmosphere (Table 1). To account for this budget imbalance (the so-called “missing” CO_2) there must be another large CO_2 sink. This sink is probably somewhere in the world’s terrestrial plants and soils, but its specific identity has eluded detection. Although we can quantify the earth’s major C reservoirs and fluxes, balancing the anthropogenic CO_2 budget requires accounting for differences that are often small relative to the natural exchange and abundance of C (Fig. 1).

The CO_2 budget problem has assumed greater urgency as the global community of nations has begun serious negotiation of measures to mitigate greenhouse warming. Budgets of atmospheric CO_2 are used not only to keep track of past and present balances, but also to construct models that forecast future trends. CO_2 is the principal contributor to the expected increase in the greenhouse effect and the inherent by-prod-

The author is with the U.S. Geological Survey, Quissett Campus, Gosnold Building, Woods Hole, MA 02543.



uct of more than 80% of the primary energy used by the world's population (1). Thus international attention is focused on questions about the impact of reducing the present exponential increase in human production of CO_2 . Among these sweeping and profoundly difficult concerns, questions about the CO_2 budget are fundamental. How will the balance of CO_2 sources and sinks be affected by a stabilization or reduction of anthropogenic CO_2 production? What CO_2 production strategies can be accommodated if we want to limit future atmospheric CO_2 concentrations? How long will anthropogenic CO_2 persist in the atmosphere? Where are the important CO_2 sinks, and can they be manipulated? The CO_2 budget has become a basic issue in international negotiations concerning global environmental problems.

Biogeochemists have not confined their search for answers to analysis of industrial-era CO_2 budgets. Well-documented examples of past imbalances among natural sources and sinks of CO_2 are evident in the record of atmospheric CO_2 increase and climate change at the end of the last ice age about 10,000 to 20,000 years ago. An inspection of the CO_2 budget for this period demonstrates the complexity of the interactions that control the balance in the atmosphere and sets the stage for examination of the recent CO_2 budget. This analysis reveals that anthropogenic CO_2 is a biogeochemical perturbation of truly geologic proportions.

CO_2 Budget During Deglaciation

The changing atmospheric CO_2 balance at the end of the Pleistocene is accurately defined by the record of air bubbles trapped in polar ice. The best ice core record to date (from the Byrd station in Antarctica) shows that CO_2 concentrations rose from 200 ppm between 17,000 and 18,000 years ago to 280 ppm between 10,000 and 11,000 years ago (2). This increase amounted to an accumulation of 170 Gt of C (1 Gt = 10^{15}

g) in the atmosphere at an average rate of about 0.02 to 0.03 Gt of C per year. For comparison, atmospheric CO_2 concentrations have increased by almost the same amount since the 18th century, but the rate of CO_2 accumulation in the modern atmosphere amounts to more than 3 Gt of C per year. It is difficult to imagine any natural process that could release CO_2 to the atmosphere as rapidly as have human activities. On the other hand, many processes must be considered possible sources of the relatively sedate increase in atmospheric CO_2 levels at the end of the Pleistocene (3).

Terrestrial plants and soils were probably a sink rather than a source of atmospheric CO_2 at this time. Vegetation advanced into the areas uncovered by the retreating ice sheets, and tropical forests may also have expanded into formerly dry regions (4). The size of this CO_2 sink is difficult to assess. Maps and models of the deglacial (5) migration of vegetation and soils have yielded widely disparate estimates (6). These estimates are particularly susceptible to misinterpretation of effects of coastline retreat. As sea level rose more than 100 m due to the melting ice sheets, nearshore terrestrial ecosystems were progressively flooded out of the terrestrial C budget. However, these areas were blanketed by a transgressive sequence of organic-rich nearshore sediments that must also be tallied in the global C budget. An approach that yields the net effect of both terrestrial and coastal changes is based on the change in the ratio of the carbon isotopes ^{13}C and ^{12}C in the atmosphere and ocean. Because photosynthesis preferentially removes $^{12}\text{CO}_2$ from the atmosphere, a significant deglacial accumulation of plant biomass and debris would have left the atmosphere relatively enriched in $^{13}\text{CO}_2$. This enrichment would have affected the $^{13}\text{C}/^{12}\text{C}$ ratios in seawater and in the calcareous shells of organisms

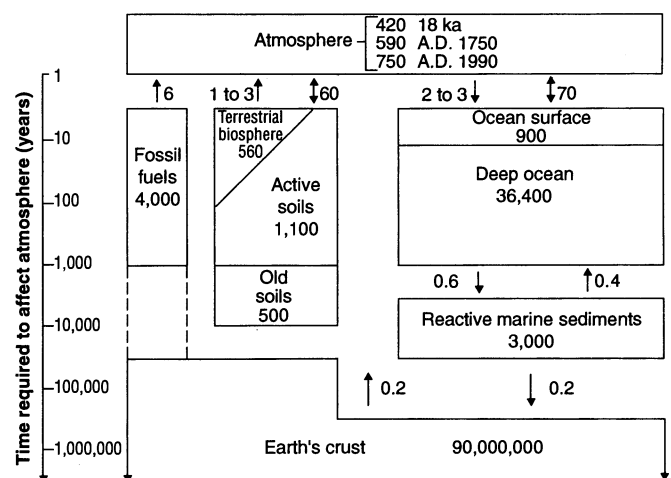
deposited in sediments. The expected atmospheric and oceanic shifts in $^{13}\text{C}/^{12}\text{C}$ ratios have been documented in ice core and marine sediment records (4, 7). They suggest that during deglaciation about 450 to 750 Gt of C were transferred from the oceans and atmosphere to terrestrial plants and soils and nearshore organic sediments (8). Thus the CO_2 budget for this period must account for not only the CO_2 increase in the atmosphere, but also several times more C that passed through the atmospheric CO_2 reservoir on its way to assimilation and storage on land and in nearshore sediments.

The CO_2 fluxes associated with both chemical weathering and volcanism are too small to contribute significantly to the deglacial CO_2 increase. The present global rate of CO_2 emission from volcanoes is estimated at about 0.04 to 0.05 Gt of C per year (9). Thus an increase of at least 50% in volcanic CO_2 emissions would have been necessary to account for only the rate of CO_2 accumulation in the deglacial atmosphere. An even greater increase would have been necessary to support the additional accumulation of C in the terrestrial biosphere, and still more to account for extra CO_2 that would have been dissolved in the oceans. There is no evidence for such a drastic increase in global volcanism at the end of the Pleistocene. There is some evidence for a significant deglacial decrease in terrestrial chemical weathering (10). Weathering consumes CO_2 at a rate that is thought to maintain a long-term geochemical steady state with respect to volcanic and other geologic CO_2 emissions (11). If geologic CO_2 production remained constant while weathering decreased, the effect would have been the same as a small source of atmospheric CO_2 , comparable in order of magnitude to an increased volcanic source. However, model simulations of the C cycle suggest that such changes are at least an

Table 1. IPCC global CO_2 budget for 1980–1989 [as adapted from (38) by (56)].

Reservoir	Average flux (Gt of C year ⁻¹)
Sources	
Fossil fuels	5.4 ± 0.5
Deforestation and land use	1.6 ± 1.0
Total	7.0 ± 1.2
Sinks	
Atmosphere	3.2 ± 0.1
Oceans (modeled uptake)	2.0 ± 0.8
Total	5.2 ± 0.8
Imbalance (sources – sinks)	1.8 ± 1.4

Fig. 1. Principal reservoirs and fluxes (arrows) in the global carbon cycle. Vertical placements relative to scale on left show approximate time scales required for reservoirs and fluxes to affect atmospheric CO_2 . Most estimates are from (13). Double arrows represent bidirectional exchange. Single arrows to and from the atmosphere are approximate estimates of anthropogenic CO_2 fluxes for 1990. Terrestrial uptake of anthropogenic CO_2 is likely (see text) but not shown because of large uncertainties.



order of magnitude too small to account for the increase of atmospheric CO₂ levels during the deglaciation (12).

The probable source of the deglacial CO₂ was the ocean. The glacial ocean contained approximately 38,000 Gt of C, whereas the atmosphere contained about 420 Gt of C (13). As in the modern ocean, the glacial ocean C pool was not distributed homogeneously. Studies of marine sediments show that the distribution of oceanic C has shifted in concert with glacial-interglacial climatic oscillations for millions of years (14). During these shifts in the massive marine C reservoir, some CO₂ might have leaked through the ocean surface to cause significant changes in the much smaller reservoir of atmospheric CO₂. The longest ice core record to date (from the Vostok site in Antarctica) reveals not only that atmospheric CO₂ levels increased at the time of the most recent deglaciation, but also that a similar oscillation in CO₂ levels accompanied the earlier glacial-interglacial cycle more than 100,000 years ago (15). It seems reasonable to infer that atmospheric CO₂ levels were also affected by the many earlier glacial-interglacial C redistributions recorded in marine sediments. Such changes in CO₂ and C reservoirs have become integral components of theories that attempt to explain Pleistocene climatic oscillations (16).

The ocean surface mixed layer cannot be a large source or sink in the deglacial CO₂ budget. Gas exchange with the atmosphere is so rapid that, for purposes of calculating global budgets, the ocean surface mixed layer can be assumed to be effectively in chemical equilibrium with atmospheric CO₂ (17). This equilibrium involves not only the concentration of dissolved CO₂ but also the much larger pool of other dissolved inorganic C species (carbonic acid, bicarbonate and carbonate ions, and various complexes and ion pairs). At equilibrium the proportional change in total dissolved inorganic C concentrations is much smaller than the proportional change in CO₂ levels. Thus transfer of only about 30 Gt of dissolved inorganic C from the deep sea to the mixed layer was required to raise the ocean surface equilibrium CO₂ concentration from 200 to 280 ppm (18). The deglacial CO₂ budget can be estimated as a deep ocean CO₂ source balancing the sum of equilibrium ocean surface enrichment, the increase in atmospheric CO₂, and the increased storage of organic C in vegetation, soils, and sediments (Table 2).

This budget does not tell us much about the mechanisms for delivering CO₂ from the deep sea. Several processes act to hold the equilibrium CO₂ concentration of the ocean surface substantially below that for

Table 2. Deglacial global CO₂ budget, 18,000 to 11,000 years ago. These estimates do not include any net transfer of C to or from the oceans as CaCO₃ (see text and Eq. 1).

Reservoir	Total flux (Gt of C)
Source	
Deep ocean	650 to 950
Sinks	
Ocean surface	30
Atmosphere	170
Plants and organic debris	450 to 750
Total	650 to 950

the oceans as a whole. Dissolved CO₂ is consumed in the mixed layer by photosynthesis. Some of this assimilated C sinks as organic debris to the deep ocean, where it is largely remineralized to dissolved inorganic C. Dissolved CO₂ is also carried downward by the sinking of polar surface waters, which are the principal source for replenishing the ocean's deep waters. These downward pumps are balanced by upwelling and other forms of vertical mixing between deep and surface waters. Subtle changes in the efficiencies of these pumping and mixing processes may have caused CO₂ to leak to and from the deep waters of the Pleistocene oceans. However, no single mechanism seems to be consistent with all of the evidence in the sediment record. For example, although there is evidence for enhanced low-latitude upwelling and productivity during the last glacial period (19), suggesting more rapid vertical ocean mixing, there is also evidence for reduced glacial CO₂ exchange between the deep ocean and the atmosphere (20). Model simulations of glacial-interglacial changes in CO₂ levels have repeatedly shown that simple hypothesized mechanisms cannot reproduce both the atmospheric CO₂ record and the sedimentary evidence (21). Instead, an intricate combination of interdependent changes seems to be required.

A significant difficulty in understanding the oceanic origins of the deglacial increase in CO₂ levels—and in calculating the CO₂ budget properly—is the unknown contribution of changes in the cycling of marine C as CaCO₃. Like dissolved CO₂, this compound is selectively removed from ocean surface waters. CaCO₃ is the primary material of coral reefs and the shells of many marine organisms. Much of the CaCO₃ precipitated in the ocean surface is eventually deposited in sediments or dissolved in the deep sea. Unlike other ocean C transformations (22), the production and dissolution of CaCO₃ significantly affect oceanic alkalinity, as illustrated by the co-occurrence of dissolved bicarbonate and calcium ions in the reaction



This alkalinity effect gives a paradoxical twist to the role of CaCO₃ in oceanic C cycling. As exemplified by the above reaction, production of CaCO₃ in the ocean surface mixed layer decreases the alkalinity and thus has the same effect as adding dissolved CO₂: an increase in the equilibrium CO₂ concentration, which can cause CO₂ to be released to the atmosphere. Thus the transfer of CaCO₃ to sediments and the deep sea partially offsets the downward pumping of oceanic CO₂ by other processes.

Although CaCO₃ is produced by organisms nearly everywhere in the ocean surface, its overall effect on the global CO₂ budget also depends on the amount of CaCO₃ that dissolves in the deep sea because of its enhanced solubility there. Like the CO₂ pumps, the CaCO₃ pump is balanced by mixing between the ocean surface and deep waters. A change in deep sea CaCO₃ dissolution will affect alkalinity. Changes in deep ocean alkalinity will be mixed upward to the ocean surface, where they may act as positive or negative feedbacks in combination with other influences on atmospheric CO₂. These feedbacks are governed by the equilibrium relations between alkalinity and dissolved inorganic C species, which imply that removal of a given amount of C as CaCO₃ from the mixed layer will add about 0.6 times as much C to the CO₂ budget of the atmosphere and ocean surface mixed layer (23). Thus the role of CaCO₃ in the deglacial CO₂ budget can be accommodated by the approximate equation

$$0.6 F_{\text{CaCO}_3} + F_{\text{CO}_2} = 650 \text{ to } 950 \text{ Gt of C} \quad (1)$$

where F_{CaCO_3} is the net excess of C in CaCO₃ removed from the ocean (that is, the deglacial change in CaCO₃ production minus the change in dissolution) and F_{CO_2} is the amount of C in CO₂ transferred from the deep sea to the ocean surface and atmosphere by mechanisms independent of the CaCO₃ balance. The right-hand side of this equation is the total amount of C removed from the deep sea during the deglaciation (Table 2).

The marine sediment record displays abundant evidence for widespread but complex climate-related changes in oceanic CaCO₃ production and dissolution (24). Changes appear to have been most pronounced during the transitions between glacial and interglacial periods (25), whereas global mean glacial and interglacial CaCO₃ patterns are less distinct (26). Like other sediment evidence, the CaCO₃ record does not seem to be consistent with



a single mechanism for increasing CO_2 during the last deglaciation. For example, an increase in CaCO_3 production on carbonate reefs and banks—caused by the rise in sea level that accompanied destruction of large ice sheets—has been suggested as a way of leaking oceanic CO_2 to the atmosphere [the so-called “coral reef hypothesis” (27)]. The accompanying decrease in oceanic alkalinity would have enhanced deep-sea CaCO_3 dissolution, a negative feedback to the hypothesized influences of increased CaCO_3 production on reefs and banks. In contrast, a deglacial leak of CO_2 from the deep ocean to the ocean surface and atmosphere would have attenuated deep-sea CaCO_3 dissolution, a positive feedback to the transfer of CO_2 to the atmosphere. It is quite possible that both of these hypothesized mechanisms—with their opposing effects on CaCO_3 dissolution—may have affected the deglacial rise in atmospheric CO_2 levels. To further complicate matters, CaCO_3 solubility in the deep sea does not behave like a simple chemistat, which would tend to maintain the deep ocean at some easily calculated mean saturation state. Instead, it responds in a way that tends to maintain the overall balance between oceanic alkalinity sources and sinks. These include the transport of dissolved bicarbonate to the oceans by rivers (the main alkalinity source) and burial of CaCO_3 in sediments (the main sink). Thus a change in the river bicarbonate source or in the amount of CaCO_3 buried will alter the state of CaCO_3 saturation for the entire deep sea. The sediment record of deep-sea CaCO_3 dissolution, and its implications for oceanic alkalinity, are among the most important and complex keys to understanding the geologic history of atmospheric CO_2 .

In summary, the deglacial CO_2 budget reflects nothing less than a major reorganization of the earth surface C cycle. The increase in atmospheric CO_2 levels during this period was not a sudden perturbation but a systematic manifestation of vast changes throughout the oceans and over the land surface. Of course, CO_2 was not a passive participant in these changes. Its greenhouse effect likely contributed to the deglacial global warming, which in turn contributed to changes in ocean circulation, plant growth, sea level rise, and other factors affecting the C cycle. One measure of the intensity of this interdependence is the difficulty of separating cause from effect in the relations between climate indices and CO_2 concentrations in ice cores (28). Climate and the C cycle appear to have been so tightly coupled that they must be considered as parts of the same global system (29).

Historical and Recent CO_2 Budget

The anthropogenic CO_2 perturbation did not begin against a background of steady

Table 3. Historical to recent global CO_2 budgets. All totals are in gigatons of C. Two estimates are given for ocean sinks in each time period: left-hand entry is from figure 42 of (37) (I extrapolated from 1988 to 1990 by assuming a constant modeled residual in 1989 and 1990); right-hand entry is from (62). Right-hand and left-hand entries in rows following ocean sinks are calculated from the corresponding ocean sink estimates.

Reservoir	Year			
	1750 to 1850	1850 to 1950	1950 to 1990	1750 to 1990
Sources				
Fossil fuels (63)	1	61 ± 6	155 ± 16	217 ± 22
Land use (64)	40 ± 12	69 ± 21	53 ± 16	162 ± 49
Total	41 ± 12	130 ± 22	208 ± 23	379 ± 54
Sinks				
Atmosphere (65)	21	50	89	160
Oceans	20 16	63 49	72 53	155 118
Total	41 37	113 99	161 142	315 278
Imbalance*	0 4	17 31	47 66	64 101
Modeled residual†	40 36	52 38	6 - 13	98 61

*Sources minus sinks.

†Land use minus imbalance.

state. The deglacial CO_2 increase involved many processes that are characterized by long response times. The e -fold response time of deep-sea CaCO_3 dissolution has been estimated at 6,000 to 14,000 years (30). Similarly, the deglacial accumulation of C in soils and sediments may be characterized by time scales of thousands of years and more (31). These long response times suggest that the 7000-year deglacial increase in CO_2 levels may not represent the full extent of the biogeochemical adjustments associated with the deglaciation. The Byrd ice core record indicates that the initial CO_2 increase to 280 ppm 11,000 years ago was followed by a reversal to perhaps 245 to 255 ppm 9,000 years ago and then a return to 260 to 280 ppm by 7,000 years ago (2). Although scattered, the data may reflect a real atmospheric response to long-term processes, such as oceanic CaCO_3 dissolution or delayed initiation of widespread peat deposition (31). Subsequent millennia are not well documented in the ice core record. By 1000 years ago atmospheric CO_2 concentrations appear to have become relatively stable at levels between 270 and 290 ppm (32, 33), but a subtle decreasing trend (on the order of a few parts per million per century) may have persisted for three to four centuries immediately preceding the modern increase in CO_2 levels (34). Although these preindustrial changes were certainly small relative to recent changes, it is not clear that early human influences can be readily distinguished from natural trends in preindustrial atmospheric CO_2 levels.

The anthropogenic CO_2 perturbation began somewhat gradually, making its onset difficult to pinpoint in view of possible subtle variations attributable to other causes. The ice core record from the Siple Station in Antarctica shows that atmospheric CO_2 concentrations rose from near

280 ppm in 1750 to just below 290 ppm in 1850 and about 310 ppm in 1950 (35). This record beautifully overlaps the modern record of atmospheric CO_2 monitoring begun in the late 1950's at Mauna Loa and the South Pole (36, 37). In 1990 the mean global CO_2 concentration was 353 ppm (38). These values define an accumulation of 160 Gt of C as atmospheric CO_2 from 1750 to 1990 (Table 3). More than half of this amount accumulated after 1950.

The principal source of this atmospheric increase was the production of CO_2 by burning fossil fuels. Industrial activities (including calcining limestone in the production of cement) yielded about 220 Gt of C as CO_2 between 1750 and 1990. Virtually all of this production occurred after 1850, and more than two-thirds occurred after 1950. Thus the production of industrial CO_2 did not begin as early or increase as gradually as the rise in atmospheric CO_2 .

Before industrial activities began to contribute to the CO_2 budget, human activities of another sort probably released significant quantities of CO_2 to the atmosphere. Between 1750 and 1850 the conversion of forests to agricultural use, particularly in North America, may have released about 40 Gt of C as CO_2 from trees and soils (39). This form of CO_2 release has likely grown with population increase and agricultural expansion in other areas, most recently in the tropics. The effects of human land use on the CO_2 budget are much more difficult to assess than the amount of industrial CO_2 released. Effects of diverse changes in land use must be accounted for in many different ecosystems. Although the harvesting of wood and conversion of forests to pasture and crops will always produce CO_2 , some may be released immediately by burning, while some may be released slowly by decay of wood and soil organic matter. Some CO_2 may be reassimilated through afforestation

Table 4. Net annual CO₂ budgets by latitude. All fluxes are in gigatons of C per year. Negative sign indicates uptake from atmosphere. Scenario labels are 1, from (50), 1980 scenario; 2, from (55), scenario 6; 3, from (56), revision of (55) scenario 6; 4, from (50), preindustrial scenario; 5, from (56), preindustrial scenario; see text for discussion and (66).

Reservoir	Scenario				
	1	2	3	4	5
<i>Extratropical Northern Hemisphere</i>					
Ocean	-2.6	-0.6	-0.7	-1.9	-0.3
Land	-0.5	-2.4	-2.3	0.0	
Total	-3.1	-3.0	-3.0	-1.9	
<i>Equatorial</i>					
Ocean	1.4	1.3	1.2	2.0	1.7
Land	0.3	0.7	0.8	0.0	
Total	1.7	2.0	2.0	2.0	
<i>Extratropical Southern Hemisphere</i>					
Ocean	-1.0	-1.4	-1.6	-0.1	-0.8
Land	-0.1	0.1	0.3	0.0	
Total	-1.1	-1.3	-1.3	-0.1	
<i>All latitudes</i>					
Ocean	-2.2	-0.7	-1.1*	0.0	0.6
Land	-0.3	-1.6	-1.2†	0.0	-0.6
Total	-2.5	-2.3	-2.3	0.0	0.0

*Subtract 0.6 river flux for total net oceanic uptake of anthropogenic CO₂ (-1.7).
 †Add 0.6 river flux for total net land uptake of anthropogenic CO₂ (-0.6).

and regrowth after logging or abandonment of agricultural land. Thus an accurate budget requires accounting for not only the shifting geographic patterns of human land use, but also the temporal fate of vegetation, soils, debris, and wood products following disturbance (40). For example, although northern nontropical forests are currently accumulating CO₂ due to regrowth and afforestation (41), their net effect on the CO₂ budget may be significantly reduced because of oxidation of debris and wood products from earlier harvests (42, 59). There is general agreement that tropical deforestation is a significant source of CO₂, but estimating the magnitude of this source is still hindered by uncertainties in the extent of deforestation, the contribution of soil C, and the interpretation of long-term reduction of biomass by selective harvest of wood within forests (43). Complexities such as these make the effects of human land use one of the most uncertain components of the global CO₂ budget.

Another area of significant uncertainty is the amount of anthropogenic CO₂ that has been absorbed by the oceans. Between 1750 and 1990 the ocean surface mixed layer absorbed close to 20 Gt of C as CO₂, the amount necessary to maintain equilibrium with the increase in atmospheric CO₂ concentrations (18). The uptake of additional anthropogenic CO₂ is limited by its downward transport below the mixed layer. This penetration would be easily detectable with current analytical techniques if it could be measured relative to a well-defined background. However, just as the complex-

ities of ocean C distribution obscure the mechanisms underlying the deglacial CO₂ budget, they prevent easy discrimination of the anthropogenic CO₂ signal from natural trends. Estimates of oceanic CO₂ uptake based on direct measurements are thus tentative (44). Valuable constraints may be provided by measured trends in ¹³C/¹²C ratios and atmospheric O₂ concentrations (45). Such estimates will inevitably improve as the signal becomes larger and as more measurements are made.

Even as more direct estimates improve, the principal basis for calculating oceanic CO₂ uptake will remain ocean models, which are required to integrate all of the available measurements into global uptake estimates. Such models vary widely in complexity, ranging from box models [which compute fluxes and amounts of C for large averaged ocean regions; for example, see (46)] to so-called "box-diffusion" models [which combine box model calculations with computation of vertical mixing using diffusion equations; for example, see (47)] to ocean general circulation models [which compute ocean mixing from fluid dynamic principles; for example, see (48)]. Models designed to simulate CO₂ changes over time scales of decades to centuries rely most critically on formulations of gas exchange and ocean mixing. Measurements of dissolved ¹⁴C are used to calibrate model gas exchange and mixing rates (49). Because ¹⁴C is produced only in the atmosphere it is a particularly useful tracer for calibrating the transfer of CO₂ from the atmosphere to the oceans. The radiodecay of ¹⁴C in deep

ocean waters is a measure of their age with respect to exchange at the surface with atmospheric CO₂. An additional injection of anthropogenic ¹⁴C was produced as a result of atmospheric nuclear weapons testing in the 1960's. Although this "bomb" ¹⁴C obscures the natural ¹⁴C distribution at relatively shallow depths, it provides a useful tracer for transport on a decadal time scale, which is more appropriate for modeling anthropogenic CO₂ uptake.

Ocean models calibrated with the use of both bomb and natural ¹⁴C distributions can be used with the ice core record of atmospheric CO₂ levels to impose significant constraints on the amount of CO₂ that has been taken up by the oceans. The models can be run with atmospheric CO₂ concentrations forced to follow the ice core record. This technique (sometimes called deconvolution) yields not only an estimate of CO₂ uptake but also a compatible estimate of the time-dependent CO₂ source necessary to account for both the modeled oceanic uptake and the prescribed trend in atmospheric CO₂ concentrations. By subtracting the reasonably well-known rate of industrial CO₂ production from the computed source, it is possible to derive a residual term that represents nonindustrial CO₂ produced (or consumed) by processes not included explicitly in the models. Comparison of this residual term with independently estimated sources—particularly estimates of CO₂ produced by changes in human land use—is a telling test of our ability to balance the global CO₂ budget.

Table 3 compares independent source estimates with results from two recent ocean model deconvolutions for the years 1750 to 1850, 1850 to 1950, and 1950 to 1990. The results from these models reasonably represent the current range of estimates for oceanic CO₂ uptake. The modeled residual terms (the last row in the table) compare favorably to recent estimates of CO₂ emissions caused by changes in land use (the second row in the table) only for the period 1750 to 1850. Subsequent increases in the estimated land-use source are not matched by the modeled residual. In the period after 1950 when the estimated emission rate from land use increases to its highest level (primarily as a result of tropical deforestation), the residual terms approach zero. This trend toward increasing disparity is reflected in an increasing CO₂ budget imbalance between known sources and identified sinks (the second row from the bottom in Table 3). The imbalance is equivalent in magnitude to one-third to one-half of the cumulative industrial CO₂ source, an amount too large to be accommodated by uncertainties in the other CO₂ budget terms. The imbalance requires a large unaccounted CO₂ sink of



about 60 to 100 Gt of C for the period 1750 to 1990. The identity of this sink could theoretically be sought in either oceanic or terrestrial processes not encompassed by the other budget terms (or the models used to calculate them). A terrestrial organic sink is suggested by ocean model deconvolution of the ice core record of stable carbon isotopes in atmospheric CO_2 (50, 51). However, efforts to model the processes responsible for this sink have not yielded a satisfactory explanation, even when likely terrestrial perturbations, such as effects of global temperature variations and the hypothesized fertilization of the biosphere by increasing atmospheric CO_2 concentrations, are combined (37, 52, 59).

Computation of the modern annual CO_2 budget is inherently grounded in historical trends. Estimates of both ocean uptake and emissions resulting from land use require accounting for effects that are integrated over periods much longer than 1 year. Thus it is not surprising that the historical CO_2 budget imbalance is also conspicuous in the modern annual budget (Table 1). Some have pointed to numerous hypothetical CO_2 sinks (such as forest growth or fertilization of plants by anthropogenic N) that might account for the annual imbalance (38, 53). However, such potential sinks must be considered to be tentative until they can be documented historically in a manner consistent with the historical origins of other modern CO_2 budget estimates.

The modern annual CO_2 budget is subject to additional constraints derived from relatively recent measurements of the detailed distribution of CO_2 in the atmosphere. Industrial CO_2 accumulates in the atmosphere of the Northern Hemisphere more rapidly than it can be mixed southward. The resultant north-to-south gradient in atmospheric CO_2 concentrations, combined with estimates of the rate of interhemispheric atmospheric exchange, constrains the rate at which CO_2 reaches the Southern Hemisphere through the northern atmosphere. This constraint applies to most of the industrial CO_2 , because nearly all of it is produced in the Northern Hemisphere. The constrained southward atmospheric transfer seems to imply that ocean and land CO_2 sinks in the Southern Hemisphere are relatively modest and, conversely, that CO_2 sinks in the Northern Hemisphere are large (50, 54, 55). This result was not predicted by models of historical CO_2 uptake, which have generally assumed that ocean CO_2 uptake is simply proportional to ocean surface area.

The enhanced Northern Hemisphere CO_2 sink has been attributed to both land and ocean uptake. For example, two recent studies (50, 55) used the observed distribution and modeled transport of atmospheric

CO_2 to constrain the distribution of sinks and nonindustrial sources (Table 4). These studies yielded similar latitudinal distributions of total sources and sinks, but Tans *et al.* (55) attributed the large Northern Hemisphere sink to land, whereas Keeling *et al.* (50) attributed it to the oceans. Both budgets are defensible but also subject to large uncertainties. Keeling *et al.* (50) constrained their simulations using atmospheric $^{13}\text{C}/^{12}\text{C}$ ratios as well as CO_2 data and suggested that this double constraint favors a large northern ocean sink. Tans *et al.* (55) did not use $^{13}\text{C}/^{12}\text{C}$ data, but showed that the Northern Hemisphere uptake suggested by Keeling *et al.* does not appear to be consistent with the most extensive ocean surface data set available for directly estimating net exchange of CO_2 between the oceans and the atmosphere. Both budgets do suggest, however, that the global biosphere is a net sink for CO_2 , in spite of the significant quantities of CO_2 released by deforestation. The budgets differ in their estimates of the magnitude of this sink, particularly in the Northern Hemisphere.

What do these modern annual budgets imply about the historical CO_2 budget? The inference of a small net biosphere sink is consistent with estimates of the CO_2 budget imbalance since 1950 (Table 3), if the imbalance is assumed to represent a terrestrial biosphere sink. The small ocean sink inferred from ocean surface CO_2 measurements (Table 4, column 2) was originally interpreted as a fundamental challenge to the ocean models used to estimate both historical and modern CO_2 uptake. However, corrections in the interpretation of the ocean surface data appear to have minimized this inconsistency (56, 57). The principal correction (Table 4, column 3) was derived from consideration of the long-term geochemical balance among CO_2 uptake by weathering on land, delivery of C by rivers to the oceans, and the ocean C budget. Geochemists have long recognized that this balance required a net flux of CO_2 from the oceans to the atmosphere (58). Part of the transfer of anthropogenic CO_2 to the oceans simply offsets this long-term flux, which must therefore be added to the observed ocean surface CO_2 exchange to yield an estimate of the anthropogenic flux (56). Likewise, the land CO_2 budget derived from such observations must be adjusted to account for long-term geochemical CO_2 uptake on land. When these adjustments are applied, the total annual oceanic CO_2 uptake is larger than that estimated by Tans *et al.* and is within the range predicted by ocean models.

Despite this corrected interpretation of the data, the adjusted latitudinal distribution of oceanic uptake remains a significant problem. The problem is most conspicuous

in comparing the pre-1750 scenarios implied by the modern annual CO_2 budgets shown in Table 4. These scenarios (Table 4, columns 4 and 5) were calculated by subtracting the modeled oceanic uptake of anthropogenic CO_2 from the total oceanic fluxes in the modern budgets for each latitude zone. Whereas Keeling *et al.* postulated a large pre-1750 northern ocean CO_2 sink (Table 4, column 4), no such sink is observed in the pre-1750 scenario derived from the budget constrained by Tans *et al.* to fit modern CO_2 observations for the ocean surface (Table 4, column 5). Although the Keeling *et al.* scenario does not include the long-term geochemical ocean CO_2 source, no reasonable latitudinal allocation of this source could resolve the discrepancies between these pre-1750 scenarios. Thus, the small ocean CO_2 sink in the Northern Hemisphere inferred from ocean surface observations still appears to require a large northern land sink. No models of historical land use can accommodate this sink, yet it is difficult to understand how such a large amount of CO_2 could be accumulating unobserved on land not affected by human use (59). These problems must limit our confidence in our understanding of both the modern and historical CO_2 budgets.

CO_2 Budget Prognoses

Forecasts of future CO_2 emissions vary widely, depending on assumptions about such factors as population, economic growth, energy supplies and technologies, and land use. A recent summary listed cumulative emissions estimates for the years 1990 to 2100 ranging from about 700 to 2100 Gt of C as CO_2 (60). Such diverse estimates lead to comparably uncertain scenarios for future atmospheric CO_2 concentrations (38). Estimates of future CO_2 emissions are therefore viewed by many as the major uncertainty in anticipating atmospheric trends. On the other hand, much more confidence is generally placed in the ability of C cycle models to forecast atmospheric CO_2 for a given emissions scenario. For example, the recent update report of the Intergovernmental Panel on Climate Change stated, "Future atmospheric CO_2 concentrations resulting from given emissions scenarios may be estimated by assuming that the same fraction remained airborne as has been observed during the last decade, that is, $46 \pm 7\%$ " (38, p. 35). Analysis of the deglacial and historical to modern CO_2 budgets suggests that uncertainties in net emissions forecasts should be even greater and that confidence in modeled CO_2 predictions should be much less.

The deglacial and recent CO_2 budgets represent global perturbations of comparable

magnitude but vastly different rates. Within the next century the cumulative amount of anthropogenic CO₂ (60) will probably exceed the amount of CO₂ transferred from the deep sea over a period of 7000 years at the end of the last ice age. Whereas the deglacial change appears to represent a collective transition involving virtually all aspects of climate and the global C cycle in ensemble, anthropogenic CO₂ is a singular top-down forcing mechanism. We are injecting CO₂ directly into the atmosphere, from whence it works its way downward into the land and sea by assimilation and gas exchange. Likewise, the greenhouse effect of anthropogenic CO₂ (and other anthropogenic gases) is translated downward from the atmosphere in the form of heat transport through the ocean and land surface. These changes may eventually lead to broad adjustments in the C cycle and climate system that are analogous in some ways to those that occurred during the deglacial period. However, the fundamentally downward forcing mode of the present CO₂ climate transient is intrinsically different from the nature of the deglacial transition.

In spite of these dissimilarities, the deglacial and recent CO₂ budgets reveal an important shared problem. In both cases the magnitude of large terrestrial CO₂ sinks must be inferred from indirect evidence rather than direct observations or records. The deglacial CO₂ sink is best estimated from changes in sediment ¹³C/¹²C ratios, and the modern sink is best estimated from the imbalances calculated from atmospheric and oceanic models. Our reliance on these indirect methods is an inevitable consequence of the difficulty of assessing small differences between large and heterogeneous terrestrial assimilation and respiration fluxes. Careful analysis of atmospheric and oceanic CO₂ records may always constrain the magnitude of net terrestrial CO₂ exchange at least as accurately as direct monitoring of the land surface. Neither the deglacial nor the modern CO₂ budget will be satisfactorily balanced, however, until it can be related to specific identifiable CO₂ exchange processes. Forecasts of future CO₂ budgets cannot be based on empirical extrapolation of present unexplained imbalances but must be based on an understanding of the processes that control CO₂ sources and sinks. This understanding requires intensive direct observation of terrestrial ecosystems and their record of past behavior.

Understanding the modern CO₂ budget also depends intrinsically on understanding the historical and deglacial CO₂ budgets. For example, the geochemical balance among weathering, river transport, and sedimentation affected deglacial CO₂ through burial of organic C in soils and nearshore sediments and through control on the net CaCO₃ feedback. The same geochemical balance contributes terms that must be accounted in the

terrestrial and oceanic components of the modern annual CO₂ budget. Deglacial changes in the accumulation of soil C and marine CaCO₃ may not have reached a steady state before the period of historical CO₂ budget accounting. Even if these non-steady-state fluxes did not contribute to significant changes in atmospheric CO₂ before 1750, their place in the modern CO₂ budget is difficult to evaluate without the underpinnings of steady-state assumptions. Estimates of modern CO₂ sources and sinks must be consistent with models that integrate historical and geological effects.

Finally, analysis of the deglacial to recent CO₂ budget illuminates the tremendous diversity in processes and feedbacks that control and respond to atmospheric CO₂. The oceanic and terrestrial contributions to the deglacial CO₂ budget—and the large imbalance in the recent CO₂ budget—suggest that both land and sea will respond dynamically, not passively, to anthropogenic increases in atmospheric CO₂ levels. Several important feedbacks will extend to periods of millennia and longer. Even the most straightforward and effective geochemical CO₂ sink—marine CaCO₃ dissolution—is revealed to be not so straightforward and perhaps not totally effective (61). Thus, fundamental uncertainties about the effects of anthropogenic CO₂ extend to time scales well beyond the period of foreseeable management policies.

REFERENCES AND NOTES

1. C. Starr, M. F. Searl, S. Albert, *Science* **256**, 981 (1992).
2. The CO₂ data are from A. Neftel, H. Oeschger, T. Staffelbach, and B. Stauffer [*Nature* **331**, 609 (1988)] and T. Staffelbach, B. Stauffer, A. Sigg, and H. Oeschger [*Tellus* **43B**, 91 (1991)]. The chronology used here is the "Hammer Ice Age" scale from T. Sowers, M. Bender, J. M. Barnola, D. Raynaud, Y. S. Korotkevich, *J. Geophys. Res.* **97**, 15683 (1992). All concentrations given in this paper refer to the volume of dry air.
3. Bubble occlusion in the Byrd ice core probably took about 50 years, so more rapid changes might not be apparent in this record [J. Schwander and B. Stauffer, *Nature* **311**, 45 (1984)]. There is evidence from other ice cores suggesting that very rapid changes in atmospheric CO₂ of up to 50 ppm occurred during the last glaciation [B. Stauffer, H. Hofer, H. Oeschger, J. Schwander, U. Siegenthaler, *Ann. Glaciol.* **5**, 160 (1984); H. Oeschger, A. Neftel, T. Staffelbach, B. Stauffer, *ibid.* **10**, 215 (1988)]. There is also growing evidence for abrupt climate changes during the last glaciation and the subsequent deglaciation [S. J. Johnsen, *et al.*, *Nature* **359**, 311 (1992); R. B. Alley *et al.*, *Eos* **73**, 259 (1992); K. Taylor, R. Alley, G. Lamoirey, *ibid.*, p. 259]. If the rapid CO₂ events are confirmed they will require explanations that lie outside the realm of current understanding.
4. N. J. Shackleton, in *The Fate of Fossil Fuel CO₂ in the Oceans*, N. R. Anderson and A. Malahoff, Eds. (Plenum, New York, 1977), pp. 401–427.
5. Throughout this article, the term "deglacial" is used to refer loosely to the period of the most recent continental deglaciation. Use of this term is not meant to imply a direct relationship to deglaciation.
6. K. C. Prentice and I. Y. Fung, *Nature* **346**, 48 (1990); J. M. Adams, H. Faure, L. Faure-Denard, J. M. McGlade, F. I. Woodward, *ibid.* **348**, 711 (1990).
7. J. C. Duplessy, N. J. Shackleton, R. G. Fairbanks, L. Labeyrie, D. Oppo, N. Kallel, *Paleoceanography* **3**, 343 (1988); W. B. Curry, J. C. Duplessy, L. D. Labeyrie, N. J. Shackleton, *ibid.*, p. 317; M. K. Samthein, K. Winn, J.-C. Duplessy, M. Fontugne, *ibid.*, p. 361; M. Leuenberger, U. Siegenthaler and C. C. Langway, *Nature* **357**, 488 (1992).
8. M. K. Samthein, K. Winn, J.-C. Duplessy, M. Fontugne, *Paleoceanography* **3**, 361 (1988); T. J. Crowley, *Nature* **352**, 575 (1991); T.-L. Ku and S. Luo, *Paleoceanography* **7**, 543 (1992). These studies document estimates of the deglacial shift in ¹³C/¹²C ratios ranging from 0.3 to 0.5 per mil. The calculation of organic C assimilation assumes that the glacial ocean and atmosphere contained 37,000 Gt of C as CO₂ and dissolved inorganic C, that isotope fractionation during terrestrial C assimilation was 25 per mil, and that virtually all of the assimilated C was terrestrial in origin.
9. T. M. Gerlach, *Eos* **72**, 249 (1991).
10. A. N. Dia, A. S. Cohen, R. K. O'Nions, N. J. Shackleton, *Nature* **356**, 786 (1992); P. N. Froelich and R. A. Mortlock, *Eos* **73**, 271 (1992).
11. R. A. Berner, A. C. Lasaga, R. M. Garrels, *Am. J. Sci.* **283**, 641 (1983).
12. K. Caldeira and M. R. Rampino [*Nature* **355**, 401 (1992)] implied that glacial-interglacial fluctuations in volcanism might account for atmospheric CO₂ changes as large as 60 ppm. However, this value was calculated from a steady-state geochemical weathering relationship that has little relevance to changes over time scales shorter than about 10⁵ years. E. T. Sundquist [*Quat. Science Rev.* **10**, 283 (1991)] examined an identical scenario using a time-dependent model. He showed that the e-fold time of approach to the steady-state CO₂ increase was 380,000 years, and the atmospheric CO₂ change in 7,000 years was less than 3 ppm.
13. A conservative estimate of preindustrial ocean C is 37,180 Gt of C, calculated as 36,600 Gt of C as dissolved inorganic carbon [E. T. Sundquist, in *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archaean to Present*, E. T. Sundquist and W. S. Broecker, Eds. (American Geophysical Union, Washington, DC, 1985), pp. 5–59] plus 700 Gt of C as dissolved organic C minus 120 Gt of C, which is the estimated historical ocean uptake. Glacial ocean carbon (38,000 Gt of C) is estimated as preindustrial ocean C plus 620 to 920 Gt of C as estimated in this paper. Any contribution of the CaCO₃ pump to the deglacial CO₂ increase would imply an increase in this estimate of glacial oceanic C.
14. M. E. Raymo, W. F. Ruddiman, N. J. Shackleton, D. W. Oppo, *Earth Planet. Sci. Lett.* **97**, 353 (1990); W. F. Ruddiman, A. McIntyre, M. Raymo, *Init. Rep. Deep Sea Drill. Proj.* **44**, 855 (1986).
15. J. M. Barnola, D. Raynaud, Y. S. Korotkevich, C. Lorius, *Nature* **329**, 408 (1987).
16. N. G. Pisias and N. J. Shackleton, *ibid.* **310**, 757 (1984); B. Saltzman, *Clim. Dynam.* **1**, 77 (1987); C. Genthon *et al.*, *Nature* **329**, 414 (1987); B. Saltzman and K. A. Maasch, *Global Biogeochem. Cycles* **2**, 177 (1988); C. Lorius, J. Jouzel, D. Raynaud, J. Hansen, H. Le Treut, *Nature* **347**, 139 (1990).
17. E. T. Sundquist and L. N. Plummer, in *Carbon Cycle Modelling*, B. Bolin, Ed. (Wiley, New York, 1981), pp. 259–331.
18. This calculation assumes an average ocean surface total alkalinity of 2.3 meq/kg, a salinity of 35 per mil, a temperature of 15°C, and a mixed layer volume of 3.6 × 10¹⁶ m³. There is no reason to believe that air-sea gas exchange rates were so different during the last glacial period that this equilibrium approach would be invalidated. The effects of deglacial changes in temperature and salinity approximately offset one another [W. S. Broecker, *Geochim. Cosmochim. Acta* **46**, 1689 (1982)]. The calculation ignores the minor (<15%) effect of the alkalinity change that would accompany CO₂ added as a result of an imbalance



- between biological soft-tissue production and remineralization.
19. M. K. Sarinthein, K. Winn, J.-C. Duplessy, M. Fontugne, *Paleoceanography* **3**, 361 (1988).
 20. N. J. Shackleton *et al.*, *Nature* **335**, 708 (1988).
 21. W. S. Broecker and T. H. Peng, *Radiocarbon* **28**, 309 (1986); C. Heinze, E. Maier-Reimer, K. Winn, *Paleoceanography* **6**, 395 (1991).
 22. There is a relatively modest alkalinity effect associated with biological production and remineralization of soft tissue.
 23. This value is an approximation estimated from calculation of two values: (i) The amount of CaCO_3 that would have to be removed from the ocean surface mixed layer to change its equilibrium CO_2 concentration from 200 to 280 ppm without gas exchange. This amount is about 1.7 times (in moles) the amount of CO_2 that would have to be added to the mixed layer to cause the same change under conditions of no CaCO_3 addition or removal. (ii) The ratio of CaCO_3 removal to simultaneous CO_2 loss required to maintain a constant equilibrium CO_2 concentration in the range 200 to 280 ppm. The molar ratio of CaCO_3 removal to CO_2 loss ranged from near 1.55 at 280 ppm to about 1.75 at 200 ppm. The ocean surface was assumed to have an average temperature of 15°C , an average salinity of 35 per mil, and a range of total alkalinities consistent with a modern value of 2.3 meq/kg.
 24. J. D. Milliman, *Marine Carbonates* (Springer-Verlag, New York, 1974).
 25. J. W. Farrell and W. L. Prell, *Paleoceanography* **4**, 447 (1989).
 26. W. S. Broecker and T.-H. Peng, *Global Biogeochem. Cycles* **3**, 215 (1989).
 27. W. H. Berger, *Naturwissenschaften* **69**, 87 (1982); B. N. Opdyke and J. C. G. Walker, *Geology* **20**, 733 (1992).
 28. C. Genthon *et al.*, *Nature* **329**, 414 (1987); T. Sowers, M. Bender, J. M. Barnola, *Eos* **73**, 260 (1992).
 29. E. T. Sundquist, *Nature* **329**, 389 (1987).
 30. E. A. Boyle, *J. Geophys. Res.* **88**, 7667 (1983); E. T. Sundquist, *Philos. Trans. Roy. Soc. London Ser. A* **331**, 155 (1990).
 31. J. W. Harden, E. T. Sundquist, R. F. Stallard, R. K. Mark, *Science* **258**, 1921 (1992).
 32. B. Stauffer and H. Oeschger, *Ann. Glaciol.* **7**, 54 (1985).
 33. U. Siegenthaler *et al.*, *ibid.* **10**, 1 (1988).
 34. D. Raynaud and J. M. Barnola, *Nature* **315**, 309 (1985).
 35. A. Neftel, E. Moor, H. Oeschger, B. Stauffer, *ibid.*, p. 45; H. Friedli, H. Löttscher, H. Oeschger, U. Siegenthaler, B. Stauffer, *ibid.* **324**, 237 (1986).
 36. C. D. Keeling, *Tellus* **12**, 200 (1960); —, J. A. Adams, Jr., C. A. Ekdahl, Jr., P. R. Guenther, *ibid.* **28**, 552 (1976); C. D. Keeling *et al.*, *ibid.*, p. 538.
 37. C. D. Keeling *et al.*, in *Aspects of Climate Variability in the Pacific and the Western Americas*, D. H. Peterson, Ed. (American Geophysical Union, Washington, DC, 1989), pp. 165–236.
 38. R. T. Watson, L. G. Meira Filho, E. Sanhueza, A. Janetos, in *Climate Change 1992: The Supplementary Report to the IPCC Scientific Assessment*, J. T. Houghton, B. A. Callander, S. K. Varney, Eds. (Cambridge Univ. Press, Cambridge, 1992), pp. 29–46.
 39. R. A. Houghton and D. L. Skole, in *The Earth as Transformed by Human Action*, B. L. Turner *et al.*, Eds. (Cambridge Univ. Press, Cambridge, 1990), pp. 393–408.
 40. R. A. Houghton *et al.*, *Ecol. Monogr.* **53**, 235 (1983).
 41. H. R. Delcourt and W. F. Harris, *Science* **210**, 321 (1980); T. V. Armentano and C. W. Ralston, *Can. For. Res.* **10**, 53 (1980); J. M. Melillo, J. R. Fruci, R. A. Houghton, B. I. Moore, D. L. Skole, *Tellus* **40B**, 116 (1988); P. E. Kauppi, K. Mielikäinen, K. Kuusela, *Science* **256**, 70 (1992); R. A. Sedjo, *Ambio* **21**, 274 (1992).
 42. E. B. Rastetter and R. A. Houghton, *Science* **258**, 382 (1992).
 43. R. P. Detwiler and C. A. S. Hall, *ibid.* **239**, 42 (1988); S. Brown and A. E. Lugo, *Interciencia* **17**, 8 (1992); R. A. Houghton and J. L. Hackler, in *Effects of Land Use Change on Atmospheric CO_2 Concentrations: Southeast Asia as a Case Study*, V. H. Dale, Ed. (Springer-Verlag, New York, in press).
 44. P. G. Brewer, *Geophys. Res. Lett.* **5**, 997 (1978); G.-T. Chen and F. J. Millero, *Nature* **277**, 205 (1979); W. S. Broecker, T. Takahashi, T.-H. Peng, "Reconstruction of past atmospheric CO_2 contents from the chemistry of the contemporary ocean: an evaluation" (*DOR Report OR-857*, National Technical Information Service, Springfield, VA, 1985); P. G. Brewer, C. Goyet, D. Dyrssen, *Science* **246**, 477 (1989); J. L. Sarmiento, *Global Biogeochem. Cycles* **5**, 309 (1991).
 45. P. D. Quay, B. Tilbrook, C. S. Wong, *Science* **256**, 74 (1992); R. F. Keeling and S. R. Shertz, *Nature* **358**, 723 (1992).
 46. C. D. Keeling, in *Chemistry of the Lower Atmosphere*, S. I. Rasool, Ed. (Plenum, New York, 1973), pp. 251–329.
 47. H. Oeschger, U. Siegenthaler, U. Schotterer, A. Gugliemann, *Tellus* **27**, 168 (1975).
 48. E. Maier-Reimer and K. Hasselman, *Clim. Dyn.* **2**, 63 (1987).
 49. W. S. Broecker and T. H. Peng, *Tracers in the Sea* (Eldigio Press, Lamont-Doherty Geological Observatory, Columbia University, Palisades, NY, 1982).
 50. C. D. Keeling, S. C. Piper, M. Heimann, in *Aspects of Climate Variability in the Pacific and the Western Americas*, D. H. Peterson, Ed. (American Geophysical Union, Washington, DC, 1989), pp. 305–363.
 51. U. Siegenthaler and H. Oeschger, *Tellus* **39B**, 140 (1987); U. Siegenthaler and F. Joos, *ibid.* **44B**, 186 (1992); T.-H. Peng and W. S. Broecker [*J. Geophys. Res.* **89**, 8170 (1984)] showed that a marine organic sink is not likely to contribute significantly to the historical CO_2 budget.
 52. I. G. Enting, *Tellus* **44B**, 23 (1992).
 53. S. Brown, A. E. Lugo, J. Wisniewski, *Science* **257**, 11 (1992).
 54. I. G. Enting and J. V. Mansbridge, *Tellus* **43B**, 156 (1991).
 55. P. P. Tans, I. Y. Fung, T. Takahashi, *Science* **247**, 1431 (1990).
 56. J. L. Sarmiento and E. T. Sundquist, *Nature* **356**, 589 (1992).
 57. J. E. Robertson and A. J. Watson, *ibid.* **358**, 738 (1992).
 58. R. M. Garrels and F. T. Mackenzie, *Mar. Chem.* **1**, 27 (1972); R. A. Berner, *Am. J. Sci.* **282**, 451 (1982); S. V. Smith and F. T. Mackenzie, *Global Biogeochem. Cycles* **1**, 187 (1988).
 59. R. A. Houghton, paper presented at workshop on Biotic Feedbacks in the Global Climatic System, Woods Hole, MA, 25–29 October 1992, sponsored by the Intergovernmental Panel on Climatic Change.
 60. From table A3.6 in J. Leggett, W. J. Pepper, R. J. Swart, in *Climate Change 1992: The Supplementary Report to the IPCC Scientific Assessment*, J. T. Houghton, B. A. Callander, S. K. Varney, Eds. (Cambridge Univ. Press, Cambridge, 1992), pp. 73–95.
 61. E. T. Sundquist, in *The Changing Carbon Cycle*, J. R. Trabalka and D. E. Reichle, Eds. (Springer-Verlag, New York, 1986), pp. 371–402; in *Sea-Level Change*, R. Revelle, Ed. (National Research Council, Washington, DC, 1990), pp. 193–207; J. C. G. Walker and J. F. Kasting, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **97**, 151 (1992).
 62. From simulation A1.1 of J. L. Sarmiento, J. C. Orr, U. Siegenthaler, [*J. Geophys. Res.* **97**, 3621 (1992)]. Yearly data were provided by the authors. To be consistent with the authors' estimates of atmospheric plus oceanic CO_2 sinks and the atmospheric sink values in Table 4, I adjusted the ocean sink estimates for 1850 to 1950 and 1950 to 1990 by +1 Gt of C. The estimates for 1750 to 1850 could not be used because their simulation was affected numerically by initial conditions for years before about 1800. The ocean sink for 1850 to 1950 was 78% (49/63) of the ocean sink estimated by (37) for the same time period. I estimated the ocean sink for 1750 to 1850 by assuming an identical ratio between this simulation and that of (37).
 63. From C. D. Keeling, *Tellus* **25**, 174 (1973) and G. Marland and T. A. Boden, in *Trends '91: A Compendium of Data on Global Change*, T. A. Boden, R. J. Sempanski, F. W. Stoss, Eds. (Oak Ridge National Laboratory, Oak Ridge, TN, 1991), pp. 386–389. Uncertainties are estimated at $\pm 10\%$.
 64. From (59). Uncertainties are estimated at $\pm 30\%$.
 65. From estimated global mean atmospheric CO_2 concentrations of (37): 278 ppmv in 1750, 287 ppmv in 1850, 311 ppmv in 1950. Concentration in 1990 estimated at 353 ppmv by (38).
 66. Scenarios 1 and 4 are taken from estimates of (50), table 10. The equatorial zone for these estimates extends from 15.65°N to 15.65°S . I rounded the original figures to be consistent with the given rounded global totals. Scenario 2 is from estimates of (55), table 4. The equatorial zone for these estimates is 15°N to 15°S . I assumed that the given temperate uptake and boreal source fluxes occur in the extratropical Northern Hemisphere. I calculated the latitudinal distribution of the authors' tropical deforestation flux by assuming that the biospheric destruction terms in (50) were distributed proportionally to latitude. Ocean fluxes for scenarios 3 and 5 are from (56), table 3. I calculated land fluxes in scenario 3 from the differences between the ocean fluxes and the total fluxes, which I assumed to have the same latitudinal distribution as in scenario 2.
 67. I am grateful to A. Berger and his colleagues at the Université Catholique de Louvain for a stimulating visit that catalyzed many of the ideas expressed here. R. A. Houghton, J. L. Sarmiento, and J. C. Orr kindly supplied data from their models and calculations. Helpful comments were provided by E. A. Boyle, R. A. Houghton, I. J. Winograd, and two anonymous reviewers. The paper also benefited from discussions with I. Enting, I. Fung, and T. Sowers. This work was supported by the Global Change Hydrology Program of the U.S. Geological Survey.