

Carbon and Climate System Coupling on Timescales from the Precambrian to the Anthropocene*

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Abstract

Over a range of geological and historical timescales, warmer climate conditions are associated with higher atmospheric levels of CO₂, an important climate-modulating greenhouse gas. Coupled carbon-climate interactions have the potential to introduce both stabilizing and destabilizing feedback loops into Earth's system. Here we bring together evidence on the dominant climate, biogeochemical and geological processes organized by timescale, spanning inter-annual to centennial climate variability, Holocene millennial variations and Pleistocene glacial-interglacial cycles, and million-year and longer variations over the Precambrian and Phanerozoic. Our focus is on characterizing, and where possible quantifying, internal coupled carbon-climate system dynamics and responses to external forcing from tectonics, orbital dynamics, catastrophic events, and anthropogenic fossil-fuel emissions. One emergent property is clear across timescales: atmospheric CO₂ can increase quickly, but the return to lower levels through natural processes is much slower. The consequences of human carbon cycle perturbations will far outlive the emissions that caused them.

Contents

INTRODUCTION AND	
MOTIVATION.....	32
CLIMATE AND CARBON	
SYSTEM PRIMER.....	33
INTERACTIONS ON	
GEOLOGICAL	
TIMESCALES.....	36
Precambrian (Earth's Formation	
to 542 Mya).....	36
Phanerozoic (542 Mya to	
Present).....	38
Pleistocene Glacial-Interglacial	
Cycles (1 Million to	
10,000 Years Ago).....	41
The Holocene (10,000 Years	
Ago to 1700).....	47
INTERACTIONS ON HUMAN	
TIMESCALES.....	48
The Modern Observational	
Record and Interannual	
Carbon-Climate Variability....	48
The Future and Anthropogenic	
Climate Change.....	51

INTRODUCTION AND MOTIVATION

The carbon cycle is one of the fundamental processes in the functioning of Earth's system, intimately connected with both planetary climate and ecology. On the timescale of the human experience, the carbon cycle links human economic activity directly to the geophysical system owing to the sensitivity of atmospheric carbon dioxide (CO₂) and methane (CH₄) levels to fossil-fuel combustion, agriculture, and land use (1). Rising atmospheric CO₂ and, to a lesser extent, CH₄ over the past two centuries have driven substantial global warming (2, 3), which in turn could trigger the release to the atmosphere of additional carbon from ocean and terrestrial reservoirs, thus accelerating climate change. The complex, but currently poorly resolved, dynamics of the modern coupled planetary

climate and carbon systems thus introduces significant uncertainty in future climate (4, 5) and economic (6) projections.

Major scientific discoveries over the past few decades demonstrate that the carbon cycle has also undergone dramatic variations in the geological and historical past in close concert with changing climate (7). A striking CO₂-climate relationship arises with higher atmospheric CO₂ levels under warmer conditions, a correlation found from interannual El Niño-Southern Oscillation (ENSO) events (8) to glacial-interglacial oscillations (9) and geological variations on hundreds of millions of years (10). Given these observations, an obvious question is to what extent can we use the geological and historical record to better predict possible future trajectories of the carbon-climate system over the next several centuries? This exercise is made more difficult because, in many cases, the underlying mechanisms of past carbon-climate variations are not fully deciphered, nor are all processes relevant on the timescales of the anthropogenic climate transient.

Intellectually, studying the carbon cycle demands that scholars link economics, demography, physics, biology, geology, chemistry, meteorology, oceanography, and ecology. Further, as societal concerns grow over climate change, carbon cycle research of modern condition is morphing from a pure academic pursuit to a more operational field, up to and including deliberate manipulation of planetary carbon reservoirs (11). This is too broad a canvas for any pair of scholars to cover in depth, and we restrict our review to the interplay of large-scale biogeochemical dynamics and climate but informed, hopefully, by the broader perspective of the full suite of human-environmental interactions (12). Because of the size and diversity of the scientific literature on the topic, our review is by design also somewhat selective and illustrative rather than comprehensive, concentrating primarily on results published in the last five years or so.

To set the stage, we begin with a brief primer on climate and carbon system

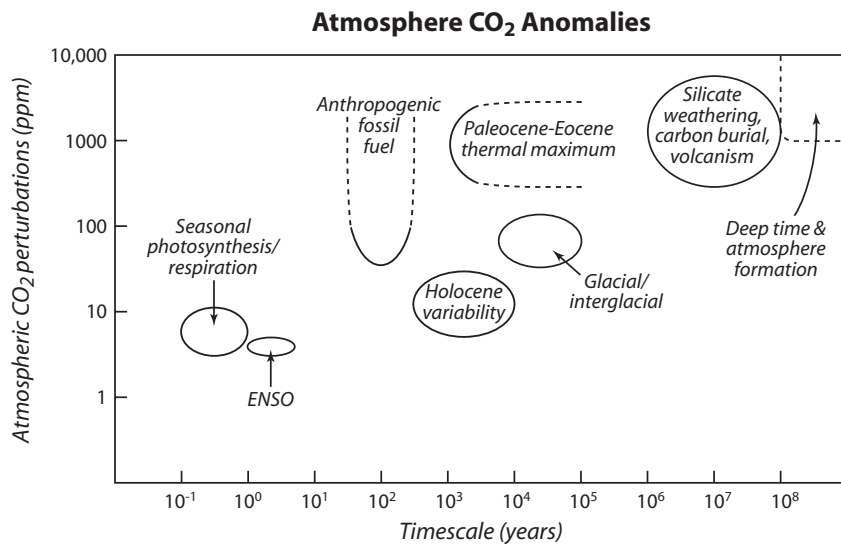


Figure 1

Schematic illustrating the magnitude of atmospheric CO₂ perturbations (in ppm) against approximate timescale (years) for various climate process. The axes are plotted on a logarithmic scale. Abbreviation: ENSO, El Niño-Southern Oscillation.

dynamics. The remainder of the review is organized by timescale (**Figure 1**), starting with the Precambrian (Earth's formation to 542 Mya) and the Phanerozoic (the past 542 million years). The Phanerozoic exhibits gradual multimillion-year variations in atmospheric CO₂ owing to the balance of weathering, volcanism, and organic carbon burial; we also discuss emerging geological evidence for abrupt carbon-climate perturbations during the Precambrian and Phanerozoic. We then overview recent advances on the late Pleistocene glacial-interglacial cycles (the past 1 million years), illuminating the links between orbital variability, cryosphere dynamics, ocean circulation, and the marine carbon cycle. The postglacial Holocene period (the past 10,000 years) reveals subtler interactions between climate and carbon and shows responses resulting from more regional changes in climate modes and events such as volcanism. We conclude with sections on the transition from the preindustrial to modern conditions, the recent observation record, and projected trends for the near future under anthropogenic climate change. The industrial period shows the imprint of human use of fossil fuels and, through process studies, allows quantification of the dynamics

of terrestrial and marine carbon cycles to both natural climate variations (e.g., ENSO) and human perturbations.

CLIMATE AND CARBON SYSTEM PRIMER

Atmospheric CO₂ and CH₄ concentrations are key from a climate perspective because they are greenhouse gases that can absorb infrared radiation, trapping heat that would otherwise be lost to space (13). Both long-lived trace gases are relatively well mixed in the atmosphere, though more subtle time and space variations can be used to reconstruct surface sources and sinks. Atmospheric CO₂ rose from a preindustrial level of ~280 parts per million by volume (ppmv) to ~380 ppmv by 2007 (**Figure 2**); over the same period, CH₄ rose from ~650 parts per billion by volume (ppbv) to ~1800 ppbv. Although the absolute increase in CH₄ is much smaller than that of CO₂, molecule for molecule CH₄ is about 50 times more potent as a greenhouse gas.

Planetary heat balance occurs when the incoming solar radiation absorbed at the surface and in the atmosphere is matched by the loss to space of an equal amount of outgoing infrared radiation from blackbody

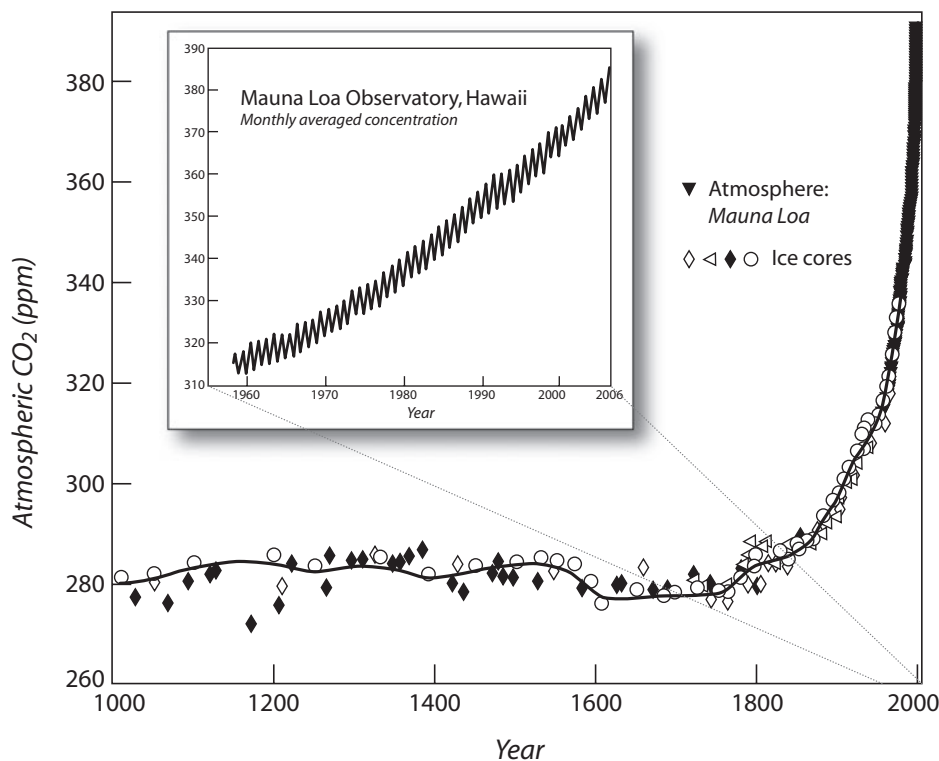


Figure 2

Atmospheric CO₂ concentration for the past 1000 years derived from high-deposition ice cores (194, 195) and direct atmospheric observations. Adapted from Sarmiento & Gruber (16). The inset displays the direct atmospheric CO₂ observations from Mauna Loa, Hawaii, beginning in 1958 at approximately monthly resolution from C.D. Keeling and the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (CO₂ data publicly available from <http://www.cmdl.noaa.gov>).

emissions. Because of water vapor absorption, the atmosphere is transparent to infrared radiation in only a few windows of the wavelength spectrum, and the climate potency of CO₂, CH₄, and other radiative gases (N₂O, chlorofluorocarbons) arises because they can absorb radiation in those windows. As atmospheric CO₂ levels grow, CO₂ absorption begins to saturate specific bands, increasing the mean elevation at which infrared radiation can escape to space. Because the atmospheric vertical temperature gradient and the planetary effective blackbody radiative temperature are relatively fixed, this leads to an increase in surface temperature. The radiative impact of changing CO₂ varies in an approxi-

mate logarithmic fashion with concentration; that is, each doubling of atmospheric CO₂ leads to about the same increment of warming. Biological-physical coupling also arises, particularly on land, because vegetation alters surface heat and water fluxes through evapotranspiration and changes in surface albedo (the fraction of solar radiation reflected back into space rather than absorbed).

The radiative perturbations resulting from changing trace-gas levels can be amplified further by other elements in the climate system associated with, for example, sea ice and land ice, land albedo vegetation, and cloud and water vapor feedbacks. Thus variations in atmospheric CO₂ and CH₄ can lead to substantial

changes in global and regional patterns of temperature, water cycling, and ocean circulation. The resulting greenhouse effect, along with that of water vapor, is a natural part of the climate system and keeps the planet's average temperature significantly warmer than if there were no atmosphere. Human activities that increase atmospheric CO_2 , however, are enhancing this greenhouse effect, and most of the observed warming over the twentieth century is now firmly attributed to the increase in atmospheric CO_2 , establishing one critical connection for quantifying anthropogenic climate change (3).

The exact quantitative magnitude of the climate system's sensitivity to CO_2 remains a subject of study because feedbacks affecting the temperature response to CO_2 (atmospheric water vapor, clouds, ocean heat uptake, and so on) are not fully quantified yet (3). A common measure of the planet's climate sensitivity to a carbon cycle perturbation $\partial T/\partial \text{CO}_2$ is the change in global mean temperature ΔT to a doubling in atmospheric CO_2 including all of the climate feedbacks. Climate sensitivity derived from the equilibrium response of ocean-atmosphere models for present-day conditions varies greatly from +1.5 to +4.5°C ($2 \times \text{CO}_2$), a major uncertainty in climate forecasting (3) and one where paleoclimate data may be used to shed some light. For example, Royer et al. (7) argue that climate sensitivity to a doubling of CO_2 of less than 1.5°C on geological scales is inconsistent with paleoclimate data.

The main controls on atmospheric CO_2 and CH_4 involve exchanges between the atmosphere and organic and inorganic carbon reservoirs on land, in the ocean, and on geological timescales within the crust and mantle (14). Estimates of the preindustrial geophysical fluxes and reservoir sizes for the carbon cycle are as follows. Inventory sizes are reported in Pg C (1 Pg equals 10^{15} g). The preindustrial atmosphere reservoir was about 600 Pg C. By comparison, terrestrial ecosystems are a thin skin of life on the exterior of the planet, containing about 1000–2000 Pg carbon as soils,

vegetation, and animals. The oceans contain large stores of dissolved inorganic carbon ($\sim 4 \times 10^4$ Pg C), a smaller but highly active biological carbon cycle, and deep layers of carbon-rich sediments. The largest stocks of carbon ($\sim 6 \times 10^7$ Pg C) exist in marine sediments as dispersed organic material trapped in sedimentary rocks as well as in carbonate (CaCO_3) rocks in the crust, which slowly but significantly exchange carbon with the rest of the system through geological processes (15). Finally, concentrated pockets of fossil organic carbon, carbon derived from paleovegetation, exist as deposits of coal, oil, natural gas, and other hydrocarbon-rich material in the crust. The current focus on the carbon cycle arises because humans are accelerating dramatically the transfer of very old carbon from crustal hydrocarbon reservoirs to the atmosphere-ocean-land system, leading to a rapid buildup of atmospheric CO_2 and in the process destabilizing the climate system (16).

The atmosphere-ocean-land carbon system is quite dynamic on timescales from hours to decades and even millenia, with large carbon exchanges among various pools and conversions of carbon from inorganic to organic form and vice versa. CH_4 has a well-defined atmospheric lifetime of about a decade owing to the main loss mechanism, chemical oxidation in the lower atmosphere to CO_2 . In contrast, perturbations to atmospheric CO_2 concentrations require decades to centuries to decay and have effects for millennia and longer (17, 18). CO_2 has no true atmosphere lifetime because of the multiple processes that add and remove CO_2 from the atmosphere, unlike reactive pollutants such as chlorofluorocarbons (CFCs) that are eventually chemically oxidized to some simpler and less harmful compound; the carbon released today from fossil-fuel burning will continue to circulate in the atmosphere-ocean-land system for many thousands of years, if not longer, elevating atmospheric CO_2 concentrations and warming the climate.

Currently about half of the CO_2 released by fossil-fuel combustion is removed from

the atmosphere and sequestered into land and ocean reservoirs, slowing CO₂ rise and climate change. The effectiveness of these land and ocean carbon sinks is expected to decline in the future, in part reflecting carbon-climate interactions and the release of additional CO₂ (and perhaps CH₄) to the atmosphere because of warming and hydrological cycle shifts (4, 19). Under some model scenarios, positive carbon-climate interactions could increase anthropogenic warming by an additional 1°C in 2100; carbon-climate feedbacks could also reduce sharply the amount of CO₂ that could be released and still allow humans to stabilize atmospheric CO₂ at a specified target level (3). Estimating the magnitude of such carbon-climate interactions from modern observations and paleorecords requires the deconvolution of the climate-induced change in atmospheric CO₂, δCO_2 , from the initial input ΔCO_2 that may have driven the initial climate change, in the anthropogenic case from fossil-fuel emissions. Climate sensitivity to CO₂ is thought to always be positive, $\partial T/\partial\text{CO}_2 > 0$. As discussed below, the carbon cycle sensitivity to climate perturbations, $\partial\delta\text{CO}_2/\partial T$ (taking temperature as a proxy for climate) can be both positive (destabilizing feedback) and negative (stabilizing feedback), depending upon the timescale and processes involved.

INTERACTIONS ON GEOLOGICAL TIMESCALES

Precambrian (Earth's Formation to 542 Mya)

The carbon cycle of the Precambrian was closely intertwined with the cycles of sulfur, oxygen, and iron as well as the oxidation state of the atmosphere and ocean. These geochemical cycles were, in turn, strongly influenced by the formation of life and subsequent biological activity, which for the Precambrian meant almost exclusively microbially mediated processes initially involving metabolic pathways that evolved under anoxic, reducing

conditions and later in both oxic and anoxic environments. Geological constraints on the composition of the atmosphere of the early Earth were somewhat limited of course, but a number of lines of evidence suggest that it was considerably more reduced than present conditions, with no free atmospheric oxygen (20). Current interpretations are that the early atmosphere was only weakly reducing, which was not so reduced as to convert CO₂ into CH₄, and contained only a small amount of H₂ (21). The redox state and H₂ concentration, however, remain questions of some debate (22).

The evolution of oxygenic photosynthesis and the burial of organic carbon led to the release of a considerable amount of oxidizing power, most of which was used up by oxidizing iron into iron oxides (e.g., banded iron formations) and sulfur into sulfates (23). There is some evidence for oxygenation, restricted to coastal surface waters, by the late Archean, ca. 2.6 Ga (1 Ga = 1 billion years ago) (24). Eventually, a small fraction of the oxidizing power exported by the carbon cycle started to build up as atmospheric O₂, most likely between 2.5 and 2.2 Ga (25). Some of the strongest evidence for the timing of atmosphere oxygenation comes from the disappearance of mass-independent fractionation in paleosulfur isotope records, as mass-independent fractionation can only arise under very low oxygen conditions (26); for an alternate interpretation of the sulfur isotope data, see Ohmoto et al. (27) who argue for a much earlier atmospheric oxygenation beginning ~3.8 Ga. The complete oxygenation of the ocean appears to have occurred more recently and in stages, and the deep ocean may have remained partially anoxic or euxinic (stagnant) under a more oxidized atmosphere and surface waters (28–30). The rise in atmospheric oxygen changed fundamentally the chemical state of the planet and drove biological trends including, eventually, the evolution of multicellular life (31).

Estimates of the atmospheric CO₂ and CH₄ levels for early Earth vary considerably and are only weakly bracketed by data.

Paleorecords of stable carbon isotope ratios ($^{13}\text{C}/^{12}\text{C}$) provide a powerful, if somewhat imperfect and qualitative, tool for characterizing the carbon cycle in the distant geological past. The basic concept is that carbon isotopes can be fractionated as CO_2 enters the ocean, atmosphere, and biosphere system from volcanic emissions from the mantle and crust and are removed to the crust by organic and inorganic carbon burial. Photosynthesis preferentially forms ^{13}C -depleted organic matter with low $^{13}\text{C}/^{12}\text{C}$ values (negative $\delta^{13}\text{C}$ anomaly, about -25% lower than the carbon source) enriching the ^{13}C (positive $\delta^{13}\text{C}$ anomaly) of atmospheric CO_2 , dissolved inorganic carbon in seawater, and the carbonate sediments formed from these pools. Carbon isotope values are reported in the $\delta^{13}\text{C}$ notation, which compares the ratio of $^{13}\text{C}/^{12}\text{C}$ of a sample to the $^{13}\text{C}/^{12}\text{C}$ of a standard. Complications arise because of the (a) extent to which particular samples are representative of the global environment, (b) uncertainties in the overall size and isotopic composition of the atmosphere-ocean-land-crust carbon reservoir over time, and (c) external sources and sinks such as asteroid impacts during the Hadean (>3.8 Ga) (32) and carbon exchange with the mantle via degassing and subduction (23).

Precambrian rock samples provide an admittedly incomplete, but very important, record of the variations over time in the $\delta^{13}\text{C}$ of carbonate sediments, sedimentary organic carbon, and the difference in $\delta^{13}\text{C}$ from contemporaneous organic-inorganic samples. The long-term evolution of the Precambrian carbon isotope record, when viewed as the product of carbon inputs from the mantle to the crust and redox transformations, is consistent with a relatively late oxidation of the atmosphere and surface ocean; abundant O_2 prior to 2.5 ± 0.3 Ga would have required implausibly large carbon cycle throughputs and organic carbon burial fluxes to oxidize the abundant reduced iron and sulfur species and maintain an oxygenated surface ocean (23). More abrupt $\delta^{13}\text{C}$ anomalies can be interpreted as rapid changes in external sources and

sinks to the ocean, atmosphere, and biosphere system or as internal shifts of carbon within the system from one reservoir to another (33).

Paleoclimatic data provides another line of evidence on the early composition of the atmosphere. Solar energy output was 20% to 30% weaker during the early Precambrian, and geochemical proxies, in this case $\delta^{18}\text{O}$ of marine carbonates, suggest that the planet was warmer and perhaps even much warmer (50 – 70°C) than at present (34). One resolution for the “faint Sun paradox” (35) would be strongly elevated levels of atmospheric greenhouse gases CO_2 and CH_4 , requiring atmospheric partial pressures for CO_2 approaching several bars to reach the upper end of the temperature estimates. More moderate, but still warm, climates may be consistent with reinterpretations of the $\delta^{18}\text{O}$ data (36). In contrast, silicon isotope data from cherts appear to support hot conditions (70°C) for the early Archaean ocean with a general cooling trend to 30°C by the late Proterozoic (37). On the basis of geological data such as ice-rafted debris, it appears that the generally warm conditions during the Archaean and Proterozoic were disrupted by several major cooler, glacial periods at about 2.9, 2.4–2.2 and 0.8–0.6 Ga.

The final glacial episode in the late Neoproterozoic included a number of distinct glacial advances, likely two in the Cryogenian (800–635 Mya) and one in the Ediacaran (635–542 Mya). Some of these glacial events may have involved extensive low-latitude glaciation or possibly even planetary glaciation, so-called “snowball Earth” conditions (38). One hypothesis is that rapid, planet-wide glaciation resulted from a runaway ice-albedo feedback that was only abated on timescales of about a million years by the buildup of a supergreenhouse effect from elevated atmospheric CO_2 (39). Following deglaciation, the high atmospheric CO_2 may have led to greatly enhanced continental weathering of carbonate and silicates as well as a flux of excess alkalinity into the ocean, which may explain the observed deposition of thick carbonate layers (*cap carbonates*) and large negative $\delta^{13}\text{C}$

anomalies in marine carbonate (-10‰ amplitude excursions).

On the basis of the magnitude of the carbonate $\delta^{13}\text{C}$ anomalies and fractionation between marine carbonates and organic matter, Rothman et al. (33) hypothesized that the carbon isotopic perturbations represented enhanced respiration of a large and isotopically light marine organic pool. Kennedy et al. (40) present an alternate hypothesis involving destabilization of terrestrial gas hydrates to explain the carbon isotope anomalies and cap carbonates. Although the specific triggers for the onset of the Neoproterozoic glacial episodes are not yet resolved, two geochemical mechanisms have been proposed: cooling caused by the drawdown of atmospheric CO_2 from elevated continental weathering owing to the tropical arrangement of land masses and variations in atmospheric CH_4 .

There is evidence of positive $\delta^{13}\text{C}$ anomalies in the early Proterozoic (2.4–2.2 Ga), interpreted variously as either massive organic carbon burial or shifts in the global zone of methanogenesis from aquatic to sedimentary

(23). Even earlier, about 2.78 Ga, there was a massive negative $\delta^{13}\text{C}$ anomaly in the organic carbon isotopic record, with little or no change in carbonate $\delta^{13}\text{C}$; the excursion is thought generally to represent a widespread assimilation of CH_4 into organic matter (41). The resulting removal of atmospheric CH_4 would likely have had an important climatic cooling effect. Less well agreed upon is Kopp et al.'s (42) argument that the Makganyene glacial event at 2.3–2.2 Ga was caused by the sudden collapse of atmospheric CH_4 greenhouse conditions owing to the rise of oxygenic cyanobacteria.

Phanerozoic (542 Mya to Present)

The more recent Phanerozoic eon (542 to 0 Mya) encompasses the proliferation of multicellular life, the rise of land plants, and the formation of the large fossil carbon reserves that we are now so vigorously exploiting. The Phanerozoic carbon cycle has shaped the environment and evolution of life (43) while responding to the activity of living organisms and geological processes (15, 44). Compared with the limited and at times equivocal geological record for the Precambrian, the paleoreconstructions of climate and atmospheric CO_2 for the Phanerozoic are more numerous and detailed in time and space and better constrained quantitatively (10, 45, 46) (Figure 3). Reconstructed atmospheric CO_2 levels vary dramatically over the Phanerozoic, from levels comparable to preindustrial concentrations of about 280 ppm to as high as 6000 ppm.

Several different geochemical proxies, of varying skill and covering different time periods, have been developed for estimating pre-Pleistocene atmospheric CO_2 (47). These methods include reconstructions on the basis of $\delta^{13}\text{C}$ of paleosoil and mineral deposits (48, 49), stomatal density on fossil plant stems and leaves (50, 51), $\delta^{13}\text{C}$ of alkenones (specific organic compounds produced by surface phytoplankton and found in marine sediments) (52), $\delta^{13}\text{C}$ of fossil plant material (53), and boron

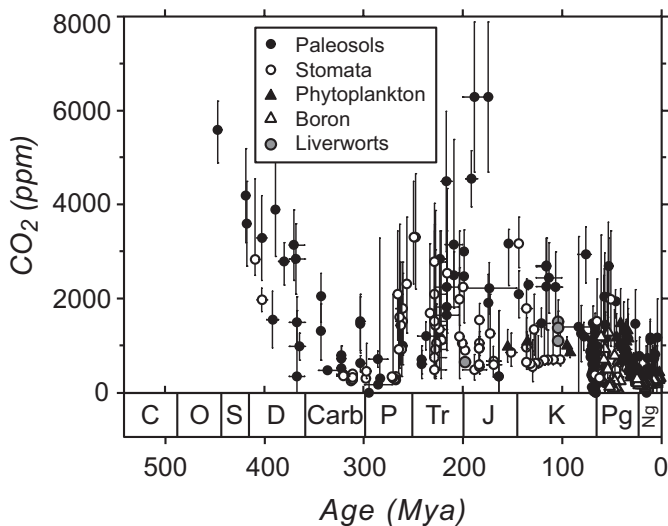


Figure 3

Paleoreconstructions of atmospheric CO_2 (ppm) versus time over the past 450 million years (Mya) of the Phanerozoic. Adapted and reprinted from a figure published in *Geochemica et Cosmochimica Acta*, Vol. 70, CO_2 -Forced Climate Thresholds During the Phanerozoic, by Dana L. Royer (10), copyright Elsevier 2006.

isotope proxies of ocean surface water pH (54, 55). Geochemical modeling studies have also been used to estimate atmospheric CO₂ levels independently and for comparison with the paleoproxy records (44, 56–58). Other important evidence on paleocarbon cycle dynamics comes from geological and geochemical estimates of net organic carbon burial, marine carbonate deposition, and atmospheric oxygen, particularly data on marine carbonate δ¹³C variations (15, 45, 59, 60). Temperature and climate reconstructions come from extensive geological evidence (e.g., presence of glacial deposits, sediment and mineral deposition environments), sea-level estimates, geochemical proxies (e.g., carbonate δ¹⁸O and Mg/Ca data), and paleontological environmental data (46, 61–63).

There is, in general, a good correlation over the Phanerozoic between higher atmospheric CO₂ and warmer climate (10, 46, 64). Periods where there is geological evidence for extensive glaciation in the Carboniferous and Permian (about 350 to 270 Mya) and during the latter part of the Cenozoic (<33 Mya) are associated with low CO₂ levels, <500 ppm. Episodes of cooler climate, but perhaps nonglaciated, tend to have atmospheric CO₂ <1000 ppm, whereas warmer periods generally exhibited atmospheric CO₂ >1000 ppm (10, 64). The geological variations in atmospheric CO₂ would have driven substantial changes in radiative forcing that would have been amplified by additional physical and biogeochemical climate feedbacks. The climatic impacts of CO₂ variations are large enough that they appear to be a primary climate driver over the Phanerozoic, rather than simply a passive response to changing climate.

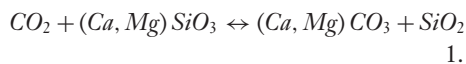
For example, the close agreement between the timing of the decline in atmospheric CO₂ in the mid-Cenozoic and the onset of permanent Antarctic glaciation at the Eocene/Oligocene boundary is highly suggestive of a CO₂-climate link (52). Other hypotheses, however, have been suggested including alterations in ocean circulation

caused by the drift of the Antarctic plate to the pole and the opening of a circumpolar channel. Recent evidence for Northern Hemisphere glaciation in late Eocene to early Oligocene (38–30 Mya) is based on extensive ice-rafted debris sediments from the Norwegian-Greenland Sea (65) and supports a more global cooling. A stronger and more direct causal link between CO₂ and climate can be drawn from coupled climate-ice sheet simulations, which show quantitatively that reductions in atmospheric CO₂, comparable to those in the geological reconstructions, induce ice-sheet growth for Cenozoic conditions (66, 67). In fact, these studies suggest that there may be an atmospheric threshold of 2× to 4× preindustrial atmospheric CO₂ levels below which CO₂ must fall before large-scale glaciation can be triggered.

Numerical climate models have also been used to explore the impact of a CO₂-rich atmosphere during warmer climate periods. Kiehl & Shields (68) describe how elevated CO₂ levels during the late Permian resulted in warm high-latitude temperatures, less vigorous ocean circulation, and low ocean oxygen levels, which are in broad agreement with geological data. In fact, paleoclimate models are reaching a state of maturity where one may be able to invert the problem using the model to estimate what range of atmospheric CO₂ levels are consistent with the climate record (69). This ideal is hindered, however, by remaining uncertainties in paleoclimate proxies and deficiencies in climate models (70).

What caused the large variations in atmospheric CO₂ on geological timescales? And to what extent do climate-carbon cycle feedbacks occur? The major biogeochemical processes influencing the carbon cycle on million-year and longer timescales during the Phanerozoic include the venting of volcanic CO₂, the weathering of silicate rocks on land, the deposition of carbonate sediments in the ocean, the weathering and oxidation of fossil organic matter, and the formation and burial of organic matter. These processes can be

encapsulated by the following two equations (15, 45):



and



The forward reaction of Equation 1 captures the effects of silicate weathering on land and the deposition of marine carbonates and biogenic silica; the reverse reaction indicates crustal metamorphism and release of CO_2 from volcanism. Equation 2 represents oxygenic photosynthesis and respiration and the release of O_2 to the environment owing to net burial of organic matter; it also represents thermal decomposition of organic matter to CO_2 and volcanic emission. A third important process is the weathering of terrestrial carbonate rocks and changes in ocean alkalinity:



As discussed below, the carbonate cycle represented by Equation 3 plays an important role in modulating atmospheric CO_2 over 10^3 – 10^5 years, but not on the million-year timescale.

The importance of chemical weathering arises because CO_2 dissolves in water to form carbonic acid that accelerates dissolution of silicate and carbonate rocks, and elevated atmospheric CO_2 can enhance weathering, driving Equation 1 to the right and thus drawing down atmospheric CO_2 . Chemical and physical weathering are coupled, each enhancing the rate of the other (71). Chemical weathering is also sensitive to climate, increasing with warmer temperature and the strength of the hydrological cycle, which are in turn coupled back to atmospheric CO_2 . This CO_2 -silicate weathering-climate coupling is the basis for a stabilizing feedback mechanism that is thought to be a key factor controlling gradual geological variations in atmospheric CO_2 and climate (72, 73). Most theories to explain long-term evolution of atmospheric CO_2 , therefore, require external perturbations to disrupt this CO_2 -weathering-climate feedback, with hypothe-

ses ranging in timescale from plate tectonics (10^5 – 10^7 years) and orbital forcing (10^4 – 10^6 years) to abrupt catastrophic geological events with durations of 10^3 – 10^5 years (62, 74).

Periods of tectonically driven mountain building increase weathering rates and CO_2 drawdown. A period of rapid uplift of the Tibetan Plateau around 8–10 Mya initiated the summer monsoon cycle; the combination of increased topographic gradients and rainfall is thought to have caused accelerated continental erosion, atmospheric CO_2 decline, and cooling in the late Cenozoic (75, 76). Gradual changes in paleogeography, the arrangement of landmasses, caused by plate tectonics also appear to have played a role by altering surface hydrology, temperature, and weathering rates (77). Donnadieu et al. (78) argue, for example, that enhanced continental runoff from the breakup of the supercontinent Pangea triggered a global cooling of about 10°C in continental temperatures and a reduction of atmospheric CO_2 from above 3000 ppm to around 400 ppm. Other researchers have attributed changes in atmospheric CO_2 to net organic carbon burial in the massive sediment wedges that develop along passive continental margins, such as those that formed during the most recent opening of the Atlantic Basin (59, 60). Squire et al. (79) suggest that the extreme erosion and sedimentation rates from a Transgondwanan Supermountain during the Neoproterozoic (650–500 Mya) may have contributed to the net burial of organic carbon and may have supplied large amounts of nutrients, calcium, and alkalinity to the ocean that supported the rapid radiation of marine life at the beginning of the Cambrian.

Biological evolution occurs on similar timescales as many tectonic processes, and both stabilizing and destabilizing biological-geochemical feedbacks have been identified (43). The expansion of land plants brought about a significant drop in atmospheric CO_2 via two mechanisms. Of primary importance, the evolution of deeply rooted vascular plants

(e.g., trees) in the Devonian accelerated the weathering rates of silicate rocks (80). Also contributing, the later introduction of woody plant material, resistant to microbial degradation, increased net organic carbon storage and created the massive Carboniferous and Permian coal beds (15). Retallack (50) argues that the transition to grasslands during the Cenozoic increased soil carbon storage and contributed to climatic cooling. Geological variations in atmospheric CO_2 may influence life directly, a commonly cited example being the evolution of marine and terrestrial C4 photosynthesis during the Cenozoic presumably because of low CO_2 levels (59, 81).

The geological history of the Phanerozoic is also replete with more abrupt events ($\ll 10^6$ years), often with large perturbations occurring in both climate and biogeochemistry. The more extreme climate episodes are associated with minor to major biological extinction events, which because of the way the geological timescale was originally developed using paleofossils, often fall at the boundaries of geological periods. One of the best-documented events occurred during the Paleocene-Eocene thermal maximum (PETM) about 55 Mya. The PETM is marked by rapid (10^3 – 10^4 years) increase in temperature (5 – 6°C), drop in marine carbonate $\delta^{13}\text{C}$ (3 – 4%), and shoaling of the calcite compensation depth (CCD) (>2 km) followed by a more gradual relaxation over several hundred thousand years (82–84). The CCD is the level in the ocean where dissolution of CaCO_3 overwhelms particle deposition to the seafloor; no burial of carbonate sediments occurs below the CCD. The temperature and carbon isotope signals at the PETM could be explained by the rapid release of a large amount of isotopically light carbon to the atmosphere as CO_2 or CH_4 (greenhouse warming), the oxidation of any CH_4 to CO_2 , and the acidification of the ocean via CO_2 , which lowers pH, increases CaCO_3 solubility, and shoals the CCD. The hundred-thousand-year relaxation timescale could then be explained as the amount of time required for the ocean alkali-

city cycle to come back into balance through carbonate and silicate weathering (Equation 3) (18).

The carbon source and the trigger for the PETM are still debated. One hypothesis, suggested by Dickens et al. (85), focuses on the destabilization of CH_4 hydrates in continental margin sediments, most likely caused by some initial warming or intrusion of magmatic sills into sediments. Methane is appealing because it is a strong greenhouse gas and is depleted in $\delta^{13}\text{C}$ (about -60% for bacterially produced CH_4), thus limiting the amount of carbon required to ~ 1200 Pg C (86). Subsequent studies have shown that the warming and ocean acidification signals were larger than originally thought, suggesting a much larger carbon source ($\gg 2000$ Pg C) that is inconsistent with a CH_4 hydrate signal because the resulting isotopic depletion would be bigger than observed (83). Alternate hypotheses have been advanced using organic carbon reserves with more typical isotopic values (-30 to -20%), for example, the burning of large amounts of high-latitude peatlands (87), thermogenic CO_2 and CH_4 production resulting from magma intrusion into a sediment-rich basin (88), or comet impact (89), but the mechanism remains an area of active research (90). The same suite of biogeochemical mechanisms, as well as others (volcanic CO_2 release from flood basalts, mass mortality, and organic matter decomposition), have been proposed for other abrupt climatic events such as the massive extinction at the Permian-Triassic boundary (91) and Jurassic ocean anoxic episodes (92, 93).

Pleistocene Glacial-Interglacial Cycles (1 Million to 10,000 Years Ago)

Late Pleistocene climate is dominated by a series of large-amplitude glacial-interglacial cycles that are readily apparent in climate and biogeochemical paleorecords. One particularly intriguing puzzle is the large and rapid increase during deglaciation in atmospheric CO_2 ($+80$ – 100 ppmv or $\sim +40\%$) (9, 94) and

Atmospheric CO₂ over late Pleistocene

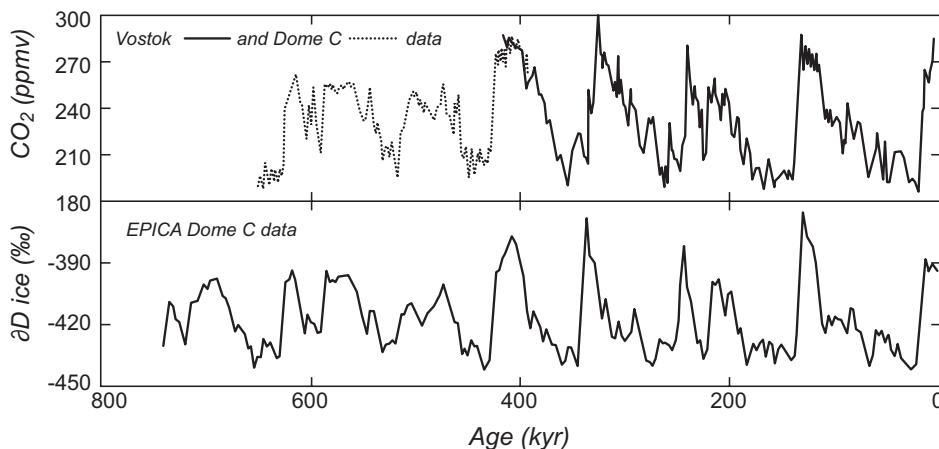


Figure 4

Glacial-interglacial variations of atmospheric CO₂ (ppmv) and ice deuterium ($\delta^2\text{H}$ or δD in ‰), a proxy for temperature (higher δD reflects warmer conditions), from Antarctic ice cores for the last 650,000 years. Created using CO₂ data from the Vostok (9) and Dome C (125) cores as well as δD data from Dome C (126). Abbreviations: EPICA, European Project for Ice Coring in Antarctica; kyr, 1000 years; ppmv, parts per million by volume.

CH₄ (+250 ppbv or $\sim+60\%$) (95) (**Figure 4**). As outlined below, considerable progress has been made in characterizing the timing and magnitude of the climate and CO₂ signals. Yet a complete mechanistic understanding of the initial triggers and underlying coupled carbon-climate dynamics remains somewhat elusive.

The Pleistocene paleorecord available to address such questions is considerably richer than that of prior geological periods, with higher temporal resolution records (10–10³ years), better spatial mapping of paleoenvironmental patterns, tighter chronological controls for determining lead/lag relationships among properties, and an expanded suite of paleoproxies. Some of the most notable advances have come from the recovery of long ice cores, which cover most of the past million years, from the Greenland and Antarctica ice sheets. Ice cores record temperature via $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic variations in the ice (96, 97); borehole temperatures and gas isotopic fraction (see below) provide additional information on thermal history (98). Ice cores

can be used to quantify dust deposition to the Greenland and Antarctic ice sheets (9, 99). Air bubbles trapped within the ice can be measured for paleolevels of CO₂, $\delta^{13}\text{C}$ of CO₂ (organic carbon redistribution), $\delta^{18}\text{O}$ of O₂ (ice volume), and other trace gases (e.g., CH₄, N₂O, sulfur compounds) (9, 95, 100). The isotope and trace-gas records can be recovered quantitatively and “calibrated” to present-day records to allow quite quantitative reconstruction of paleoenvironmental conditions.

Corresponding temporal records of ice sheet volume and ocean surface and deepwater temperatures have been reconstructed from marine sediment cores and corals using carbonate $\delta^{18}\text{O}$, Mg/Ca, and Sr/Ca (101–104), alkenones (105, 106), pore fluid composition (107), and plankton species assemblages (108–111). Detailed records of sea level variations can be derived for some periods with exposed and subaerial corals using uranium-thorium radiodecay dating methods (112, 113). There are also extensive data on glacial advance and retreat, land temperature and water cycle variations, and changes in the distributions of

land vegetation (114). Reconstructions of past marine biogeochemistry conditions have been developed from numerous marine sediment proxies for nutrient distributions from $\delta^{13}\text{C}$ and Cd/Ca (115, 116), bulk and diatom-bound $\delta^{15}\text{N}$ measures of surface nutrient utilization (117, 118) and ocean nitrogen budget (119), the depth profile and rate of ocean CaCO_3 dissolution (120), and export production (121), among others. Radiocarbon ^{14}C , a radioactive isotope of carbon, which is produced naturally by cosmic rays primarily in the upper atmosphere and decays with about a 5700 year half-life, provides a powerful tool for dating events and deciphering carbon cycle variations over the past 50,000 years (122–124).

The close coupling of the carbon cycle and climate is strikingly illustrated by the parallel rise and fall of ice core-derived temperature and atmospheric CO_2 over the late Pleistocene glacial-interglacial cycles (125). The last several cycles were marked by a 100-kyr (1 kyr is 1000 years) saw-tooth pattern with a gradual buildup of land ice and cooling followed by rapid deglaciation over about 5 to 10 kyr; the warm, interglacial periods, similar to the present climate, were relatively short, typically about 10 kyr (126). The Antarctic Vostok core shows these relationships over approximately 420,000 years and four cycles (9). The more recent Antarctic Dome C core shows similar trends over the last eight glacial-interglacial cycles (125, 126). Prior to about 1 Mya, the dominant glacial-interglacial periodicity was about 41 kyr, transitioning to about 100 kyr only over the last 0.5 million years. At the 100-kyr periodicity, atmospheric CO_2 and temperature and deepwater temperature are approximately in phase, with ice volume lagging by several thousand years (102).

The cause of glacial-interglacial oscillations is commonly attributed to orbital variations on surface solar insolation, the so-called Milankovitch forcing owing to changes in Earth's orbital obliquity (41 kyr), eccentricity (100 kyr), and precession (19–23 kyr) (127). However, the direct solar changes are too small to explain the observed peak glacial-

interglacial amplitudes, particularly comparing the variations in eccentricity with the amplitude of the 100-kyr signal. The glacial-interglacial response would have to be modulated and amplified by complex interactions of ice-sheet dynamics, ocean circulation, and biogeochemistry (128–130). The details of the correlations between paleoclimate data and the planet's orbit are still a subject of some debate, and some researchers invoke the stochastic internal variability of the climate system in addition to deterministic orbital triggers (131, 132). The reality may be in between. Huybers & Wunsch (133), for example, find a statistically significant relationship between obliquity and the timing of deglaciations; see also the discussion of nonlinear phase locking to orbital forcing by Tziperman et al. (134).

Analysis of specific paleoclimate events with high temporal resolution records allows for better quantification of the “leads” and “lags” between temperature, atmospheric CO_2 , and other climate properties, providing important clues about carbon-climate coupling. One complication for ice cores arises because air spaces in the firn near the surface of the ice sheet do not seal off immediately from the atmosphere when snow is deposited, and thus the air in ice-core bubbles is actually younger than the surrounding ice. This age offset between air-bubble CO_2 and ice $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic signals can be addressed by age models that attempt to align the records. A recently developed approach takes advantage of the fact that the gases in the firn (the ice prior to bubble closure) can diffuse vertically through the ice until the air spaces are fully sealed off. Diffusion can cause isotopic fractionation. When there is a large temperature gradient in the ice, introduced for example by a change in surface temperature, the gases will be fractionated isotopically in the vertical because of thermal diffusion. The signature of thermal isotopic fractionation in nitrogen and argon in the bubbles can then be used to mark rapid temperature fluctuations (135, 136). The chronology of ice cores in different locations can be matched using well-mixed

atmospheric gases such as CH₄ and δ¹⁸O in O₂ in air bubbles (137). The problem of correlating ice cores with other records, such as marine sediment cores, is even more difficult and involves either independent age measures (e.g., layer counting in ice cores and in varved marine sediments that occur in some anoxic basins, radiometric ages using ¹⁴C and U-Th) or simultaneous climate proxies that are evident in both records (138, 139).

Comparing the age-corrected bubble and ice-core δ²H time series for the last glacial termination (when CO₂ rose by 76 ppmv in only 6000 years), Monnin et al. (140) found that the CO₂ changes lagged slightly behind the Southern Hemisphere temperature changes by 800 (+/- 600) years (Figure 5). Caillon et al. (141) found similar results with CO₂ lagging Antarctic warming by 800 +/- 200 years for glacial termination III [~240 ka (1 ka is 1000 years before present)]. Alley et al. (142) argue that Northern Hemisphere warming during the most recent termination occurred, if anything, slightly earlier than Southern Hemisphere warming. Because the onset of Southern Hemisphere thermal warming precedes CO₂ changes in both cases, we can infer that initial elevated Southern Hemisphere temperatures affect Earth's system in some way that releases CO₂ to the atmosphere. The Southern Ocean is thought generally to be the primary CO₂ source (9, 143), but see Johnston & Alley (144) for a countersuggestion for Northern Hemisphere control on atmospheric CO₂. A CO₂-climate lag time of 800 years is consistent with the mixing time of the deep ocean and is much longer than the time required for warming and degassing of the surface ocean.

The rise in atmospheric CO₂ affects radiative forcing in the atmosphere and will cause surface warming, other factors being equal. Thus carbon-climate feedbacks amplify the original physical climate perturbation, accelerate deglaciation, and transform small radiative changes from orbital forcing to large glacial-interglacial climate state shifts (145, 146). The similarity of orbital-scale north-

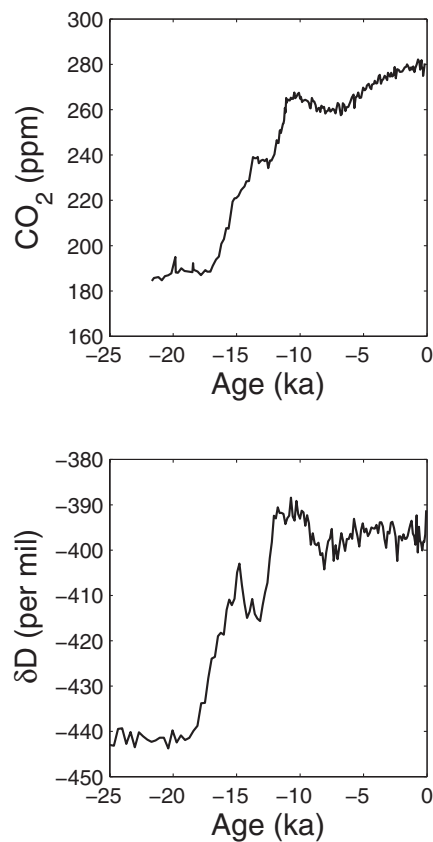


Figure 5

Variations of atmospheric CO₂ (ppm) and ice deuterium (δ²H or δD in ‰), a proxy for temperature (higher δD reflects warmer conditions), from Antarctic ice cores for the last glacial termination and Holocene. Created using data from Dome C core for δD (126) and CO₂ (126a). Abbreviations: 1 ka, 1000 years ago; mil, isotopic fractionation relative to reference material in parts per thousand (‰).

ern and southern climate records, despite the hemispheric asynchrony of some of the orbital forcing, argues for such a global feedback from orbital forcing, and atmospheric CO₂ provides quantitatively the only plausible global process (145). Close correlations between ice-core CO₂ and CH₄ changes also indicate synchrony between Southern Hemisphere and tropical and/or Northern Hemisphere climate (140). Elevated atmospheric CH₄ is usually interpreted as arising from

warmer and wetter terrestrial conditions, which lead to increased CH₄ release from both tropical and boreal wetlands (147). Paleoclimate simulations suggest that radiative impact of the atmospheric CO₂, CH₄, and N₂O variations contributes about half of the estimated cooling that occurred at glacial maxima compared with interglacial periods (146, 148); the remainder is due to changes in surface albedo (sea ice, ice sheets, vegetation) and surface topography (ice sheets).

The interpretation of CO₂ and CH₄ during the most recent glacial termination is complicated, somewhat, by a large millennial climate oscillation with the Bolling-Allerod warm phase (13.8–12.3 ka) followed by the Younger Dryas cold reversal (12.3–11.2 ka), both of which are evident in the Greenland ice core synchronous with other climate proxies for the northern and tropical Atlantic (139, 149). Unlike the orbital-scale patterns where the Northern and Southern Hemisphere climate signals are broadly in phase, perhaps with a slight northern lead, the millennial-scale signals are broadly antiphase, again with a slight northern lead of the antiphased behavior. Atmospheric CO₂ was flat or slightly decreasing during the Bolling-Allerod and then increased sharply during the Younger Dryas, consistent with a positive CO₂-temperature relationship and Antarctic climate variations, which were out of phase with those in Greenland during this period (140). The pattern was opposite for CH₄ (Northern Hemisphere dominance), with near Holocene levels during the Bolling-Allerod and a sharp minimum during the Younger Dryas.

The ocean is the only likely candidate for modulating the 80–100 ppmv (160–200 Pg C) glacial-interglacial variations in atmospheric CO₂ because it is the largest reservoir of mobile carbon on these timescales. Land carbon inventories actually grew rather than shrank during deglaciation owing to revegetation of previously ice-covered surfaces and to shifts in vegetation, removing about 300–800 Pg C that must have been balanced by even greater ocean CO₂ release

(114, 150) and increasing the $\delta^{13}\text{C}$ of the ocean-atmosphere inorganic pools by 0.3–0.4‰ (151). Numerous ocean hypotheses, each with a rich scientific literature, have been proposed such as coral reef growth, temperature and salinity changes, reorganizations in North Atlantic ocean circulation, and alterations in nutrient inventories and biological productivity, among others (152, 153). As summarized in recent review articles (151, 154), no single mechanism appears to explain the entire CO₂ change while remaining consistent with the numerous paleodata constraints, and recent conceptual models argue for combinations of different processes acting during different stages of glacial-interglacial transitions (155, 156). One general caveat is that many of the recent synthesis studies have been conducted in box models, which tend to exhibit stronger changes in atmospheric CO₂ to perturbations compared with three-dimensional general circulation models (157), though uncertainties surround general circulation models as well (158, 159).

Postulated reduced biological productivity because of lower interglacial dust deposition and iron fertilization (160) now appears to account for at most only about half of the CO₂ increase (121, 161, 162). Improved paleodata sets (121) also question other biological hypotheses that require decreased interglacial Southern Ocean export production arising from depleted nitrate inventories (143), weaker nutrient utilization owing to reduced stratification (163, 164), or shifts in plankton community structure. Brzezinski et al. (165) and Matsumoto et al. (166) hypothesized that during glacial periods biological processes were less efficient at removing dissolved silicic acid from Southern Ocean surface waters, leaving more preformed silicic acid to be transported in the ocean thermocline to low-latitude upwelling regions. This silicic acid leakage would have favored the growth in the tropics of diatoms over coccolithophorids, thereby increasing the organic carbon/CaCO₃ rain ratio in key tropical regions, readjusting the ocean's alkalinity

balance, and lowering glacial atmospheric CO₂. Sediment core data from the eastern equatorial Pacific, however, provide evidence of lower opal (Si) fluxes for the last glacial period relative to the Holocene, exactly the opposite predicted from the silicic acid leakage hypothesis (167, 168).

Southern Ocean physical mechanisms likely contribute a significant fraction of the atmospheric CO₂ rise during deglaciation, including effects caused by thermal warming, a poleward shift in atmospheric westerlies, enhanced ocean overturning circulation, increased vertical mixing, and decreased sea ice (163, 169–171). Watson & Naveira-Garabato (172) argue that changes in air-sea buoyancy fluxes may have been as important as surface winds in altering glacial-interglacial upwelling circulation in the Southern Ocean. A large drop in surface ocean/atm ¹⁴C levels (a $\Delta^{14}\text{C}$ decrease of $190 \pm 10\%$) occurred during the time interval 17.5- to 14.5-kyr in the last termination; Hughen et al. (122, 123) use the ¹⁴C data to infer a period of increased deep-ocean ventilation and an injection to the surface ocean of radiocarbon-depleted, deep-ocean carbon that had built up during glacial periods with reduced ventilation. Muscheler et al. (173) compare ¹⁴C and ice-core ¹⁰Be records, a constraint on cosmogenic ¹⁴C production rates. They argue that large carbon cycle changes, including ocean circulation variations, are necessary to explain the ¹⁴C temporal evolution. In contrast, Broecker & Barker (174) question the isolated ¹⁴C reservoir explanation, arguing that it is quantitatively implausible and inconsistent with sediment ¹³C data. Understanding the relationship between climate change and ocean mixing/ventilation is critical to understanding past carbon cycle changes and potential future dynamics. Tracer paleoceanography has sought to do this for many years. Unfortunately, ambiguities and methodological problems still plague this endeavor, but progress is being made.

Kohler et al. (155) and Peacock et al. (156) argue that decreases in mean ocean alkalinity

(and phosphate in Peacock et al.) over glacial terminations lead to the final increment in the atmospheric CO₂ rise. Coral reef growth appears to be a minor contributor to overall glacial-interglacial variation, and the impact of altered terrestrial weathering, although potentially larger (175), can explain only part of the signal. In the CaCO₃ compensation hypothesis, a shift of inorganic carbon from deepwater to the surface ocean and atmosphere would result in a transient increase in deepwater carbonate ion concentration, deepening of the lysocline (the depth where noticeable CaCO₃ deposition first starts to occur), and excess CaCO₃ burial, bringing the marine CaCO₃ cycle back into balance over several thousand years. Estimates of glacial-interglacial lysocline variations have been argued as evidence for relatively small net ocean alkalinity adjustments (151), though proxy carbonate ion time series exhibit positive spikes (+25–30 $\mu\text{mol/kg}$) during deglaciation that may be consistent with a larger CaCO₃ compensation mechanism (120).

Greenland $\delta^{18}\text{O}$ ice-core records are punctuated during cold glacial periods by numerous millennial-scale events (176) that are commonly interpreted as abrupt, Northern Hemisphere climate warming events. Positive atmospheric CH₄ anomalies (+100–200 ppmv) associated with these so-called Dansgaard-Oeschger events allow temporal matching of Greenland $\delta^{18}\text{O}$ and Antarctic CO₂ signals (the millennial Greenland CO₂ record is contaminated by high dust and organic levels). Atmospheric CO₂ variations during some Dansgaard-Oeschger events were small (<10 ppmv). Larger CO₂ anomalies (~20 ppmv) occurred for those oscillations linked with Heinrich events, which are marked by extensive ice-rafted debris in North Atlantic sediment cores thought to reflect episodic ice-sheet surging (177). Martin et al. (178) suggest that larger CO₂ oscillations during this period (marine isotope stage 3) can be explained as a temperature-dependent solubility response to deep-sea temperature variations. Two mechanisms have been

proposed to explain glacial millennial climate oscillations involving either changes in ocean thermohaline overturning circulation (179) and/or in tropical ocean-atmosphere dynamics (180). The large atmospheric CH₄ signal provides a potential support for an extension of the warming into the tropics, if the CH₄ variations indeed involve wetland sources over a wide spatial extent (147, 181).

The Holocene (10,000 Years Ago to 1700)

Climate and atmospheric CO₂ variability during the Holocene interglacial is less dramatic than during the glacial-interglacial transitions but nonetheless contains intriguing information about coupled processes. For example, high-resolution Antarctic ice cores (182, 183) show a 6 ppmv decrease in atmospheric CO₂ during the early Holocene (10.5 ka to 8 ka) followed by a steady 20 ppmv increase over the ~8 kyr prior to the industrial period. Indermuhle et al.'s (182) analysis for CO₂ and δ¹³C indicates an initial terrestrial uptake of ~10 Pg C, likely through continued revegetation during the glacial retreat, followed by a terrestrial biosphere carbon release of ~200 Pg C from 8 ka on, perhaps in response to a cooling and drying of Northern Hemisphere climate after the mid-Holocene climate optimum; oceanic warming effects and marine calcite cycle feedbacks contribute but Indermuhle found them to be more minor. On the basis of surface ocean δ¹³C and deep-sea CaCO₃ dissolution records, Broecker et al. (184) suggest an alternative hypothesis where the terrestrial biosphere remained constant from 8 ka to preindustrial times. In their scenario, the 20 ppmv Holocene rise in atmospheric CO₂ resulted from the slow readjustment of ocean carbonate chemistry and alkalinity following the much larger (~500 Pg C) terrestrial biosphere uptake prior to 8 ka during the last deglaciation. Ridgwell et al. (185) provide further support that growth of coral reefs and shallow water carbonates drove the late CO₂

increase, not changes in terrestrial carbon inventory.

Joos et al. (186) simulated Holocene dynamics using climate fields derived from a coupled climate model linked to terrestrial ecosystem and ocean-ocean sediment models. They concluded that oceanic carbonate compensation and sea surface temperature dominated the Holocene CO₂ trend, whereas changes in terrestrial carbon storage, evolving vegetation distributions, and peat growth probably only influenced the atmospheric accumulation by a few ppm. Kaplan et al. (150) came to a similar conclusion from Holocene simulations of terrestrial carbon storage using a dynamic global vegetation model. A modeling study of Brovkin et al. (187) required both a modest terrestrial carbon loss and ocean carbonate adjustments. Although perhaps not having a major impact on atmospheric CO₂, the extensive reorganizations in land vegetation and biogeography during the Holocene (188) amplified and contributed to regional climate variation (146, 189).

In contrast to the previous discussed studies that invoke natural carbon-climate interactions, Ruddiman (190) argued that humans began to modify the global carbon cycle and climate much earlier than previously thought. In his scenario, anthropogenic land use beginning in the early Holocene caused the observed rising atmospheric CO₂ (<8 ka) and CH₄ (<5 ka), and a human-induced +40 ppm atmospheric CO₂ anomaly actually forestalled the onset of the next glacial period. Joos et al. (186) showed that Ruddiman's hypothesis would require a change in terrestrial storage of 700 Pg C and a decrease in atmospheric δ¹³CO₂ of 0.6‰. The isotopic change is not consistent with the observed atmospheric isotope record, and 700 Pg C is about four times larger than current estimates of historical land-use effects.

Atmospheric CH₄ underwent a large oscillation during the Holocene, with peaks around 11.5–9 ka and in the late Holocene; a minimum occurred around 5 ka (191). These variations have been attributed to changes in

tropical wetlands (191), widespread growth of peats in the early Holocene (192), and human rice irrigation (190). Using ice-core $\delta^{13}\text{CH}_4$ data for the last 2000 years, Ferretti et al. (193) found elevated biomass burning emissions for the period 2000 ka to 1000 ka and suggested that both human activities and natural climate change influenced preindustrial atmospheric CH_4 .

Detailed analyses of atmospheric CO_2 for the last millennium from high-accumulation Antarctic ice cores from Law Dome (194) and Dronning Maud Land (195) show highly suggestive relationships between the carbon cycle and recent climate trends as captured by, for example, tree-ring records (196). The records are similar, exhibiting at Dronning Maud Land a CO_2 increase from 278 to 282 ppmv (1000–1200 AD) during the Medieval Warm Period and then a gradual decline to 277 ppmv by 1700 AD during the Little Ice Age. Trudinger et al. (197, 198) applied an innovative modeling technique to deduce terrestrial and oceanic fluxes from the Law Dome ice-core CO_2 and $\delta^{13}\text{CO}_2$ observations. They suggest the CO_2 minimum from 1550 to 1800 AD arises from a land biosphere response to cooling, although they note the $\delta^{13}\text{C}$ data are too sparse to allow robust land-ocean partitioning. Modeling the carbon-climate response to solar irradiance variations and cooling from volcanic eruptions over the last millennium, Gerber et al. (199) found that warming of $+1^\circ\text{C}$ in global mean temperature results in a $+12$ ppmv anomaly in atmospheric CO_2 ; thus ice-core CO_2 data can be used to place bounds on paleotemperature.

In the Trudinger et al. (197, 198) analysis, natural variability in net land and ocean CO_2 fluxes was about 1 Pg C yr^{-1} on timescales of a decade to centuries. Similar levels of natural variability were found in a fully coupled, three-dimensional carbon climate simulation (200). The majority of the modeled internal carbon cycle variability was initiated on land in response to changing soil moisture and temperature, and the ocean acted to partially damp the land-driven oscillations in atmo-

spheric CO_2 . Trudinger et al. (197, 198) also found suggestive evidence of an ENSO correlation with carbon fluxes, possibly involving both terrestrial and marine processes as illustrated by variability studies for the past several decades (201–204), a suite of dynamics we explore in more detail in the next section for the period of instrumental records. The quantitative effects of biogeochemical versus anthropogenic changes over the past millennia remain somewhat speculative and are an active area of research. However, it is clear that the observed carbon system integrates internal and external generated climate variability and anthropogenic forcing and reflects the coupled responses of the ocean-land-atmosphere reservoirs.

INTERACTIONS ON HUMAN TIMESCALES

The Modern Observational Record and Interannual Carbon-Climate Variability

With respect to the global carbon cycle, the beginning of the modern observational period can be marked by the pioneering work of Roger Revelle and Charles David Keeling, and their establishment in 1958 of a long-term atmospheric CO_2 time series on top of Mauna Loa volcano in Hawaii (204a, 204b). Continuing through the present day, the Mauna Loa record shows, up to now, an inexorable rise of atmospheric CO_2 because of fossil-fuel combustion and thus has become one of the most iconic data sets in geophysics, if not all of science. The Mauna Loa record is now part of an extensive atmospheric CO_2 monitoring network that is used for, among many other things, the estimation of land and ocean surface CO_2 fluxes from inverse models of atmospheric transport (8, 205, 206). The combination of atmospheric data with satellite remote sensing, CO_2 flux towers and surface ocean CO_2 measurements, and marine and terrestrial processes studies is providing today unprecedented and, oftentimes, detailed

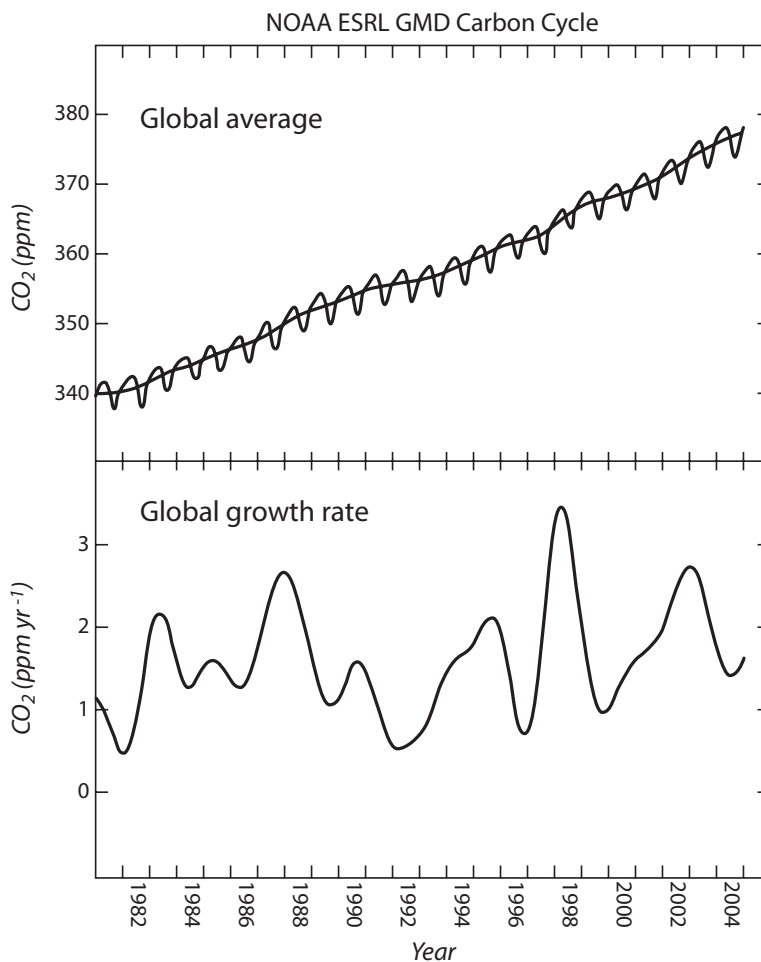


Figure 6

Global mean atmospheric CO₂ concentration and global CO₂ growth rate, $\partial CO_2/\partial t$, for 1981–2005 [adapted from publicly available data and figure courtesy of P. Tans, National Oceanic and Atmospheric Administration (NOAA), <http://www.cmdl.noaa.gov/ccgg>]. Abbreviations: ESRL GMD, NOAA's Earth System Research Laboratory Global Monitoring Division.

information about carbon-climate coupling on multiple space scales and timescales from the diurnal cycle to decades.

The long-term trend in atmospheric CO₂ has remained positive; however, subtle variations in the annual increase in concentration indicate the response of terrestrial and marine processes to climate variability (207) (**Figure 6**). Statistical and modeling analyses of this variation in growth rate of CO₂ have proved a fruitful source of insight. Although arguably the analysis of interannual variations has come to fruition recently, Bacastow et al. (208) first noted a relationship between the Mauna Loa CO₂ record and the weak El

Niño of 1975, suggesting a link between the ocean carbon cycle and atmospheric CO₂. An oceanic causation for the El Niño-CO₂ correlation was first considered because the ENSO is a coupled ocean-atmosphere phenomenon originating in the tropical Pacific. By the 1990s, this was questioned because observed changes in marine CO₂ and air-sea CO₂ fluxes were too small and of the wrong sign to explain the atmospheric changes (201, 209). El Niño events reduce upwelling of cold, CO₂-rich water in the tropical Pacific causing an effective transient increase in ocean carbon uptake (210, 211). Climate variability induces variations in other ocean regions, such as the

Southern Ocean (212), but the magnitude appears to be smaller than the ENSO signal (213, 214).

Much of the El Niño effect on CO₂ seems instead to be associated with terrestrial processes and linked to tropical drought (215). For example, the Amazon Basin experiences droughts during El Niño years. Tian et al. (216) argued that soil drought causes increases in respiratory carbon emission, and Nepstad et al. (217) showed that biomass burning of forest slash during deforestation is higher during El Niño droughts. Vukicevic et al. (202) used data assimilation and a simple model of ecosystem carbon responses to temperature and showed that, although some amount of interannual biogeochemical variability could be explained, large residuals were associated with El Niño periods. The residuals show processes not correlated with temperature through ecosystem metabolism and indicated uptake early in the El Niño period and emissions later. This pattern could arise from ocean uptake early with land emissions following, as El Niño droughts affect biomass burning (215).

Early work focused on drought effects on biological carbon exchange (photosynthesis and respiration) (218); more recent interpretations emphasize wildfires triggered by drought as the cause for much of the observed terrestrial El Niño emission of carbon. Langenfelds et al. (219) used atmospheric measurements of CO₂, ¹³CO₂, and several chemical tracers of biomass burning. They concluded that most of the interannual variability in the growth rate of CO₂ during the 1990s was caused by wildfire. In parallel studies, several groups began to focus on the extremely large wildfires in Indonesia during the 1997–1998 El Niño. Page et al. (220) calculated emissions from these fires of 0.8 to 2.6 Pg of carbon. The emissions were large because the fires burned peatlands, where vast amounts of soil carbon were stored. The Indonesian fires were triggered by El Niño drought but occurred in areas where naturally waterlogged soils had been drained for de-

velopment and so were unusually vulnerable. These huge fluxes were thus caused by an interaction of climate and human land-use practices. Subsequent work using global satellite data has confirmed the importance of wildfire in the interannual variability of the carbon cycle (204). The extent of fires is controlled by ignition and climatic conditions, although as described in Amazonia and Indonesia, prior land management greatly affects the fires' severity and the amount of carbon released.

A large literature focuses on the terrestrial impacts of temperature and temperature increases as a result of global warming (221), but more recent work has highlighted the interaction of temperature and water balance changes as controls over terrestrial carbon exchange. Numerous studies (222, 223) have reported a "greening" trend from satellite data, suggesting increases in terrestrial plant growth, which correspond to a trend in the amplitude of the seasonal cycle of CO₂ that also suggests increased photosynthetic activity. Angert et al. (224) using global CO₂ and satellite data products showed that early spring photosynthetic activity seems to increase (from changes in the spring drawdown of CO₂) but that summer activity is decreased. Using satellite data, they argue that warm springs are typically followed by dry summers, which cancel out the beneficial aspects of the spring warming. This study is highly inferential, as it used aggregated global responses. Direct studies of the impacts of drought on carbon exchange support the potential of dry summers to reduce carbon uptake. Ciais et al. (225) showed that the Europe-wide heat wave and accompanying drought conditions significantly reduced carbon uptake across a large number of in situ observing sites. Using carbon flux data over seven years at a mid-continental site, Sacks et al. (226) showed support for the Angert et al. (224) model by determining that warmer springs increased early carbon uptake but were typically followed by drier summers. The early springs tended to lengthen the growing season, but because of the warm spring-dry summer

pattern, actually reduced the annual carbon uptake.

The Future and Anthropogenic Climate Change

Human activities have altered profoundly many aspects of Earth's system, including climate and biogeochemistry, to the point where some argue that we are entering a new geological era, the Anthropocene (227). The modern atmospheric CO₂ of 380 ppmv is higher than it has been for at least the last 650 ka, and the Intergovernmental Panel on Climate Change projections for 700–1000 ppm by the end of this century have not been observed on Earth for tens of millions of years. In conjunction with the rise in CO₂ and other greenhouse gases, global surface temperature has increased at about 0.2°C/decade over the past several decades, and current temperatures are within about 1°C of the warmest conditions observed for the past 1 million years (228). Archer & Ganopolski (229) pose the provocative idea that anthropogenic fossil fuel or clathrate emissions of 5000 PgC could prevent the planet from entering the next ice age. What coupled carbon cycle climate processes might operate in this high-CO₂, greenhouse world?

In the late 1990s, a large and somewhat speculative literature (221) began to be replaced by quantitative modeling, which examined the terrestrial (230–232) and oceanic responses (233–235) to elevated CO₂ and warmer climate. Evaluating such models is sometimes difficult because much of the signal linking climate variability to surface CO₂ fluxes arises from seasonal and interannual variability. These high-frequency dynamics overlay the lower-frequency processes governing net CO₂ storage on the decadal to centennial scales that are most relevant for the anthropogenic climate and CO₂ perturbation and that may be strongly affected by past historical events such as agriculture, deforestation, and fire management practices (236, 237).

In a seminal paper, Cox et al. (4) used a coupled carbon–climate model, which used an atmosphere–ocean general circulation model to address this question, and found that coupled processes could significantly accelerate climate change. This was because climate change weakened the ability of the oceans and biosphere to take up carbon and could even trigger large emissions in some regions. Specifically, they found in their simulations that tropical drying led to massive losses of carbon from tropical forest regions. This study was followed by a large effort using multiple models to test this hypothesis (238). Friedlingstein et al. (239) used a similar model and found a quantitatively similar but quantitatively smaller response. In their model, the coupled carbon–climate system accelerated warming but to a much smaller degree. Their models had similar marine responses but different sensitivities in the terrestrial biosphere.

An international collaborative project organized by the World Climate Research and International Geosphere–Biosphere Programs inspired 11 modeling teams to repeat these experiments in a multimodel intercomparison. The C⁴MIP project (19) found essentially the same results as Cox et al. (4) and Friedlingstein et al. (239), reporting (a) a consensus on a positive feedback such that carbon–climate coupling accelerates climate change and (b) a great quantitative spread in the magnitude of that feedback. Most of the models simulated a terrestrially dominated effect, but three had a significant ocean feedback. Also, most of the models had terrestrial effects that were dominated by the effects of tropical drying on ecosystem carbon storage. In some of the models, reduced plant growth caused this effect, whereas in others, enhanced respiration or wildfire were the dominant responses. This uncertainty reflects the weak empirical basis and relative recent development of these coupled models. As work progresses, these uncertainties should be reduced through targeted comparisons of the underlying mechanisms in the models against process study data.

The importance of the interplay between temperature and water cycle changes was highlighted by Fung et al. (5). In their coupled model, they found that warming caused increased productivity and enhanced carbon uptake in mid- and high-latitude northern regions. They found that warmer and drier conditions decreased carbon uptake in the tropics. The net carbon cycle feedback resulted from the balance of these two processes, with the tropical reduction dominating over the northern increases. The key drivers for the tropical response were neither temperature nor precipitation but their joint effect on soil moisture. This latitudinal pattern, in fact, holds across the C⁴MIP suite of models (19); the wide range of results on the carbon-climate feedback reflects differences in the relative magnitude of extratropical uptake and tropical emission. Although intriguing, these results should not be treated as the last word on the subject. The terrestrial and marine ecosystem models were generally simple, neglecting a number of potentially important processes such as nitrogen limitation on the land and dust-iron fertilization in the ocean.

The model used by Fung et al. (5) also revealed a critical atmosphere-ocean coupling mechanism. In a study of the model's nat-

ural variability, Doney et al. (200) showed that whereas most of the variability in atmospheric CO₂ was the result of the land biosphere, the variability was damped by ocean processes on decadal to centennial timescales. That is, climate-triggered changes in terrestrial carbon storage caused atmospheric CO₂ concentration-driven changes in ocean uptake. Testing of the key quantitative and qualitative assumptions in these models is in an early stage, and comparisons on the El Niño timescale or using flux time series are just beginning. This analysis shows that the atmosphere-ocean coupling that dominates many of the long timescales of the paleorecord is likely to remain important on the timescales of global change. Caveats are that the current generation of coupled carbon-climate models leave out a number of important biogeochemical processes, for example, nitrogen limitation on land and iron fertilization of the ocean, and neglect peats (240) and CH₄ hydrates (241), two large carbon reservoirs that could be destabilized under a warmer climate. Although the likelihood of a large catastrophic CO₂ release in response to anthropogenic warming may be small, the present estimates of positive carbon-climate feedbacks are also likely to underestimate the true values.

SUMMARY POINTS

1. The coupled carbon-climate system has important dynamics on a wide range of timescales, many of which need to be captured in order to model the anthropogenic transient caused by fossil-fuel emissions and land use. As we push the planet into a new warmer, high-CO₂ state, two important questions arise: What is the climate sensitivity to elevated CO₂? How does warming impact atmospheric CO₂? Historical and paleoclimate records are providing constraints, if somewhat broad, on physical climate sensitivity of about +1.5–6°C in global temperature for a doubling of CO₂ (57, 242, 243).
2. We are less far along addressing the second question, which will require understanding how slow (>10 years) biogeochemical processes set the background that may determine abrupt responses. For example, the tropical and temperate climate-carbon responses are of opposite sign in the current generation of coupled carbon-climate models, reflecting differential net responses to soil moisture and temperature changes. Forecasting future coupled carbon-climate changes also requires understanding how abrupt changes can “excite” responses of slower components of the system, as when

rapid changes to freshwater inputs to the oceans trigger long-lasting changes in circulation and chemistry. The geological record often provides useful pictures of the equilibrium state of the carbon system under different climate conditions, but more research is needed to understand the transient dynamics on the decadal to centennial timescales that control how the system moves from one state to another. As an example, terrestrial vegetation models were originally constructed for static climate conditions. More difficult, but relevant, is the question of how species ranges shift in time in response to changing climate.

3. We also need to incorporate people more specifically into the equation. Humans already manipulate a large fraction of the global carbon system through agriculture, forestry, fisheries, and urbanization, and the human footprint will only grow in the future to confront increased demands for water, food, and energy (biofuels) for a rising world population. Geoengineering approaches are also under consideration, such as reforestation, soil carbon management, ocean iron fertilization, and carbon sequestration into the deep-ocean and geological reservoirs, such as old oil and natural gas fields. Gaining a predictive understanding of the coupled carbon and climate systems requires integrating our knowledge of processes gained across all of the observational timescales, from the geological to the physiological, and including humans and social decision making processes into the dynamics of the carbon-climate system. Although an impressive body of scholarship exists, its integration into a quantitative, predictive framework is just beginning.
4. Despite these complexities, examination of the diverse range of feedbacks across all timescales from abrupt events in the deep past to the modern El Niño cycle supports one consistent finding. The time constants for carbon release are consistently faster than for uptake. Carbon can be released quickly (where the meaning of *quick* varies from days to millenia), but dropping to equilibrium atmospheric levels takes longer than the increase. As we consider the human perturbation and attempt to manage the carbon cycle through fossil-fuel emission controls and geoengineering, we need to remember that, although we can increase CO₂ in the atmosphere quickly, returning to lower levels by manipulating natural processes is likely to be much slower.

DISCLOSURE STATEMENT

The authors are not aware of any biases that might be perceived as affecting the objectivity of this review.

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LITERATURE CITED

1. Wigley TML, Richels R, Edmonds JA. 1996. Economic and environmental choices in the stabilization of atmospheric CO₂ concentrations. *Nature* 379:240–43
2. Hansen J, Nazarenko L, Ruedy R, Sato M, Willis J, et al. 2005. Earth's energy imbalance: confirmation and implications. *Science* 308:1431–35
3. Intergov. Panel Clim. Change. 2007. *Climate Change 2007: The Physical Science Basis*. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, ed. S Solomon, D Qin, M Manning, Z Chen, M Marquis, et al. Cambridge, UK/New York: Cambridge Univ. Press
4. Cox PM, Betts RA, Jones CD, Spall SA, Totterdell IJ. 2000. Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model. *Nature* 408:184–87
5. Fung I, Doney SC, Lindsay K, John J. 2005. Evolution of carbon sinks in a changing climate. *Proc. Natl. Acad. Sci. USA* 102:11201–6
6. Smith SJ, Edmonds JA. 2006. The economic implication of carbon cycle uncertainty. *Tellus B* 56:586–90
7. Royer DL, Berner RA, Park J. 2007. Climate sensitivity constrained by CO₂ concentrations over the past 420 million years. *Nature* 446:530–33
8. Bousquet P, Peylin P, Ciais P, Le Quéré C, Friedlingstein P, Tans PP. 2000. Regional changes in carbon dioxide fluxes of land and oceans since 1980. *Science* 290:1342–46
9. Petit JR, Jouzel J, Raynaud D, Barkov NI, Barnola JM. 1999. Climate and atmospheric history of the past 420000 years from the Vostok ice core, Antarctica. *Nature* 399:429–36
10. Royer DL. 2006. CO₂-forced climate thresholds during the Phanerozoic. *Geochim. Cosmochim. Acta* 70:5665–75
11. Dilling L, Doney SC, Edmonds J, Gurney KR, Harriss R, et al. 2003. The role of carbon cycle observations and knowledge in carbon management. *Annu. Rev. Environ. Resour.* 28:521–58
12. Raupach MR, Marland G, Ciais P, Le Quéré C, Canadell JG, et al. 2007. Global and regional drivers of accelerating CO₂ emissions. *Proc. Natl. Acad. Sci. USA* 104:10288–93
13. Hansen JE, Sato M, Lacis A, Ruedy R, Tegen I, Matthews E. 1998. Climate forcings in the industrial era. *Proc. Natl. Acad. Sci. USA* 95:12753–58
14. Sundquist ET. 1986. Geologic analogs: their value and limitations in carbon dioxide research. In *The Changing Carbon Cycle: A Global Analysis*, ed. JR Trabalka, DE Reichle, pp. 371–402. New York: Springer-Verlag
15. Berner RA. 2003. The long-term carbon cycle, fossil fuels and atmospheric composition. *Nature* 426:323–26
16. Sarmiento JL, Gruber N. 2002. Sinks for anthropogenic carbon. *Phys. Today* 55:30–36
17. Moore B, Braswell BH. 1994. The lifetime of excess atmospheric carbon-dioxide. *Glob. Biogeochem. Cycles* 8:23–38
18. Archer D, Kheshgi H, Maier-Reimer E. 1998. Dynamics of fossil fuel CO₂ neutralization by marine CaCO₃. *Glob. Biogeochem. Cycles* 12:259–76
19. Friedlingstein P, Cox P, Betts R, Bopp L, von Bloh W, et al. 2006. Climate-carbon cycle feedback analysis: results from the C⁴MIP model intercomparison. *J. Climate* 19:3337–53
20. Holland HD. 1984. *The Chemical Evolution of the Atmosphere and Oceans*. Princeton, NJ: Princeton Univ. Press
21. Kasting JF, Howard MT. 2006. Atmospheric composition and climate on the early Earth. *Philos. Trans. R. Soc. London Ser. B* 361:1733–42

22. Tian F, Toon OB, Pavlov AA, De Sterck H. 2005. A hydrogen rich early Earth atmosphere. *Science* 308:1014–17
23. Hayes JM, Waldbauer JR. 2006. The carbon cycle and associated redox processes through time. *Philos. Trans. R. Soc. London Ser. B* 361:931–50
24. Eigenbrode JL, Freeman KH. 2006. Late Archean rise of aerobic microbial ecosystems. *Proc. Natl. Acad. Sci. USA* 103:15759–64
25. Farquhar J, Wing BA. 2003. Multiple sulfur isotopes and the evolution of the atmosphere. *Earth Planet. Sci. Lett.* 213:1–13
26. Bekker A, Holland HD, Wang P-L, Rumble III D, Stein HJ, et al. 2004. Dating the rise of atmospheric oxygen. *Nature* 427:117–20
27. Ohmoto H, Watanabe Y, Ikemi H, Poulson SR, Taylor BE. 2006. Sulphur isotope evidence for an oxic Archean atmosphere. *Nature* 442:908–11
28. Canfield DE. 1998. A new model for Proterozoic ocean chemistry. *Nature* 396:450–53
29. Poulton SW, Fralick PW, Canfield DE. 2004. The transition to a sulphidic ocean ~1.84 billion years ago. *Nature* 431:173–77
30. Fike DA, Grotzinger JP, Pratt LM, Summons RE. 2006. Oxidation of the Ediacaran Ocean. *Nature* 444:744–47
31. Canfield DE, Poulton SW, Narbonne GM. 2007. Late-Neoproterozoic deep-ocean oxygenation and the rise of animal life. *Science* 315:92–95
32. Catling DC, Zahnle KJ, McKay CP. 2001. Biogenic methane, hydrogen escape, and the irreversible oxidation of the early Earth. *Science* 293:839–43
33. Rothman DH, Hayes JM, Summons RE. 2003. Dynamics of the Neoproterozoic carbon cycle. *Proc. Natl. Acad. Sci. USA* 100:8124–29
34. Kasting JF, Ono S. 2006. Paleoclimates: the first two billion years. *Philos. Trans. R. Soc. London Ser. B* 361:917–29
35. Sagan C, Mullen G. 1972. Earth and Mars: evolution of atmospheres and surface temperatures. *Science* 177:52–56
36. Kasting JF, Howard MT. 2006. Atmospheric composition and climate on the early Earth. *Philos. Trans. R. Soc. London Ser. B* 361:1733–42
37. Robert F, Chaussidon M. 2006. A palaeotemperature curve for the Precambrian oceans based on silicon isotopes in cherts. *Nature* 443:969–72
38. Kirschvink JL. 1992. Late Proterozoic low-latitude global glaciation: the snowball Earth. In *The Proterozoic Biosphere: A Multidisciplinary Study*, ed JW Schofp, C Klein, pp. 51–52. New York: Cambridge Univ. Press
39. Hoffman PF, Schrag DP. 2002. The snowball Earth hypothesis: testing the limits of global change. *Terra Nova* 14:129–55
40. Kennedy MJ, Christie-Blick N, Sohl LE. 2001. Are Proterozoic cap carbonates and isotopic excursions a record of gas hydrate destabilization following Earth's coldest intervals? *Geology* 29:443–46
41. Hayes JM. 1994. Global methanotrophy at the Archean-Proterozoic transition. In *Early Life on Earth*. Nobel Symp. 84, ed S Bengtson, pp. 220–36. New York: Columbia Univ. Press
42. Kopp RE, Kirschvink JL, Hilburn IA, Nash CZ. 2005. The paleoproterozoic snowball Earth: a climate disaster triggered by the evolution of oxygenic photosynthesis. *Proc. Natl. Acad. Sci. USA* 102:11131–36
43. Beerling DJ, Berner RA. 2005. Feedbacks and the coevolution of plants and atmospheric CO₂. *Proc. Natl. Acad. Sci. USA* 102:1302–5
44. Berner RA. 1991. A model for atmospheric CO₂ over Phanerozoic time. *Am. J. Sci.* 291:339–76

45. Berner RA. 2004. *The Phanerozoic Carbon Cycle: CO₂ and O₂*. Oxford: Oxford Univ. Press. 150 pp
46. Crowley TJ, Berner RA. 2001. CO₂ and climate change. *Science* 292:870–72
47. Royer DL, Berner RA, Beerling DJ. 2001. Phanerozoic CO₂ change: evaluating geochemical and paleobiological approaches. *Earth Sci. Rev.* 54:349–92
48. Cerling TE. 1991. Carbon dioxide in the atmosphere; evidence from Cenozoic and Mesozoic paleosols. *Am. J. Sci.* 291:377–400
49. Ekart DD, Cerling TE, Montanez IP, Tabor NJ. 1999. A 400 million year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide. *Am. J. Sci.* 299:805–27
50. Retallack GJ. 2001. A 300-million-year record of atmospheric carbon dioxide from fossil plant cuticles. *Nature* 411:287–90
51. Beerling DJ. 2002. Low atmospheric CO₂ levels during the Permo-Carboniferous glaciation inferred from fossil lycopsids. *Proc. Natl. Acad. Sci. USA* 99:12567–71
52. Pagani M, Zachos JC, Freeman KH, Tipple B, Bohaty S. 2005. Marked decline in atmospheric carbon dioxide concentrations during the Paleogene. *Science* 309:600–3
53. Fletcher BJ, Beerling DJ, Royer DL, Brentall SJ. 2005. Fossil bryophytes as recorders of ancient CO₂ levels: experimental evidence and a Cretaceous case study. *Glob. Biogeochem. Cycl.* 19:GB3012, doi:10.1029/2005GB002495
54. Pearson PN, Palmer MR. 2000. Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature* 406:695–99
55. Pagani M, Lemarchand D, Spivack A, Gaillardet J. 2005. A critical evaluation of the boron isotope-pH proxy: the accuracy of ancient ocean pH estimates. *Geochim. Cosmochim. Acta* 69:953–61
56. Berner RA, Kothavala Z. 2001. GEOCARB III: a revised model of atmospheric CO₂ over Phanerozoic time. *Am. J. Sci.* 301:182–204
57. Wallmann K. 2001. Controls on the Cretaceous and Cenozoic evolution of seawater composition, atmospheric CO₂ and climate. *Geochim. Cosmochim. Acta* 65:3005–25
58. Bergman NM, Lenton TM, Watson AJ. 2004. COPSE: a new model of biogeochemical cycling over Phanerozoic time. *Am. J. Sci.* 304:397–437
59. Katz ME, Wright JD, Miller KG, Cramer BS, Fennel K, Falkowski PG. 2005. Biological overprint of the geological carbon cycle. *Mar. Geol.* 217:323–38
60. Falkowski PG, Katz ME, Milligan AJ, Fennel K, Cramer BS, et al. 2005. The rise of oxygen over the past 205 million years and the evolution of large placental mammals. *Science* 309:2202–4
61. Crowley TJ, North GR. 1991. *Paleoclimatology*. New York: Oxford Univ. Press
62. Zachos J, Pagani M, Sloan L, Thomas E, Billups K. 2001. Trends, rhythms, and aberrations in global climate 65 Ma to present. *Science* 292:686–93
63. Miller KG, Komazin MA, Browning JV, Wright JD, Mountain GS, et al. 2005. The Phanerozoic record of global sea-level change. *Science* 310:1293–98
64. Royer DL, Berner RA, Montanez IP, Tabor NJ, Beerling DJ. 2004. CO₂ as a primary driver of Phanerozoic climate. *GSA Today* 14:4–10
65. Eldrett JS, Harding IC, Wilson PA, Butler E, Roberts AP. 2007. Continental ice in Greenland during the Eocene and Oligocene. *Nature* 446:176–79
66. DeConto RM, Pollard D. 2003. Rapid Cenozoic glaciation of Antarctica induced by declining atmospheric CO₂. *Nature* 421:245–49
67. Pollard D, DeConto RM. 2005. Hysteresis in Cenozoic Antarctic ice-sheet variations. *Glob. Planet. Change* 45:9–21

68. Kiehl JT, Shields CA. 2005. Climate simulation of the latest Permian: implications for mass extinction. *Geology* 33:757–60
69. Hyde WT, Grossman EL, Crowley TJ, Pollard D, Scotese CR. 2006. Siberian glaciation as a constraint on Permian–Carboniferous CO₂ levels. *Geology* 34:421–24
70. Bice KL, Birgel D, Meyers PA, Dahl KA, Hinrichs KU, Norris RD. 2006. A multiple proxy and model study of Cretaceous upper ocean temperatures and atmospheric CO₂ concentrations. *Paleoceanography* 21:PA2002
71. Gaillardet J, Dupre B, Louvat P, Allegre CJ. 1999. Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* 159:3–30
72. Walker JCG, Hays PB, Kasting JF. 1981. A negative feed back mechanism for the long-term stabilization of Earth's surface temperature. *J. Geophys. Res.* 86:9776–82
73. Berner RA, Lasaga AC, Garrels RM. 1983. The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.* 283:641–83
74. Palike H, Norris RD, Herrle JO, Wilson PA, Coxall HK, et al. 2006. The heartbeat of the Oligocene climate system. *Science*. 314:1894–98
75. Raymo ME, Ruddiman WF, Froelich PN. 1988. Influence of late Cenozoic mountain building on ocean geochemical cycles. *Geology* 16:649–53
76. Molnar P, England P, Martinod J. 1993. Mantle dynamics, uplift of the Tibetan Plateau, and the Indian monsoon. *Rev. Geophys.* 31:357–96
77. Gibbs MT, Bluth GJS, Fawcett PJ, Kump LR. 1999. Global chemical erosion over the last 250 My: variations due to changes in paleogeography, paleoclimate, and paleogeology. *Am. J. Sci.* 299:611–51
78. Donnadieu Y, Godderis Y, Pierrehumbert R, Dromart G, Fluteau F, Jacob R. 2006. A GEOCLIM simulation of climatic and biogeochemical consequences of Pangea breakup. *Geochem. Geophys. Geosystems* 7:Q11019, doi:10.1029/2006GC001278
79. Squire RJ, Campbell IH, Allen CM, Wilson CJL. 2006. Did the Transgondwanan Supermountain trigger the explosive radiation of animals on Earth? *Earth Planet. Sci. Lett.* 250:116–33
80. Berner RA. 1998. The carbon cycle and carbon dioxide over Phanerozoic time: the role of land plants. *Philos. Trans. R. Soc. London Ser. B* 353:75–82
81. Ehleringer JR, Sage RF, Flanagan LB, Pearcy RW. 1991. Climate change and the evolution of C4 photosynthesis. *Trends Ecol. Evol.* 6:95–99
82. Zachos JC, Wara MW, Bohaty S, Delaney ML, Petrizzo MR, et al. 2003. A transient rise in tropical sea surface temperature during the Paleocene-Eocene thermal maximum. *Science* 302:1551–54
83. Zachos JC, Rohl U, Schellenberg SA, Hodell D, Thomas E, et al. 2005. Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. *Science* 308:1611–15
84. Thomas DJ, Zachos JC, Bralower TJ, Thomas E, Bohaty S. 2002. Warming the fuel for the fire: evidence for the thermal dissociation of methane during the Paleocene-Eocene thermal maximum. *Geology* 30:1067–70
85. Dickens GR, O'Neil JR, Rea DK, Owen RM. 1995. Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography* 10:965–71
86. Dickens GR, Castillo MM, Walker JCG. 1997. A blast of gas in the latest Paleocene; simulating first-order effects of massive dissociation of oceanic methane hydrate. *Geology* 25:259–62

87. Kurtz AC, Kump LR, Arthur MA, Zachos JC, Paytan A. 2003. Early Cenozoic decoupling of the global carbon and sulfur cycles. *Paleoceanography* 18:1090, doi:10.1029/2003PA000908
88. Svensen H, Planke S, Malthe-Sorensen A, Jamtveit B, Myklebust R, et al. 2004. Release of methane from a volcanic basin as a mechanism for initial Eocene global warming. *Nature* 429:542–45
89. Kent DV, Cramer BS, Land L, Wang D, Wright JD, Van der Voo R. 2003. A case for a comet impact trigger for the Paleocene/Eocene thermal maximum and carbon isotope excursion. *Earth Planet. Sci. Lett.* 211:13–26
90. Higgins JA, Schrag DP. 2006. Beyond methane: towards a theory for the Paleocene-Eocene thermal maximum. *Earth Planet. Sci. Lett.* 245:523–37
91. Berner RA. 2002. Examination of hypotheses for the Permo-Triassic boundary extinction by carbon cycle modeling. *Proc. Natl. Acad. Sci. USA* 99:4172–77
92. Hesselbo SP, Grocke DR, Jenkyns HC, Bjerrum CJ, Farrimond P, et al. 2000. Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. *Nature* 406:392–95
93. Weissert H, Erba E. 2004. Volcanism, CO₂ and palaeoclimate: a Late Jurassic-Early Cretaceous carbon and oxygen isotope record. *J. Geol. Soc.* 161:695–702
94. Barnola JM, Raynaud D, Korotkevich YS, Lorius C. 1987. Vostok ice core provides 160,000-year record of atmospheric CO₂. *Nature* 329:408–14
95. Spahni R, Chappellaz J, Stocker TF, Loulergue L, Hausammann G, et al. 2005. Atmospheric methane and nitrous oxide of the late Pleistocene from Antarctic ice cores. *Science* 310:1317–21
96. Jouzel J, Lorius C, Petit JR, Genthon C, Barkov NI, et al. 1987. Vostok ice core: a continuous isotope temperature record over the last climatic cycle (160,000 years). *Nature* 329:403–8
97. Jouzel J, Vimeux F, Caillon N, Delaygue G, Hoffmann G, et al. 2003. Magnitude of isotope/temperature scaling for interpretation of central Antarctic ice cores. *J. Geophys. Res.* 108D:4361
98. Alley RB, Cuffey KM. 2001. Oxygen- and hydrogen-isotopic ratios of water in precipitation: beyond paleothermometry. In *Stable Isotope Geochemistry, Reviews in Mineralogy and Geochemistry*, Vol. 43, ed. JW Valley, D Cole, pp. 527–53. Chantilly, VA: Mineral. Soc. Am.
99. Wolff EW, Fischer H, Fundel F, Ruth U, Twarloh B, et al. 2006. Southern Ocean sea-ice extent, productivity and iron flux over the past eight glacial cycles. *Nature* 440:491–96
100. Sowers T, Alley RB, Jubenville J. 2003. Ice core records of atmospheric N₂O covering the last 106,000 years. *Science* 301:945–48
101. Shackleton NJ. 1987. Oxygen isotopes, ice volume and sea level. *Quat. Sci. Rev.* 6:183–90
102. Shackleton NJ. 2000. The 100,000-year ice-age cycle identified and found to lag temperature, carbon dioxide, and orbital eccentricity. *Science* 289:1897–902
103. Elderfield H, Ganssen G. 2000. Past temperature and delta O-18 of surface ocean waters inferred from foraminiferal Mg/Ca ratios. *Nature* 405:442–45
104. Siddall M, Rohling EJ, Almogi-Labin A, Hemleben C, Meischner D, et al. 2003. Sea-level fluctuations during the last glacial cycle. *Nature* 423:853–58
105. Bard E, Rostek F, Sonzogni C. 1997. Interhemispheric synchrony of the last deglaciation inferred from alkenone palaeothermometry. *Nature* 385:707–10
106. Mollenhauer G, Eglinton TI, Ohkuchi N, Schneider RR, Muller PJ, et al. 2003. Asynchronous alkenone and foraminifera records from the Benguela Upwelling System. *Geochim. Cosmochim. Acta* 67:2157–71

107. Adkins JF, McIntyre K, Schrag DP. 2002. The salinity, temperature, and $\delta^{18}\text{O}$ of the glacial deep ocean. *Science* 298:1769–73
108. CLIMAP Proj. Memb. 1976. The surface of the ice-age Earth. *Science* 191:1131–37
109. CLIMAP Proj. Memb. 1981. Seasonal reconstructions of the of the Earth's surface at the Last Glacial Maximum. *Geol. Soc. Am. Map Chart Ser. Rep. MC-36*, Geol. Soc. Am., Boulder CO, pp. 18
110. Pflaumann U, Sarnthein M, Chapman M, d'Abreu L, Funnell B, et al. 2003. Glacial North Atlantic: sea-surface conditions reconstructed by GLAMAP 2000. *Paleoceanography* 18:1065
111. Gersonde R, Crosta X, Abelmann A, Armand L. 2005. Sea-surface temperature and sea lee distribution of the Southern Ocean at the EPILOG Last Glacial Maximum: a circum-Antarctic view based on siliceous microfossil records. *Quat. Sci. Rev.* 24:869–96
112. Bard E, Hamelin B, Fairbanks RG. 1990. U-Th ages obtained by mass-spectrometry in corals from Barbados: sea level during the past 130,000 years. *Nature* 346:456–58
113. Thompson WG, Goldstein SL. 2005. Open-system coral ages reveal persistent suborbital sea-level cycles. *Science* 308:401–4
114. Crowley TJ. 1995. Ice age terrestrial carbon changes revisited. *Glob. Biogeochem. Cycles* 9:377–89
115. Boyle EA, Keigwin LD. 1982. Deep circulation of the North Atlantic over the last 200,000 years: geochemical evidence. *Science* 218:784–87
116. Curry WB, Oppo DW. 2005. Glacial water mass geometry and the distribution of $\delta^{13}\text{C}$ of ΣCO_2 in the western Atlantic Ocean. *Paleoceanography* 20:PA1017, doi:10.1029/2004PA001021
117. Sigman DM, Altabet MA, Francois R, McCorkle DC, Gaillard J-F. 1999. The isotopic composition of diatom-bound nitrogen in Southern Ocean sediments. *Paleoceanography* 14:118–34
118. Robinson R, Sigman D, DiFiore P, Rohde M, Mashiotta T, Lea D. 2005. Diatom-bound $^{15}\text{N}/^{14}\text{N}$: new support for enhanced nutrient consumption in the ice age subantarctic. *Paleoceanography* 20:PA3003, doi:10.1029/2004PA001114
119. Deutsch C, Sigman DM, Thunell RC, Meckler AN, Haug GH. 2004. Isotopic constraints on glacial/interglacial changes in the oceanic nitrogen budget. *Glob. Biogeochem. Cycles* 18:GB4012, doi:10.1029/2003GB002189
120. Marchitto TM, Lynch-Stieglitz J, Hemming SR. 2005. Deep Pacific CaCO_3 compensation and glacial-interglacial atmospheric CO_2 . *Earth Planet. Sci. Lett.* 231:317–36
121. Kohfeld KE, Le Quéré C, Harrison S, Anderson RF. 2005. Role of marine biology in glacial-interglacial CO_2 cycles. *Science* 308:74–78
122. Hughen K, Lehman S, Southon J, Overpeck J, Marchal O, et al. 2004. C-14 activity and global carbon cycle changes over the past 50,000 years. *Science* 303:202–7
123. Hughen K, Southon J, Lehman S, Bertrand C, Turnbull J. 2006. Marine-derived ^{14}C calibration and activity record for the past 50,000 years updated from the Cariaco Basin. *Quat. Sci. Rev.* 25:3216–27
124. Robinson LF, Adkins JF, Keigwin LD, Southon J, Fernandez DP, et al. 2005. Radiocarbon variability in the western North Atlantic during the last deglaciation. *Science* 310:1469–73
125. Siegenthaler U, Stocker TF, Monnin E, Luthi D, Schwander J, et al. 2005. Stable carbon cycle-climate relationship during the late Pleistocene. *Science* 310:1313–17
126. Eur. Proj. Ice Coring Antarct. (EPICA) Community Memb. 2004. Eight glacial cycles from an Antarctic ice core. *Nature* 429:623–28

- 126a. Monnin E, Steig EJ, Siegenthaler U, Kawamura KK, Schwander J, et al. 2004. Evidence for substantial accumulation rate variability in Antarctica during the Holocene, through synchronization of CO₂ in the Taylor Dome, Dome C and DML ice cores. *Earth Planet. Sci. Lett.* 224:45–54
127. Hays JD, Imbrie J, Shackleton NJ. 1976. Variations in the Earth's orbit: pacemaker of the ice ages. *Science* 194:1121–32
128. Imbrie J, Imbrie JZ. 1980. Modeling the climatic response to orbital variations. *Science* 207:943–53
129. Imbrie J, Berger A, Boyle EA, Clemens SC, Duffy A, et al. 1993. On the structure and origin of major glaciation cycles 2. The 100,000-year cycle. *Paleoceanography* 8:699–735
130. Gildor H, Tziperman E. 2000. Sea ice as the glacial cycles' climate switch: role of seasonal and orbital forcing. *Paleoceanography* 15:605–15
131. Pelletier J. 2003. Coherence resonance and ice ages. *J. Geophys. Res.* 108:4645, doi:10.1029/2002JD003120
132. Wunsch C. 2003. The spectral description of climate change including the 100 ky energy. *Clim. Dyn.* 20:353–63
133. Huybers P, Wunsch C. 2005. Obliquity pacing of the late Pleistocene glacial terminations. *Nature* 434:491–94
134. Tziperman E, Raymo ME, Huybers P, Wunsch C. 2006. Consequences of pacing the Pleistocene 100 kyr ice ages by nonlinear phase locking to Milankovitch forcing. *Paleoceanography* 21:PA4206
135. Severinghaus JP, Sowers T, Brook EJ, Alley RB, Bender ML. 1998. Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice. *Nature* 391:141–46
136. Severinghaus JP, Brook EJ. 1999. Abrupt climate change at the end of the last glacial period inferred from trapped air in polar ice. *Science* 286:930–34
137. Brook EJ, White JWC, Schilla ASM, Bender ML, Barnett B, et al. 2005. Timing of millennial-scale climate change at Siple Dome, West Antarctica, during the last glacial period. *Quat. Sci. Rev.* 24:1333–43
138. Hughen KA, Southon JR, Lehman SJ, Overpeck JT. 2000. Synchronous radiocarbon and climate shifts during the last deglaciation. *Science* 290:1951–54
139. Hughen KA, Eglinton TI, Xu L, Makou M. 2004. Abrupt tropical vegetation response to rapid climate changes. *Science* 304:1955–59
140. Monnin E, Indermuhle A, Dallenbach A, Fluckiger J, Stauffer B, et al. 2001. Atmospheric CO₂ concentrations over the last glacial termination. *Science* 291:112–14
141. Caillon N, Severinghaus JP, Jouzel J, Barnola J-M, Kang J, Lipenkov VY. 2003. Temperature changes across termination III. *Science* 299:1728–31
142. Alley RB, Brook EJ, Anandakrishnan S. 2002. A northern lead in the orbital band: North-South phasing of Ice-Age events. *Quat. Sci. Rev.* 21:431–41
143. Broecker WS, Henderson G. 1998. The sequence of events surrounding termination II and their implications for the cause of glacial-interglacial CO₂ changes. *Paleoceanography* 13:352–64
144. Johnston TC, Alley RB. 2006. Possible role for dust or other northern forcing of ice-age carbon dioxide changes. *Quat. Sci. Rev.* 25:3198–206
145. Lorius C, Jouzel J, Raynaud D, Hansen J, Le Treut H. 1990. The ice-core record: climate sensitivity and future greenhouse warming. *Nature* 347:139–45
146. Otto-Bliesner BL, Brady EC, Clauzet G, Tomas R, Levis S, Kothavala Z. 2006. Last Glacial Maximum and Holocene climate in CCSM3. *J. Clim.* 19:2526–44

147. Brook EJ, Harder S, Severinghaus JP, Steig EJ, Sucher CM. 2000. On the origin and timing of rapid changes in atmospheric methane during the last glacial period. *Glob. Biogeochem. Cycles* 14:559–72
148. Shin S-I, Liu Z, Otto-Bliessner B, Brady EC, Kutzbach JE, Harrison SP. 2003. A simulation of the Last Glacial Maximum climate using the NCAR-CCSM. *Clim. Dyn.* 20:127–51
149. Lea DW, Pak DK, Peterson LC, Hughen KA. 2003. Synchronicity of tropical and high-latitude Atlantic temperatures over the last glacial termination. *Science* 301:1361–64
150. Kaplan JO, Prentice IC, Knorr W, Valdes PJ. 2002. Modeling the dynamics of terrestrial carbon storage since the Last Glacial Maximum. *Geophys. Res. Lett.* 29:2074, doi:10.1029/2002GL015230
151. Sigman DM, Boyle EA. 2000. Glacial/interglacial variations in atmospheric carbon dioxide. *Nature* 407:859–69
152. Broecker WS. 1982. Glacial to interglacial changes in ocean chemistry. *Prog. Oceanogr.* 2:151–97
153. Broecker WS, Denton GH. 1989. The role of ocean-atmosphere reorganizations in glacial cycle. *Geochim. Cosmochim. Acta* 53:2465–501
154. Archer D, Winguth A, Lea D, Mahowald N. 2000. What caused the glacial/interglacial atmospheric pCO₂ cycles? *Rev. Geophys.* 38:159–89
155. Kohler P, Fischer H, Munhoven G, Zeebe RE. 2005. Quantitative interpretation of atmospheric carbon records over the last glacial termination. *Glob. Biogeochem. Cycles* 19:GB4020
156. Peacock S, Lane E, Restrepo JM. 2006. A possible sequence of events for the generalized glacial-interglacial cycle. *Glob. Biogeochem. Cycle* 20:GB2010, doi:10.1029/2005GB002448
157. Archer D, Martin P, Brovkin V, Plattner G-K, Ashendel C. 2003. Model sensitivity in the effect of Antarctic sea ice and stratification on atmospheric pCO₂. *Paleoceanography* 18:1012, doi:10.1029/2002PA000760
158. Toggweiler JR, Gnanadesikan A, Carson S, Murnane R, Sarmiento JL. 2003. Representation of the carbon cycle in box models and GCMs: 1. Solubility pump. *Glob. Biogeochem. Cycles* 17:1026, doi:10.1029/2001GB001401
159. Toggweiler JR, Murnane R, Carson S, Gnanadesikan A, Sarmiento JL. 2003. Representation of the carbon cycle in box models and GCMs: 2. Organic pump. *Glob. Biogeochem. Cycles* 17:1027, doi:10.1029/2001GB001841
160. Martin J. 1990. Glacial-interglacial CO₂ change: the iron hypothesis. *Paleoceanography* 5:1–13
161. Bopp L, Kohfeld KE, Le Quéré C, Aumont O. 2003. Dust impact on marine biota and atmospheric CO₂ during glacial periods. *Paleoceanography* 18:1046
162. Rothlisberger R, Bigler M, Wolff EW, Joos F, Monnin E, Hutterli MA. 2004. Ice core evidence for the extent of past atmospheric CO₂ change due to iron fertilization. *Geophys. Res. Lett.* 31:L16207
163. Francois R, Altabet MA, Yu E-F, Sigman DM, Bacon MP, et al. 1997. Contribution of Southern Ocean surface-water stratification to low atmospheric CO₂ concentrations during the last glacial period. *Nature* 389:929–35
164. Jaccard SL, Haug GH, Sigman DM, Pedersen TF, Thierstein HR, Rohl U. 2005. Glacial/interglacial changes in subarctic North Pacific stratification. *Science* 308:1003–6
165. Brzezinski M, Sarmiento J, Matsumoto K, Pride C, Sigman D, et al. 2002. A switch from Si(OH)₄ to NO₃ depletion in the glacial Southern Ocean. *Geophys. Res. Lett.* 29:1564, doi:10.1029/2001GL014349

166. Matsumoto K, Sarmiento JL, Brzezinski MA. 2002. Silicic acid leakage from the Southern Ocean: a possible explanation for glacial atmospheric pCO₂. *Glob. Biogeochem. Cycles* 16:1031, doi:10.1029/2001GB001442
167. Bradtmiller LI, Anderson RF, Fleisher MQ, Burckle LH. 2006. Diatom productivity in the equatorial Pacific Ocean from the last glacial period to the present: a test of the silicic acid leakage hypothesis. *Paleoceanography* 21:PA4201, doi:10.1029/2006PA001282
168. Kienast SS, Kienast M, Jaccard S, Calvert SE, François R. 2006. Testing the silica leakage hypothesis with sedimentary opal records from the eastern equatorial Pacific over the last 150 kyrs. *Geophys. Res. Lett.* 33:L15607, doi:10.1029/2006GL026651
169. Toggweiler JR, Russell JL, Carson SR. 2006. Midlatitude westerlies, atmospheric CO₂, and climate change during the ice ages. *Paleoceanography* 21:PA2005
170. Toggweiler JR. 1999. Variation of atmospheric CO₂ by ventilation of the ocean's deepest water. *Paleoceanography* 14:571–88
171. Stephens BB, Keeling RF. 2000. The influence of Antarctic sea ice on glacial-interglacial CO₂ variations. *Nature* 404:171–74
172. Watson AJ, Naveira-Garabato AC. 2006. The role of Southern Ocean mixing and upwelling in glacial-interglacial atmospheric CO₂ change. *Tellus B* 58:73–87
173. Muscheler R, Beer J, Wagner G, Laj C, Kissel C, et al. 2004. Changes in the carbon cycle during the last deglaciation as indicated by the comparison of ¹⁰Be and ¹⁴C records. *Earth Planet. Sci. Lett.* 219:325–40
174. Broecker W, Barker S. 2007. A 190% drop in atmosphere's Δ¹⁴C during the "Mystery Interval" (17.5 to 14.5 kyr). *Earth Planet. Sci. Lett.* 256:90–99
175. Munhoven G. 2002. Glacial-interglacial changes of continental weathering: estimates of the related CO₂ and HCO₃⁻ flux variations and their uncertainties. *Glob. Planet. Change* 33:155–76
176. Dansgaard W. 1987. Ice core evidence of abrupt climatic changes. In *Abrupt Climatic Change. Evidence and Implications*, ed. WH Berger, LD Labeyrie, pp. 223–33. New York: Springer-Verlag
177. Stauffer B, Blunier T, Dallenbach A, Intermuhle A, Schwander J, et al. 1998. Atmospheric CO₂ concentration and millennial-scale climate change during the last glacial period. *Nature* 392:59–62
178. Martin P, Archer D, Lea DW. 2005. Role of deep sea temperature in the carbon cycle during the last glacial. *Paleoceanography* 20:PA2015
179. Alley RB. 2007. Wally was right: predictive ability of the North Atlantic "conveyor belt" hypothesis for abrupt climate change. *Annu. Rev. Earth Planet. Sci.* 35:241–72
180. Broecker WS. 2003. Does the trigger for abrupt climate change reside in the ocean or in the atmosphere? *Science* 300:1519–22
181. Fluckiger J, Blunier T, Stauffer B, Chappellaz J, Spahni R, et al. 2004. N₂O and CH₄ variations during the last glacial epoch: insight into global processes. *Glob. Biogeochem. Cycl.* 18:GB1020, doi:10.1029/2003GB002122
182. Intermuhle A, Stocker TF, Joos F, Fischer H, Smith HJ, et al. 1999. Holocene carbon-cycle dynamics based on CO₂ trapped in ice at Taylor Dome, Antarctica. *Nature* 398:121–26
183. Fluckiger J, Monnin E, Stauffer B, Schwander J, Stocker TF, et al. 2002. High-resolution Holocene N₂O ice core record and its relationship with CH₄ and CO₂. *Glob. Biogeochem. Cycl.* 16:1010
184. Broecker WS, Lynch-Stieglitz J, Clark E, Hajdas I, Bonani G. 2001. What caused the atmosphere's CO₂ content to rise during the last 8000 years? *Geochem. Geophys. Geosystems* 2:U1–13

185. Ridgwell AJ, Watson AJ, Maslin MA, Kaplan JO. 2003. Implications of coral reef buildup for the controls on atmospheric CO₂ since the Last Glacial Maximum. *Paleoceanography* 18:1083, doi:10.1029/2003PA000893
186. Joos F, Gerber S, Prentice IC, Otto-Bliesner BL, Valdes PJ. 2004. Transient simulations of Holocene atmospheric carbon dioxide and terrestrial carbon since the Last Glacial Maximum. *Glob. Biogeochem. Cycles* 18:GB2002
187. Brovkin V, Bendtsen J, Claussen M, Ganopolski A, Kubatzki C, et al. 2002. Carbon cycle, vegetation, and climate dynamics in the Holocene: experiments with the CLIMBER-2 model. *Glob. Biogeochem. Cycles* 16:1139
188. Williams JW, Shuman BN, Webb T, Bartlein PJ, Leduc PL. 2004. Late-quaternary vegetation dynamics in North America: scaling from taxa to biomes. *Ecol. Monogr.* 74:309–34
189. Crucifix M, Loutre MF, Tulkens P, Fichetef T, Berger A. 2002. Climate evolution during the Holocene: a study with an Earth system model of intermediate complexity. *Clim. Dyn.* 19:43–60
190. Ruddiman WF. 2003. The anthropogenic greenhouse era began thousands of years ago. *Clim. Change* 61:261–93
191. Blunier T, Chappellaz J, Schwander J, Stauffer B, Raynaud D. 1995. Variations in atmospheric methane concentration during the Holocene epoch. *Nature* 374:46–49
192. Smith LC, MacDonald GM, Velichko AA, Beilman DW, Borisova OK, et al. 2004. Siberian peatlands a net carbon sink and global methane source since the early Holocene. *Science* 303:353–56
193. Ferretti DF, Miller JB, White JWC, Etheridge DM, Lassey KR, et al. 2005. Unexpected changes to the global methane budget over the past 2000 years. *Science* 309:1714–17
194. Etheridge DM, Steele LP, Langenfelds RL, Francey RJ, Barnola J-M, Morgan VI. 1996. Natural and anthropogenic changes in atmospheric CO₂ over the last 1000 years from air in Antarctic ice and firn. *J. Geophys. Res.* 101D:4115–28
195. Siegenthaler U, Monnin E, Kawamura K, Spahni R, Schwander J, et al. 2005. Supporting evidence from the EPICA Dronning Maud Land ice core for atmospheric CO₂ changes during the past millennium. *Tellus B* 57:51–57
196. Esper J, Cook ER, Schweingruber FH. 2002. Low-frequency signals in long tree-ring chronologies for reconstructing past temperature variability. *Science* 295:2250–53
197. Trudinger CM, Enting IG, Francey RJ, Etheridge DM, Rayner PJ. 1999. Long-term variability in the global carbon cycle inferred from a high precision CO₂ and δ¹³C ice core record. *Tellus B* 51:233–48
198. Trudinger C, Enting I, Etheridge D, Francey R, Rayner P. 2005. The carbon cycle over the past 1000 years inferred from the inversion of ice core data. In *A History of Atmospheric CO₂ and Its Effect on Plants, Animals, and Ecosystems*, ed. JR Ehleringer, TE Cerling, MD Dearing, pp. 329–49. New York: Springer
199. Gerber S, Joos F, Brugger P, Stocker TF, Mann ME, et al. 2003. Constraining temperature variations over the last millennium by comparing simulated and observed atmospheric CO₂. *Clim. Dyn.* 20:281–99
200. Doney SC, Lindsay K, Fung I, John J. 2006. Natural variability in a stable 1000 year coupled climate-carbon cycle simulation. *J. Clim.* 19:3033–54
201. Feely RA, Wanninkhof R, Takahashi T, Tans P. 1999. Influence of El Niño on the equatorial Pacific contribution to atmospheric CO₂ accumulation. *Nature* 398:597–601
202. Vukicevic T, Braswell BH, Schimel D. 2001. A diagnostic study of temperature controls on global terrestrial carbon exchange. *Tellus B* 53:150–70
203. Schimel D, Baker D. 2002. Carbon cycle: the wildfire factor. *Nature* 420:29–30

204. Van der Werf GR, Randerson JT, Collatz GJ, Giglio L, Kasibhatla PS, et al. 2004. Continental-scale partitioning of fire emissions during the 1997 to 2001 El Niño/La Niña period. *Science* 303:73–76
- 204a. Keeling CD. 1960. The concentration and isotopic abundance of carbon dioxide in the atmosphere. *Tellus* 12:200–3
- 204b. Keeling CD, Bacastow RB, Bainbridge AE, Ekdahl CA Jr, Guenther PR, et al. 1976. Atmospheric carbon dioxide variations at Mauna Loa Observatory, Hawaii. *Tellus* 28:538–51
205. Rodenbeck C, Houweling S, Gloor M, Heimann M. 2003. CO₂ flux history 1982–2001 inferred from atmospheric data using a global inversion of atmospheric transport. *Atmos. Chem. Phys.* 3:1919–64
206. Peylin P, Bousquet P, Le Quéré C, Sitch S, Friedlingstein P, et al. 2005. Multiple constraints on regional CO₂ flux variations over land and oceans. *Glob. Biogeochem. Cycles* 19:GB1011, doi:10.1029/2003GB002214
207. Braswell BH, Schimel DS, Linder E, Moore B III. 1997. The response of global terrestrial ecosystems to interannual temperature variability. *Science* 278:870–73
208. Bacastow RB, Adams JA, Keeling CD, Moss DJ, Whorf TP, Wong CS. 1980. Atmospheric carbon dioxide, the Southern Oscillation, and the weak 1975 El Niño. *Science* 210:66–68
209. Lee K, Wanninkhof R, Takahashi T, Doney SC, Feely RA. 1998. Low interannual variability in recent oceanic uptake of atmospheric carbon dioxide. *Nature* 396:155–59
210. Chavez FP, Strutton PG, Friederich GE, Feely RA, Feldman G, et al. 1999. Biological and chemical response of the equatorial Pacific Ocean to the 1997–1998 El Niño. *Science* 286:2126–31
211. Feely RA, Boutin J, Cosca CE, Dandonneau Y, Etcheto J, et al. 2002. Seasonal and interannual variability of CO₂ in the equatorial Pacific. *Deep-Sea Res. II* 49:2443–69
212. Lovenduski NS, Gruber N, Doney SC, Lima ID. 2007. Enhanced CO₂ outgassing in the Southern Ocean from a positive phase of the Southern Annular Mode. *Glob. Biogeochem. Cycles* 21:GB2026, doi:10.1029/2006GB002900
213. Le Quéré C, Orr JC, Monfray P, Aumont O, Madec G. 2000. Interannual variability of the oceanic sink of CO₂ from 1979 through 1997. *Glob. Biogeochem. Cycles* 14:1247–65
214. Gruber N, Keeling CD, Bates NR. 2002. Interannual variability in the North Atlantic Ocean carbon sink. *Science* 298:2374–78
215. Baker DF, Law RM, Gurney KR, Rayner P, Peylin P, et al. 2006. TransCom 3 inversion intercomparison: impact of transport model errors on the interannual variability of regional CO₂ fluxes, 1988–2003. *Glob. Biogeochem. Cycles* 20:GB1002, doi:10.1029/2004GB002439
216. Tian H, Melillo JM, Kicklighter DW, McGuire AD, Helfrich JVK, et al. 1998. Effect of interannual climate variability on carbon storage in Amazonian ecosystems. *Nature* 396:664–67
217. Nepstad DC, Verssimo A, Alencar A, Nobre C, Lima E, et al. 1999. Large-scale impoverishment of Amazonian forests by logging and fire. *Nature* 398:505–8
218. Jones CD, Collins M, Cox PM, Spall SA. 2001. The carbon cycle response to ENSO: a coupled climate-carbon cycle model study. *J. Clim.* 14:4113–29
219. Langenfelds RL, Francey RJ, Pak BC, Steele LP, Lloyd J, et al. 2002. Interannual growth rate variations of atmospheric CO₂ and its $\delta^{13}\text{C}$, H₂, CH₄, and CO between 1992 and 1999 linked to biomass burning. *Glob. Biogeochem. Cycles* 16:1048, doi:10.1029/2001GB001466

220. Page SE, Siegert F, Rieley JO, Boehm HDV, Jaya A, Limin S. 2002. The amount of carbon released from peat and forest fires in Indonesia during 1997. *Nature* 420:61–64
221. Woodwell G, Mackenzie FT. 1995. *Biotic Feedbacks in the Global Climatic System: Will the Warming Feed the Warming?* New York: Oxford Univ. Press. 416 pp
222. Myneni RB, Keeling CD, Tucker CJ, Asrar G, Nemani RR. 1997. Increased plant growth in the northern high latitudes from 1981 to 1991. *Nature* 386:698–702
223. Lucht W, Prentice IC, Myneni RB, Sitch S, Friedlingstein P, et al. 2002. Climatic control of the high-latitude vegetation greening trend and Pinatubo effect. *Science* 296:1687–89
224. Angert A, Biraud S, Bonfils C, Henning CC, Buermann W, et al. 2005. Drier summers cancel out the CO₂ uptake enhancement induced by warmer springs. *Proc. Natl. Acad. Sci. USA* 102:10823–27
225. Ciais P, Reichstein M, Viovy N, Granier A, Ogee J, et al. 2005. Europe-wide reduction in primary productivity caused by the heat and drought in 2003. *Nature* 437:529–33
226. Sacks WJ, Schimel DS, Monson RK. 2007. Coupling between carbon cycling and climate in a high-elevation, subalpine forest: a model-data fusion analysis. *Oecologia* 151:54–68
227. Crutzen PI, Stoermer EF. 2000. The “Anthropocene.” *Int. Geosph.-Biosph. Program. Newsl.* 41:17–18
228. Hansen J, Sato M, Ruedy R, Lo K, Lea DW, Medina-Elizade M. 2006. Global temperature change. *Proc. Natl. Acad. Sci. USA* 103:14288–93
229. Archer D, Ganopolski A. 2005. A movable trigger: fossil fuel CO₂ and the onset of the next glaciation. *Geochem. Geophys. Geosystems* 6:Q05003, doi:10.1029/2004GC000891
230. Cramer W, Bondeau A, Woodward FI, Prentice IC, Betts RA. 2001. Global response of terrestrial ecosystem structure and function to CO₂ and climate change: results from six dynamic global vegetation models. *Glob. Change Biol.* 7:357–73
231. Schimel D, Melillo J, Tian H, McGuire AD, Kicklighter D, et al. 2000. Contribution of increasing CO₂ and climate to carbon storage by ecosystems in the United States. *Science* 287:2004–6
232. McGuire AD, Prentice IC, Ramankutty N, Reichenau T, Schloss A, et al. 2001. Carbon balance of the terrestrial biosphere in the twentieth century: analyses of CO₂, climate and land-use effects with four process-based ecosystem models. *Glob. Biogeochem. Cycles* 15:183–206
233. Bopp L, Monfray P, Aumont O, Dufresne J-L, Le Treut H, et al. 2001. Potential impact of climate change on marine export production. *Glob. Biogeochem. Cycles* 15:81–100
234. Boyd PW, Doney SC. 2002. Modelling regional responses by marine pelagic ecosystems to global climate change. *Geophys. Res. Lett.* 29:1806, doi:10.1029/2001GL014130
235. Sarmiento J, Slater R, Barber R, Bopp L, Doney SC, et al. 2004. Response of ocean ecosystems to climate warming. *Glob. Biogeochem. Cycles* 18:GB3003, doi:10.1029/2003GB002134
236. Pacala SW, Hurtt GC, Baker D, Peylin P, Houghton RA, et al. 2001. Consistent land-and atmosphere-based U.S. carbon sink estimates. *Science* 292:2316–20
237. Schimel DS, House JI, Hibbard KA, Bousquet P, Ciais P, et al. 2001. Recent patterns and mechanisms of carbon exchange by terrestrial ecosystems. *Nature* 414:169–72
238. Friedlingstein P, Bopp L, Ciais P, Dufresne JL, Fairhead L, et al. 2001. Positive feedback between future climate change and the carbon cycle. *Geophys. Res. Lett.* 28:1543–46
239. Friedlingstein P, Dufresne J-L, Cox PM, Rayner P. 2003. How positive is the feedback between climate change and the carbon cycle? *Tellus B* 55:692–700
240. Zimov SA, Schuur EAG, Chapin FS. 2006. Permafrost and the global carbon budget. *Science* 312:1612–13

241. Dickens GR. 2003. Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor. *Earth Planet. Sci. Lett.* 213:169–83
242. Forest CE, Stone PH, Sokolov AP, Allen MR, Webster MD. 2002. Quantifying uncertainties in climate system properties with the use of recent climate observations. *Science* 295:113–17
243. Hegerl GC, Crowley TJ, Hyde WT, Frame DJ. 2006. Climate sensitivity constrained by temperature reconstructions over the past seven centuries. *Nature* 440:1029–32



Contents

I. Earth's Life Support Systems

Feedbacks of Terrestrial Ecosystems to Climate Change
Christopher B. Field, David B. Lobell, Halton A. Peters, and Nona R. Chiariello 1

Carbon and Climate System Coupling on Timescales from the
Precambrian to the Anthropocene
Scott C. Doney and David S. Schimel 31

The Nature and Value of Ecosystem Services: An Overview
Highlighting Hydrologic Services
Kate A. Brauman, Gretchen C. Daily, T. Ka'eo Duarte, and Harold A. Mooney 67

Soils: A Contemporary Perspective
Cheryl Palm, Pedro Sanchez, Sonya Abamed, and Alex Awiti 99

II. Human Use of Environment and Resources

Bioenergy and Sustainable Development?
Ambuj D. Sagar and Sivan Kartha 131

Models of Decision Making and Residential Energy Use
Charlie Wilson and Hadi Dowlatabadi 169

Renewable Energy Futures: Targets, Scenarios, and Pathways
Eric Martinot, Carmen Dienst, Liu Weiliang, and Chai Qimin 205

Shared Waters: Conflict and Cooperation
Aaron T. Wolf 241

The Role of Livestock Production in Carbon and Nitrogen Cycles
Henning Steinfeld and Tom Wassenaar 271

Global Environmental Standards for Industry
David P. Angel, Trina Hamilton, and Matthew T. Huber 295

Industry, Environmental Policy, and Environmental Outcomes
Daniel Press 317

Population and Environment <i>Alex de Sherbinin, David Carr, Susan Cassels, and Leiwen Jiang</i>	345
---	-----

III. Management, Guidance, and Governance of Resources and Environment

Carbon Trading: A Review of the Kyoto Mechanisms <i>Cameron Hepburn</i>	375
--	-----

Adaptation to Environmental Change: Contributions of a Resilience Framework <i>Donald R. Nelson, W. Neil Adger, and Katrina Brown</i>	395
---	-----

IV. Integrative Themes

Women, Water, and Development <i>Isha Ray</i>	421
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Indexes

Cumulative Index of Contributing Authors, Volumes 23–32	451
Cumulative Index of Chapter Titles, Volumes 23–32	455

Errata

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