Carbon and climate system coupling on timescales from the Precambrian to the Anthropocene

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Abstract

The global carbon and climate systems are closely intertwined, with biogeochemical processes responding to and driving climate variations. Over a range of geological and historical time-scales, warmer climate conditions are associated with higher atmospheric levels of CO_2, an important climate-modulating greenhouse gas. The atmospheric CO_2-temperature relationship reflects two dynamics, the planet's climate sensitivity to a perturbation in atmospheric CO_2 and the stability of non-atmospheric carbon reservoirs to evolving climate. Both exhibit non-linear behavior, and coupled carbon-climate interactions have the potential to introduce both stabilizing and destabilizing feedback loops into the Earth System. Here we bring together evidence from a wide range of geological, observational, experimental and modeling studies on the dominant interactions between the carbon cycle and climate. The review is organized by time-scale, spanning interannual 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, the emergent behavior internal to the coupled carbon-climate system as well as the responses of the system to external forcing from tectonics, orbital dynamics, catastrophic events, and anthropogenic fossil fuel emissions. While there are many unresolved uncertainties and complexity in the carbon cycle, one emergent property is clear across time scales: while CO_2 can increase in the atmosphere quickly, returning to lower levels through natural processes is much slower, so the consequences of the human perturbation will far outlive the emissions that caused them.

Introduction and Motivation

The carbon cycle is one of the fundamental processes in the functioning of earth system, intimately connected with both planetary climate and ecology. On the time scale of the human experience, the carbon cycle links human economic activity directly to the geophysical system due to the sensitivity of atmospheric carbon dioxide (CO_2) and methane (CH_4) levels to fossil-fuel combustion, agriculture, and land-use (1). Rising atmospheric CO_2 and, to a lesser extent, CH_4 over the last 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 last 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 CO_2-climate relationship arises with higher atmospheric CO_2 levels under warmer conditions, a correlation found from interannual El Nino-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 time-scales of the anthropogenic climate transient.

Intellectually, studying the carbon cycle demands scholars to link economics and 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 must be 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 dynamics. The remainder of the review is organized by time-scale (Figure 1), starting with the Precambrian (Earth's formation to 542 million years ago) and the Phanerozoic (last 542 million years). The Phanerozoic exhibits gradual multi-million year variations in atmospheric CO_2 due 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 (last 1 million years), illuminating the links between orbital variability, cryosphere dynamics, ocean circulation and the marine carbon cycle. The post-glacial Holocene period (last 10,000 years) reveals subtler interactions between climate and carbon and shows responses due to 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., El Nino-Southern Oscillation) and human perturbations.

Climate and Carbon System Primer

Atmospheric CO_2 and CH_4 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 CO_2 rose from a preindustrial level of ~280 ppmv to ~380 ppmv by 2007 (Figure 2); over the same period CH_4 rose from ~650 ppbv to ~1800 ppbv. Although the absolute increase in CH_4 is much smaller than that of CO_2, molecule for molecule CH_4 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 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 CO_2, CH_4 and other radiative gases (N_2O, chlorofluorocarbons) arises because they can absorb radiation in those windows. As atmospheric CO_2 levels grow, CO_2 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 CO_2 varies in an approximate logarithmic fashion with concentration; that is, each doubling of atmospheric CO_2 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 CO_2 and CH_4 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 CO2, however, are enhancing this greenhouse effect, and most of the observed warming over the 20^{th} 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 systems' sensitivity to carbon dioxide 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 $\partial T/\partial CO_2$ 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 +1.5-4.5 K ($2xCO_2$), a major uncertainty in climate forecasting (3) and one where paleo-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 deg. C on geological scales is inconsistent with paleo-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 time-scales with the crust and mantle (14). Estimates of the pre-industrial 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 (~$4x10^4$ Pg C), a smaller but highly active biological carbon cycle, and deep layers of carbon-rich sediments. The largest stocks of carbon (~$6x10^7$ Pg C) exist in marine sediments, as dispersed organic material trapped in sedimentary rocks, and 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 paleo-vegetation, 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 build-up of atmospheric CO_2 and in the process destabilizing the climate system (16).

The atmosphere-ocean-land carbon system is quite dynamic on time-scales 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. Methane has a well-defined atmospheric life-time of about a decade due 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). Carbon dioxide has no true atmosphere life-time because of the multiple process 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 CO_2 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 CO_2 (and perhaps CH_4) to the atmosphere due to warming and hydrological cycle sifts (4, 19). Under some model scenarios, positive carbon-climate interactions could increase anthropogenic warming by an additional 1K at 2100; carbon-climate feedbacks could also reduce sharply the amount of CO_2 that could be released and still allow humans to stabilize atmospheric CO_2 at a specified target level (3). Estimating the magnitude of such carbon-climate interactions from modern observations and paleo-records requires the deconvolution of the climate-induced change in atmospheric CO_2, 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 CO_2 is thought to always be positive, $\partial T / \partial CO_2 > 0$. As discussed below, the carbon cycle sensitivity to climate perturbations, $\partial \delta CO_2 / \partial T$ (taking temperature as a proxy for climate), can be both positive (destabilizing feedback) and negative (stabilizing feedback), depending upon the time-scale and processes involved.

Precambrian (Earth's formation to 542 million years ago)

The carbon cycle of the Precambrian is closely intertwined with the cycles of sulfur, oxygen, iron and 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 are 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, that is not so reduced as to convert CO_2 into CH_4 and containing only a small amount of H_2 (21). The redox state and H_2 concentration, however, remains a question of some debate (22).

The evolution of oxygenic photosynthesis and the burial of organic carbon lead to 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 (1Ga=1 billion years ago) (24). Eventually, a small fraction of the oxidizing power exported by the carbon cycle started to build up as atmospheric O_2, 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-fraction in paleo-sulfur isotope records, as mass-independent-fraction 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, 29, 30). The rise in atmospheric oxygen changed fundamentally the chemical state of the planet and drove biological trends including, eventually, the evolution of multi-cellular life (31).

Estimates of the atmospheric CO_2 and CH_4 levels for the early Earth vary considerably and are only weakly bracketed by data. Paleorecords of stable carbon isotope ratios ($^{13}C/^{12}C$) 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, biosphere system from volcanic emissions from the mantle and crust and is removed to the crust by organic and inorganic carbon burial. Photosynthesis preferentially forms ^{13}C-depleted organic matter with low $^{13}C/^{12}C$ values (negative $\delta^{13}C$ anomaly, about -25‰ lower than the carbon source) enriching the ^{13}C (positive $\delta^{13}C$ anomaly) of atmospheric CO_2, dissolved inorganic carbon in seawater, and the carbonate sediments formed from these pools. Complications arise because of the extent to which particular samples are representative of the global environment, uncertainties in the overall size and isotopic composition of the atmosphere-ocean-land-crust carbon reservoir over time, and external sources and sinks such 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 $\delta^{13}C$ of carbonate sediments, sedimentary organic carbon, and the difference in $\delta^{13}C$ 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 $\delta^{13}C$ anomalies can be interpreted as rapid changes in external sources and sinks to the ocean, atmosphere, and biosphere system or internal shifts of carbon within the system from one reservoir to another (33).

Paleoclimatic data provides another line evidence on the early composition of the atmosphere. Solar energy output was 20-30% weaker during the early Precambrian, and geochemical proxies, in this case $\delta^{18}O$ of marine carbonates, suggest that the planet was warmer and perhaps even much warmer (50-70 deg. 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 bar to reach the upper end of the temperature estimates. More moderate, but still warm, climates may be consistent with reinterpretations of the $\delta^{18}O$ data (36). In contrast, silicon isotope data from cherts appears to support hot conditions (70 deg. C) for the early Archaean ocean with a general cooling trend to 30 deg. C by the late Proterozoic (37). Based on geological data such as ice-rafted debris, it appears that the generally warm conditions during the Archean 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 Ma, 1 Ma is 1 million) and one in the Ediacaran (635-542 Ma). Some of these glacial events may have involved extensive low-latitude glaciation or possibly even planetary glaciation, so-called "snow-ball earth" conditions (38). One hypothesis is that rapid, planet wide glaciation resulted from a runaway ice-albedo feedback that was only abated on time-scales of about a million years by the build-up of a super-greenhouse effect from elevated atmospheric CO_2 (39). Following deglaciation, the high atmospheric CO_2 may have lead to greatly enhanced continental weathering of carbonate and silicates and a flux of excess alkalinity into the ocean, which may explain the observed deposition of thick carbonate layers ("cap carbonates") and large negative $\delta^{13}C$ anomalies in marine carbonate (-10‰ amplitude excursions).

Based on the magnitude of the carbonate $\delta^{13}C$ 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. While 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 due to the tropical arrangement of land masses; and variations in atmospheric CH_4.

There is evidence of positive $\delta^{13}C$ 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 $\delta^{13}C$ anomaly in the organic carbon isotopic record, with little or no change in carbonate $\delta^{13}C$; the excursion is thought generally to represent a widespread assimilation of CH_4 into organic matter (41). The resulting removal of atmospheric methane 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 methane greenhouse conditions due to the rise of oxygenic cyanobacteria.

Phanerozoic (542 million to 1 million years ago)

The more recent Phanerozoic eon (542 to 0 Ma) encompasses the proliferation of multi-cellular 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 paleo-reconstructions 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 pre-industrial 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 based on $\delta^{13}C$ of paleo-soil and mineral deposits (48, 49), stomatal density on fossil plant stems and leaves (50, 51), $\delta^{13}C$ of alkenones---specific organic compounds produced by surface phytoplankton and found in marine sediments (52), $\delta^{13}C$ of fossil plant material (53), and boron isotope proxies of ocean surface water pH (54; but also see 55). Geochemical modeling studies have also been used to estimate atmospheric CO_2 levels independently and for comparison with the paleo-proxy records (44, 56-58). Other important evidence on paleo-carbon cycle dynamics comes from geological and geochemical estimates of net organic carbon burial, marine carbonate deposition, and atmospheric oxygen, particularly data on marine carbonate $\delta^{13}C$ 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 $\delta^{18}O$ and Mg/Ca data), and paleontological environmental data (46, 61-63).

There is, in general, a good correlation over the Phanerozoic between higher atmospheric CO_2 and warmer climate (10, 46, 64). Periods where there is geological evidence for extensive glaciation in the Carboniferous and Permian (about 350 to 270

Ma) and during the latter part of the Cenozioc (<33 Ma) are associated with low CO_2 levels, <500 ppm. Episodes of cooler climate, but perhaps non-glaciated, tend to have atmospheric CO_2 <1000 ppm while warmer periods generally exhibited atmospheric CO_2 >1000 ppm (10, 64). The geological variations in atmospheric CO_2 would have driven substantial changes in radiative forcing that would have been amplified by additional physical and biogeochemical climate feedbacks. The climatic impacts of CO_2 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 CO_2 in the mid-Cenozoic and the onset of permanent Antarctic glaciation at the Eocene/Oligocene boundary is highly suggestive of a CO_2-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 Ma), based on extensive ice-rafted debris sediments from the Norwegian–Greenland Sea (65), support a more global cooling. A stronger and more direct causal link between CO_2 and climate can be drawn from coupled climate-ice sheet simulations, which show quantitatively that reductions in atmospheric CO_2 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 2x to 4x preindustrial atmospheric CO_2 levels below which CO_2 must fall before large-scale glaciation can be triggered.

Numerical climate models have also been used to explore the impact of a CO_2 rich atmosphere during warmer climate periods. Kiehl & Shields (68) describe how elevated CO_2 levels during the late Permian resulted in warm high latitude temperatures, less vigorous ocean circulation and low ocean oxygen levels in broad agreement with geological data. In fact, paleo-climate 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 CO_2 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 CO_2 on geological time-scales? And to what extent do climate-carbon cycle feedbacks occur? The major biogeochemical processes influencing the carbon cycle on million year and longer time-scales during the Phaerozoic include the venting of volcanic CO_2, 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 two equations (15; 45):

$$CO_2 + (Ca,Mg)SiO_3 \leftrightarrow (Ca,Mg)CO_3 + SiO_2 \tag{1}$$

$$CO_2 + H_2O \leftrightarrow CH_2O + O_2 \tag{2}$$

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 due to net burial of organic matter; it also represents thermal decomposition of organic matter to CO_2 and volcanic emission. As discussed below, the weathering of terrestrial carbonate rocks and changes in ocean alkalinity:

$$CO_2 + CaCO_3 + H_2O \leftrightarrow 2HCO_3^- + Ca^{2+} \tag{3}$$

plays an important role in modulating atmospheric CO_2 over 10^3-10^5 years, but not on the million year time-scale.

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 hypotheses ranging in time-scale from plate tectonics (10^5-10^7 y) and orbital forcing to (10^4-10^6 y) to abrupt catastrophic geological events with durations of 10^3-10^5 y (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 Ma initiated the summer monsoon cycle; the combination of increased topographic gradients and rainfall are 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, due to plate tectonics also appears 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 super-continent Pangea triggered a global cooling of about 10K 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 Ma) may have contributed to the net burial organic carbon and supplied large amounts of nutrients, calcium and alkalinity to the ocean to support the rapid radiation marine life at the beginning of the Cambrian.

Biological evolution occurs on similar time-scales 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 ($<<10^6$ y), 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 time-scale was originally developed using paleofossils, often fall at the boundaries of geological periods. One of the best documented event occurred during the Paleocene-Eocene thermal maximum (PETM) about 55 Ma. The PETM is marked by rapid (10^3-10^4 y) increase in temperature (5-6 K), drop in marine carbonate $\delta^{13}C$ (3-4‰), and shoaling of the calcite compensation depth (>2 km) followed by a more gradual relaxation over several hundred thousand years (82-84). The calcite compensation depth (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 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 would lower pH, increases $CaCO_3$ solubility, and shoal the CCD. The hundred thousand year relaxation timescale could then be explain as the amount of time required for the ocean alkalinity 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 methane hydrates in continental margin sediments, most like due to some initial thermal warming or intrusion of magmatic sills into sediments. Methane is appealing because it is a strong greenhouse gas and is depleted in $\delta^{13}C$ (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 (>>2000 Pg C) that is inconsistent with a methane 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 due to 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 increases during deglaciation in atmospheric CO_2 (+80-100 ppmv or ~+40%) (9, 94) and CH_4 (+250 pbmv or ~+60%) (95) (Figure 4). As outlined below, considerable progress has been made in characterizing the timing and magnitude of the climate and CO_2 signals. Yet a complete mechanistic understanding of the initial triggers and underlying coupled coupled-carbon 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 (10-10^3 y), better spatial mapping of paleo-environmental patterns, tighter chronological controls for determining lead/lag relationships among properties, and an expanded suite of paleo-proxies. Some of the most notable advances have come from the recovery of long ice cores from the Greenland and Antarctica ice sheets now covering most of the last 1 Ma. Ice cores record temperature via $\delta^{18}O$ and $\delta^{2}H$ 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 paleo-levels of CO_2, $\delta^{13}C$ of CO_2 (organic carbon redistribution), $\delta^{18}O$ of O_2 (ice volume), and other trace gases (e.g., CH_4, N_2O, 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 paleo-environmental conditions.

Corresponding temporal records of ice sheet volume, ocean surface and deep-water temperatures have been reconstructed from marine sediment cores and corals using carbonate $\delta^{18}O$, 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 subaeriel corals using uranium-thorium radiodecay dating methods (112, 113). There is 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 $\delta^{13}C$ and Cd/Ca (115, 116), bulk and diatom-bound $\delta^{15}N$ 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 or ^{14}C, a radioactive isotope of carbon that 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 last 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 Pliestocene 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 build-up 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 8 glacial-interglacial cycles (125, 126). Prior to about 1 Ma, the dominant glacial-interglacial periodicity was about 41 kyr (1 kyr is 1000 years), transitioning to about 100 kyr only over the last 0.5 Ma. At the 100 kyr periodicity, atmospheric CO_2 and temperature and deep-water temperature are approximately in phase, with ice volume lagging be several thousand years (Shackelton, 102).

The cause of glacial-interglacial oscillations is commonly attributed to orbital variations on surface solar insolation, the so-called Milankovitch forcing due 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 paleo-climate data and the planet's orbit is still a subject of some debate, and some researchers invoke 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 discussion of non-linear 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 $\delta^{18}O$ and $\delta^{2}H$ isotopic signals can be addressed by age models that attempt align the records. A recently develop 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 fractioned isotopically in the vertical due to 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 methane and $\delta^{18}O$ in O_2 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-core and varved marine sediments that occur in some anoxic basins;

radiometric ages using ^{14}C and U-Th, etc.) or simultaneous climate proxies that are evident in both records (138, 139).

Comparing the age-corrected bubble and ice-core δ^2H time-series for the last glacial termination (when CO_2 rose by 76 ppmv in only 6000 years), Monnin et al. (140) found that the CO_2 changes lagged slightly behind the southern hemisphere temperature changes by 800 (+/- 600) years. Caillon et al. (141) found similar results with CO_2 lagging Antarctic warming by 800+/-200 years for glacial termination III (~240 ka). 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 CO_2 changes in both cases, we can infer that initial elevated southern hemisphere temperatures affect the Earth System in some way that releases CO_2 to the atmosphere. The Southern Ocean is thought to be the primary CO_2 source (9, 143), but see Johnston and Alley (144) for a counter-suggestion for northern hemisphere control on atmospheric CO_2. A CO_2–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 CO_2 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 northern 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 CO_2, provide quantitatively the only plausible global process (145). Close correlations between ice-core CO_2 and CH_4 changes also indicate synchrony between southern hemisphere and tropical and/or Northern Hemisphere climate (140). Elevated CH_4 is usually interpreted as warmer and wetter terrestrial conditions, leading to increased CH_4 release from both tropical and boreal wetlands (147). Paleoclimate simulations suggest that radiative impact of the atmospheric CO_2, CH_4 and N_2O variations, along with changes in surface albedo (sea-ice, ice-sheets, vegetation) and surface topography (ice-sheets), contribute about half of the estimated cooling that occurred at glacial maxima compared with interglacial periods (146, 148).

The interpretation of CO_2 and CH_4 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 Youger Dryas cold reversal (12.3-11.2), 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 anti-phase, again with a slight northern lead of the anti-phased behavior. Atmospheric CO_2 was flat or slightly decreasing during the Bolling-Allerod and then increased sharply during the Younger Dryas, consistent with a positive CO_2-temperature relationship and Antarctic climate variations, which were out of phase with those in Greenland during this period (140). The pattern was opposite for methane (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 CO_2 because it is the largest reservoir of mobile carbon on these time-scales. Land carbon inventories actually grew rather than shrank during deglaciation due to revegetation of previously ice-covered surfaces and shifts in vegetation, removing about 300-800 Pg C that must have been balanced by even greater ocean CO_2 release (114, 150) and increasing the $\delta^{13}C$ 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 be able to explain the entire CO_2 change while remaining consistent with the numerous paleo-data 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 CO_2 to perturbations compared with 3-D general circulation models (GCMs) (157), though uncertainties surround GCMs as well (158, 159).

Postulated reduced biological productivity due to lower interglacial dust deposition and iron fertilization (160) now appears to account for at most only about half of the CO_2 increase (121, 161, 162). Improved paleo-data sets (121) also question other biological hypotheses that require decreased interglacial Southern Ocean export production from depleted nitrate inventories (143), weaker nutrient utilization due 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/$CaCO_3$ rain ratio in key tropical regions, readjusting the ocean's alkalinity balance and lowering glacial atmospheric CO_2. Sediment core data from the eastern equatorial Pacific, however, provide evidence higher opal (Si) fluxes for the Holocene relative to the last glacial period, exactly the opposite predicted from the silicic acid leakage hypothesis (167, 168).

Southern Ocean physical mechanisms likely contribute a significant fraction of the atmospheric CO_2 rise during deglaciation, including effects due to thermal warming, a poleward shift in atmospheric westerlies and enhanced ocean overturning circulation (169), and increased vertical mixing and decreased sea-ice (163, 170, 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/atmosphere ^{14}C levels (a $\Delta^{14}C$ decrease of 190±10‰) occurred during the time-interval 17.5- to 14.5-kyr in the last termination; Hughen et al. (122, 123) use the ^{14}C 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. Comparing ^{14}C and ice-core ^{10}Be records, a constraint on cosmogenic ^{14}C production rates, Muscheler et al. (173) also need large carbon cycle changes, including ocean circulation variations, to explain the ^{14}C temporal evolution. In contrast, Broecker & Barker (174) question the isolated ^{14}C reservoir explanation, arguing that it is quantitatively implausible and inconsistent with sediment ^{13}C data. Understanding the relationship between climate change and ocean mixing/ventilation is critical to understanding past carbon cycle changes and potential future dynamics. Tracer paleooceanography 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 CO_2 rise. Coral reef growth appears to be minor contributor to overall glacial-interglacial variation, and the impact of altered terrestrial weathering, while potentially larger (175), can explain only part of the signal. In the $CaCO_3$ compensation hypothesis, a shift of inorganic carbon from deep-water to the surface ocean and atmosphere would result in a transient increase in deep-water carbonate ion concentration, deepening of the lysocline (the depth where noticeable $CaCO_3$ deposition first starts to occur), and excess $CaCO_3$ burial, bringing the marine $CaCO_3$ 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 umol/kg) during deglaciation that may be consistent with a larger $CaCO_3$ compensation mechanism (120).

Greenland $\delta^{18}O$ 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 CH_4 anomalies (+100-200 ppmv) associated with these so-called Dansgaard-Oeschger events allow temporal matching of Greenland $\delta^{18}O$ and Antarctic CO_2 signals (the millennial Greenland CO_2 record is contaminated by high dust and organic levels). Atmospheric CO_2 variations during some Dansgaard-Oeschger events were small (< 10 ppmv). Larger CO_2 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 CO_2 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 CH_4 signal provides a potential support for an extension of the warming into the tropics, if the CH_4 variations indeed involve wetland sources over a wide spatial extent (147, 181).

The Holocene (10,000 years ago to 1700)

Climate and atmospheric CO_2 variability during the Holocene interglacial is less dramatic than during the glacial-interglacial transitions, but nonetheless contain intriguing information about coupled processes. For example, high resolution Antarctic ice-cores (182, 183) show a 6 ppmv decrease in atmospheric CO_2 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 CO_2 and $\delta^{13}C$ indicates an initial terrestrial uptake of ~10 Pg C, likely due to continued revegetation post 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 terms. Based on surface ocean $\delta^{13}C$ and deep-sea $CaCO_3$ dissolution records, Broecker et al. (184) suggest an alternative hypothesis where the terrestrial biosphere remained constant from 8 ka and preindustrial times. In their scenario, the 20 ppmv Holocene rise in atmospheric CO_2 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) provides further support that growth of coral-reefs and shallow-water drove the late CO_2 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 CO_2 trend while 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 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. While perhaps not having a major impact on atmospheric CO_2, the extensive reorganizations in land vegetation and biogeography during the Holocene (188) amplified and contributed to regional climate variation (146, 189).

Contrasting 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 CO_2 (<8 ka) and CH_4 (< 5ka), and the +40 ppm atmospheric CO_2 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 $\delta^{13}CO_2$ of 0.6‰. The isotopic change is not consistent with the observed atmospheric isotope record, and 700 Pg C is about 4 times larger than current estimates of historical land-use effects.

Atmospheric methane underwent a large oscillation during the Holocene, with peaks around 11.5-9 ka and the late Holocene and a minimum 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 $\delta^{13}CH_4$ data for the last 2000 years, Ferretti et al. (193) found elevated biomass burning emissions for the period 2000-1000 years ago and suggested that both human activities and natural climate change influenced preindustrial atmospheric methane.

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 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 $\delta^{13}CO_2$

observations. They suggest the CO_2 minimum from 1550-1800 AD arises from a land biosphere response to cooling, although they note the $\delta^{13}C$ 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 +1K in global mean temperature results in +12 ppmv anomaly in atmospheric CO_2; thus ice-core CO_2 data can be used to place bounds on paleo-temperature.

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, 3-D carbon climate simulation (200). The majority of the model internal carbon cycle variability was initiated on land in response to changing soil water and temperature, and the ocean acted to partially damp the land-driven oscillations in atmospheric CO_2. Trudinger also found suggestive evidence of an El Nino-Southern Ocean correlation with carbon fluxes, possibly involving both terrestrial and marine processes (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 bigeochemical 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.

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. Continuing through present-day, the Mauna Loa record shows, up to now, an inexorable rise of atmospheric CO_2 due to fossil fuel combustion and thus has become one of the most iconic datasets 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 information about carbon-climate coupling on multiple space scales and time-scales from the diurnal cycle to decades.

While the long-term trend in atmospheric CO_2 has remained positive, subtle variations in the annual increase in concentration indicate the response of terrestrial and marine processes to climate variability (207) (Figure 5). Statistical and modeling analyses of this variation in growth rate of CO_2 have proved a fruitful source of insight. Although arguably the analysis of interannual variations have come to fruition recently, Bacastow et al. (208) first noted a relationship between the Mauna Loa CO_2 record and the weak El Nino of 1975, suggesting a link between the ocean carbon cycle and atmospheric CO_2. An oceanic causation for the El Nino-CO_2 correlation was first considered because the El Nino-Southern Oscillation (ENSO) is a coupled ocean-atmosphere phenomenon originating in the tropical Pacific. By the 1990s, this was questioned because observed changes in marine CO_2 and air-sea CO_2 fluxes were too small and of the wrong sign to explain the atmospheric changes (201, 209). El Nino events reduce upwelling of cold, CO_2-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 Nino effect on CO_2 seems instead to be associated with terrestrial processes and linked to tropical drought (215). For example, the Amazon Basin experiences droughts during El Nino years. Tian et al. (216) argued that soil drought causes increases in respiratory carbon emission, while Nepstad et al. (217) showed that biomass burning of forest slash during deforestation is higher during El Nino droughts. Vukicevic et al. (202) used data assimilation and a simple model of the responses of ecosystem carbon responses to temperature and showed that while some amount of interannual biogeochemical variability could be explained, large residuals were associated with El Nino periods. The residuals show processes not correlated with temperature through ecosystem metabolism and indicated uptake early in the El Nino period and emissions later. This pattern could arise from ocean uptake early with emissions following as El Nino droughts affect biomass burning (215).

While early work focused on drought effects on biological carbon exchange (photosynthesis and respiration) (218), wildfire triggered by drought may cause much of the observed terrestrial El Nino emission of carbon. Langenfelds et al. (219) used atmospheric measurements of CO_2, $^{13}CO_2$, and several chemical tracers of biomass burning. They concluded that most of the interannual variability in the growth rate of CO_2 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 Nino. Page et al. (220) calculated emissions from these fires of 0.8 to 2.6 Pg of carbon. The emissions were large because they burned peatlands, where vast amounts of soil carbon were stored. The Indonesian fires were triggered by El Nino drought but occurred in areas where naturally waterlogged soils had been drained for development and so were unusually vulnerable. These huge fluxes were thus caused between 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 are controlled by ignition and climatic conditions, although as described in Amazonia and Indonesia, prior land management greatly affects their 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 CO_2 that also suggests increased photosynthetic activity. Angert et al (224) using global CO_2 and satellite data products showed that while early spring photosynthetic activity seems to increase (from changes in the spring drawdown of CO_2), summer activity is decreased. Using satellite data, they suggest that warm springs are typically followed by dry summers that 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 7 years at 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 the earth 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 CO_2 of 380 ppmv is higher than it has been for at least the last 650 ka, and IPCC 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 CO_2 and other greenhouse gases, global surface temperature has increased at about 0.2^{o} C/decade over the last several decades, and current temperatures are within about 1^{o} C of the warmest conditions observed for the last 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 CO_2, greenhouse world?

A large and somewhat speculative literature (221) began to be replaced by quantitative modeling in the late 1990s examining the terrestrial (230-232) and oceanic responses to elevated CO_2 and warmer climate (233-235). Evaluating such models is sometimes difficult because much of the signal linking climate variability to surface CO_2 fluxes arises from seasonal and interannual variability. These high-frequency dynamics overlay the lower-frequency processes governing net CO_2 storage on 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 based on 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 eleven modeling teams to repeat these experiments in a multi-model inter-comparison. The C^4MIP project (19) found essentially the same results as Cox et al. (4) and Friedlingstein et al. (239), reporting a 1) consensus on a negative feedback, so that coupling accelerated climate change, and 2) great quantitative spread in the magnitude of that feedback. Most of the models simulated a terrestrially-dominated effect, but three had a larger ocean feedback. 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, while 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 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 C^4MIP 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. While 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 natural variability, Doney et al. (200) showed that while most of the variability in atmospheric CO_2 was due to the land biosphere, the variability was damped by ocean processes on decadal to centennial time-scales. That is, climate-triggered changes in terrestrial carbon storage caused atmospheric CO_2 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 Nino time scale or using flux time series are just beginning. This analysis shows that atmosphere-ocean coupling that dominates many of the long time scales of the paleo-record is likely to remain important on the time scales of global change. One caveat is that the current generation of coupled carbon-climate models neglect peats (240) and methane hydrates (241), two large carbon reservoirs that could be destabilized under warmer climate. While the likelihood of a large catastrophic CO_2 release in response to anthropogenic warming may be small, the present estimates of positive carbon-climate feedbackss are also likely underestimates of the true values.

Final Thoughts

The coupled carbon-climate system has important dynamics on a wide range of time-scales, 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-CO_2 state, two important questions arise: 1) what is the climate sensitivity to elevated CO_2? 2) how does warming impact atmospheric CO_2? Historical and paleoclimate records are providing constraints, if somewhat broad, on physical climate sensitivity of about +1.5-6 K in global temperature for a doubling of CO_2 (5, 242, 243). 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 water balance 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. Gaining a predictive understanding of the coupled carbon and climate systems requires integrating our knowledge of processes gained across all of the observational time scales, from the geological to the physiological. Although an impressive body of scholarship exists, its integration into a quantitative, predictive framework is just beginning.

Despite these complexities, examination of the diverse range of feedbacks across all time-scales from abrupt events in the deep past to the modern El Nino 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 potentially managing the carbon cycle through fossil fuel emission controls and geoengineering, we need to remember that while we can increase CO_2 in the atmosphere quickly, returning to lower levels by manipulating natural processes is likely to be much slower.

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Figures

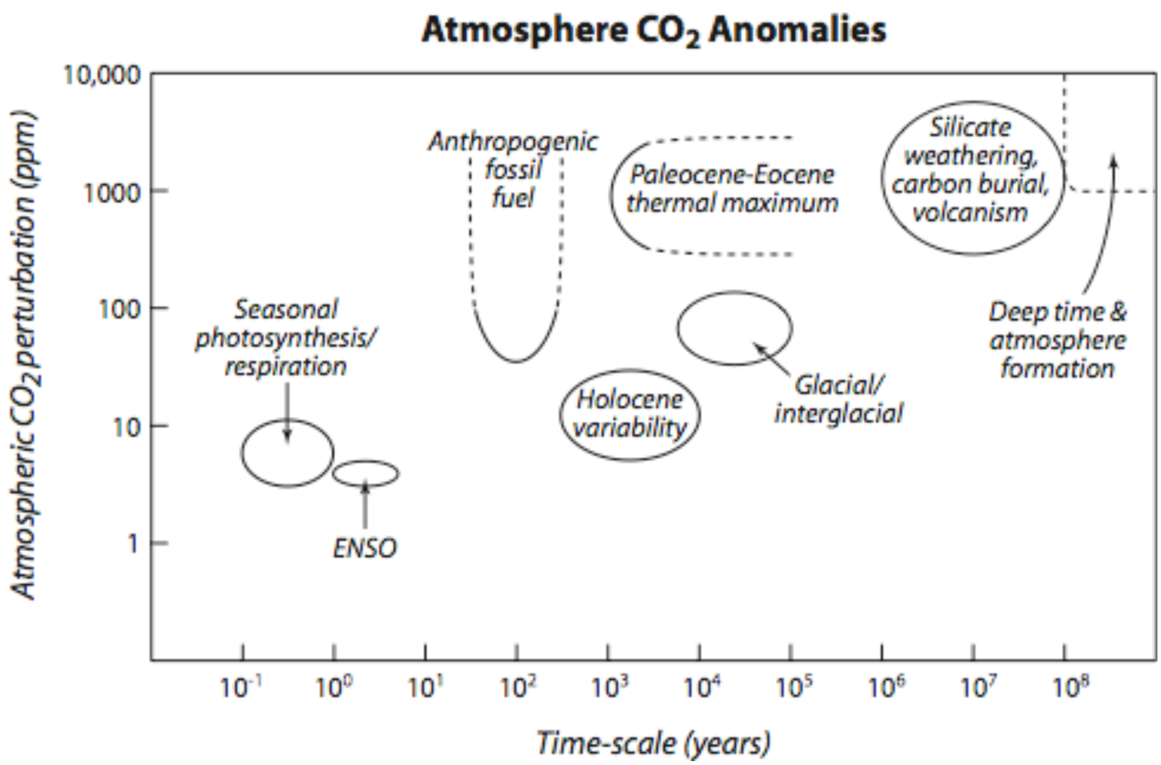

Figure 1: Schematic illustrating the magnitude of atmospheric CO_2 perturbations (ppm) against approximate time-scale (year) for various climate process. The axis are log-log.

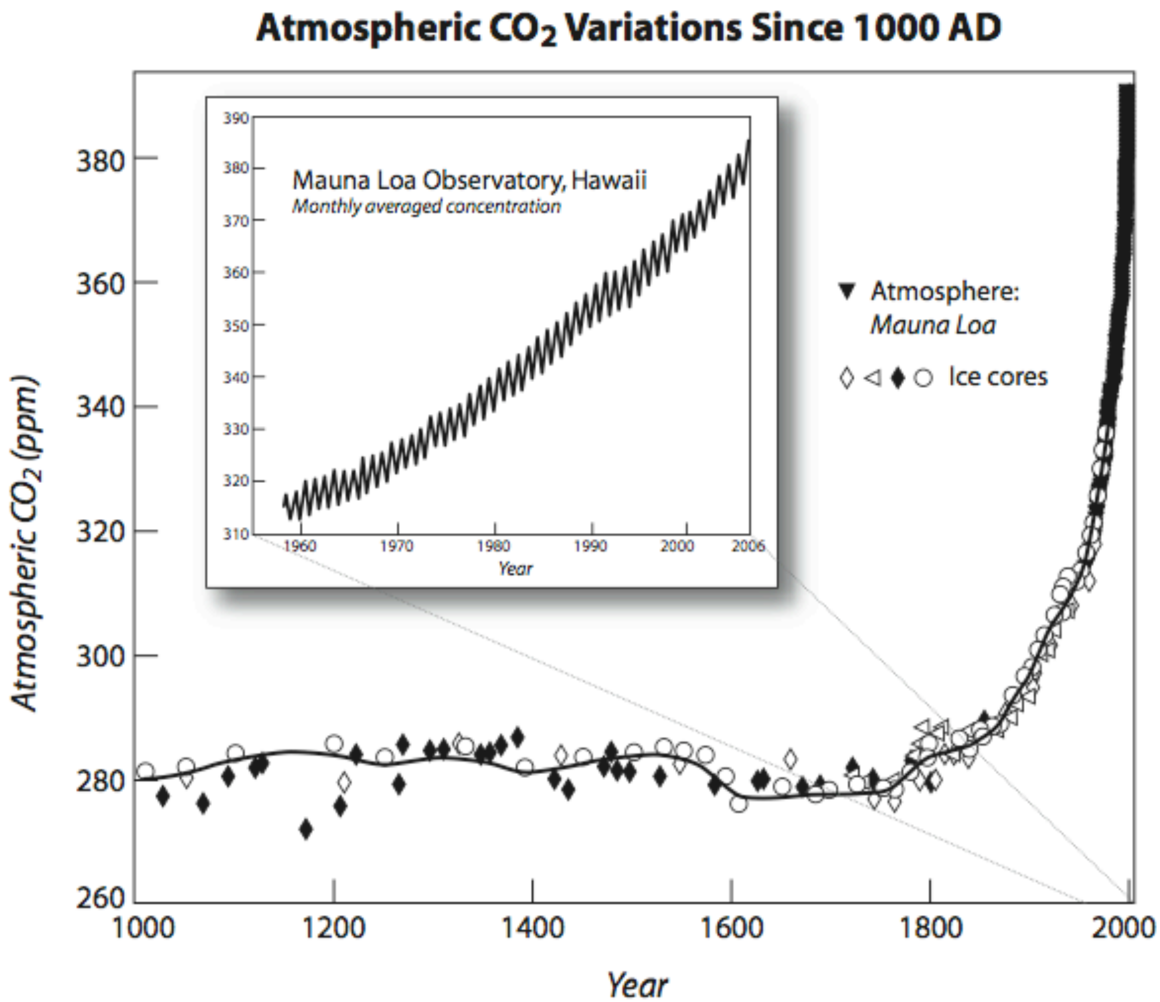

Figure 2: Atmospheric CO_2 concentration for the last 1000 years derived from high-deposition ice cores (194, 195) and direct atmospheric observations. Adapted from Sarmiento and Gruber (16). The inset displays the direct atmospheric CO_2 observations from Mauna Loa, Hawaii beginning in 1958 at approximately monthly resolution from CD Keeling and NOAA/CMDL.

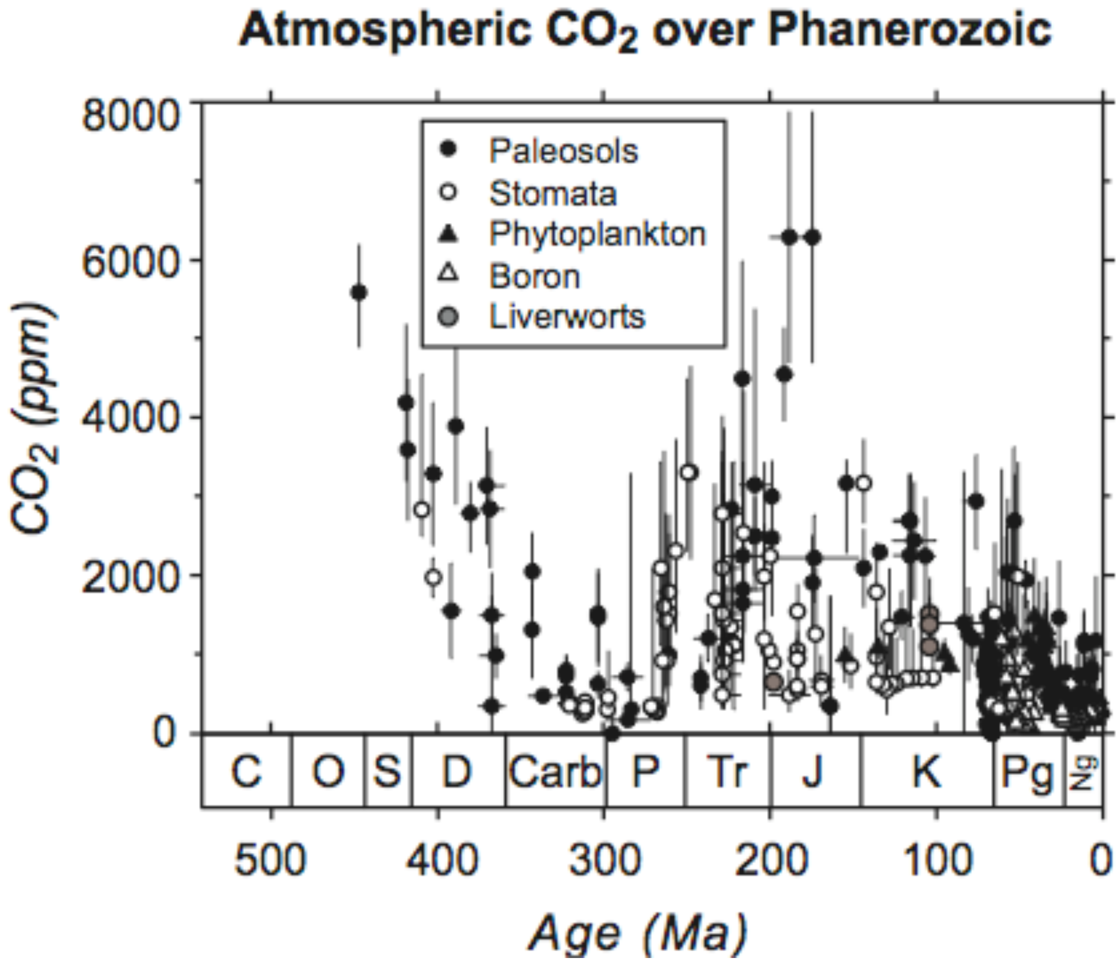

Figure 3: Paleo-reconstructions of atmospheric CO_2 (ppm) versus time over the last 450 million years (Ma) of the Phanerozoic. Adapted from Royer (10).

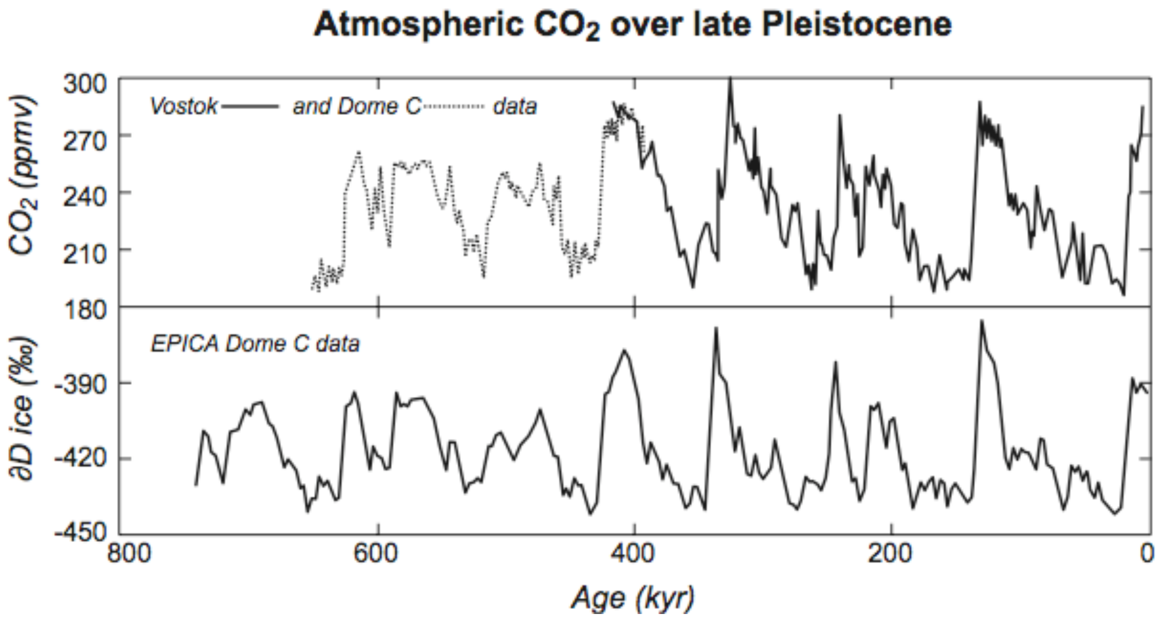

Figure 4: Glacial-interglacial variations of atmospheric CO_2 (ppm) and ice deuterium (δ^2H or δD in ‰), a proxy for temperature (higher δD reflects warmer conditions), from Antarctic ice-cores for the last 650,000 years. Based on CO_2 data from Vostok (9) and Dome C (125) cores and δD from Dome C (126).

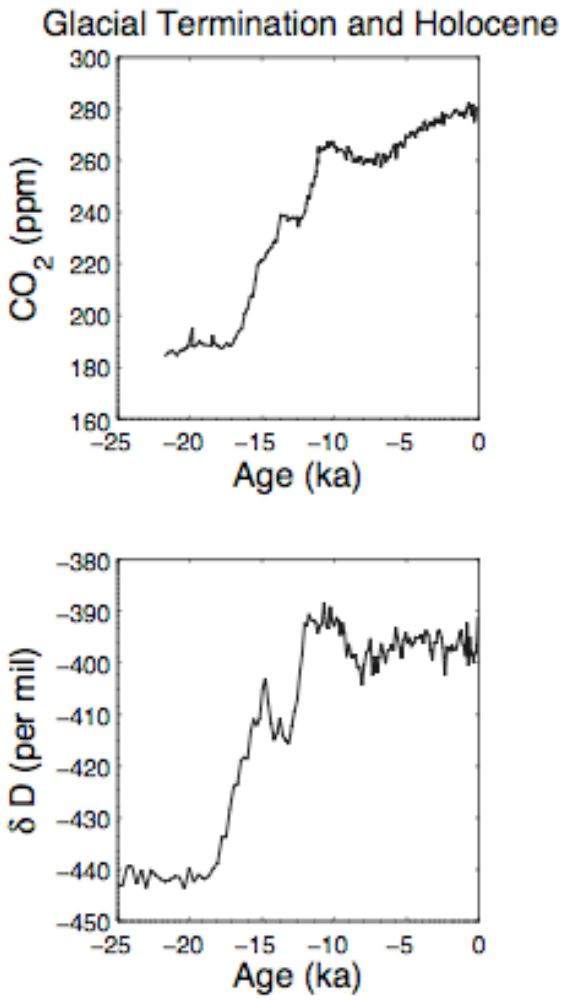

Figure 5: Variations of atmospheric CO_2 (ppm) and ice deuterium (δ^2H or δD in ‰), a proxy for temperature (higher δD reflects warmer conditions), from Antarctic ice-cores for the last glacial termination and Holocene. Based on data from Dome C core for δD (126) and .

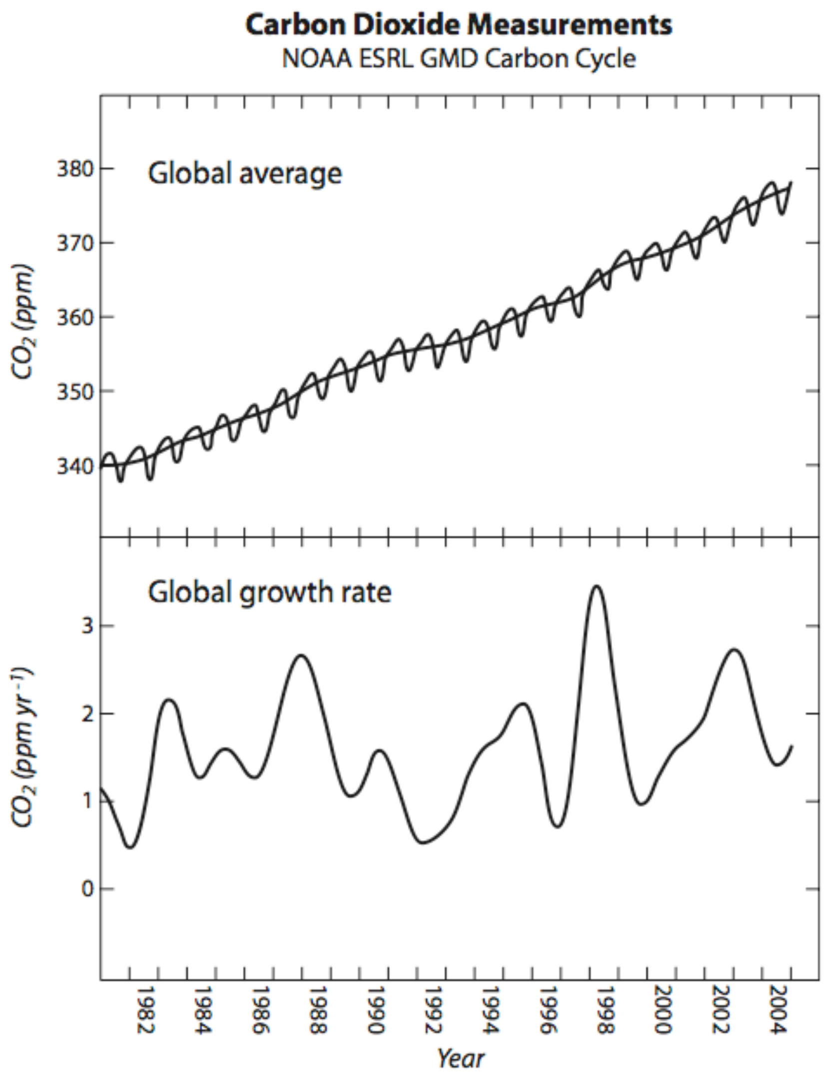

Figure 6: Global mean atmospheric CO_2 concentration and global CO_2 growth rate, $\partial CO_2/\partial t$, for 1981-2005 (adapted from publiclly available data and figure courtesy of P. Tans, NOAA/CMDL, http://www.cmdl.noaa.gov/ccgg).

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