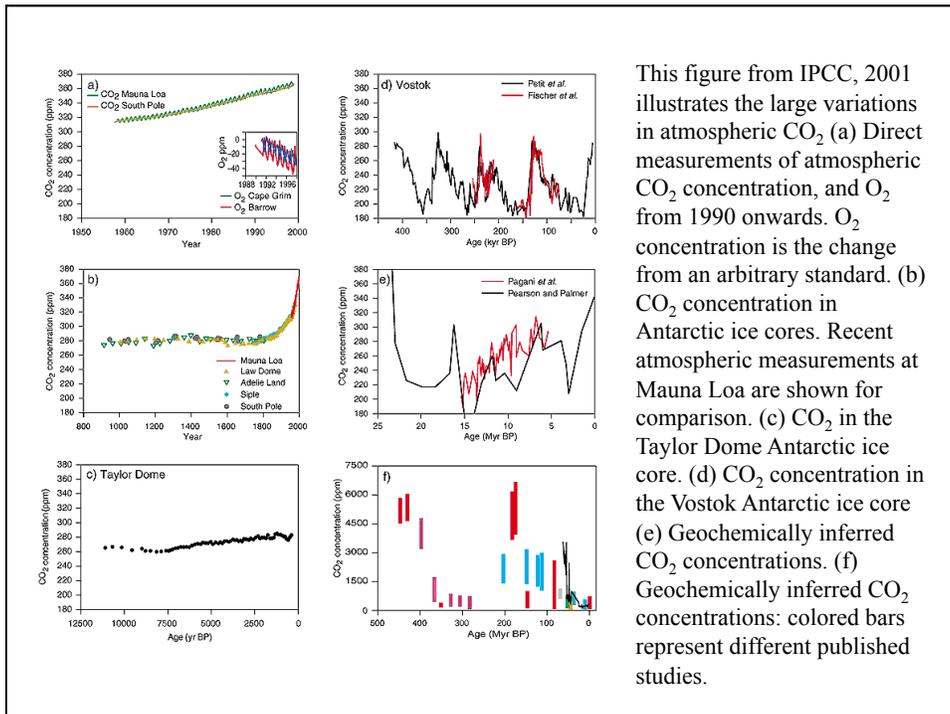


Carbon - I



The time scale matters. On tectonic time scales, volcanism and the weathering of carbonate rocks has a strong influence on atmospheric CO_2 . On glacial-interglacial timescales (and longer), the whole ocean and the ocean sediments can come into equilibrium with the atmosphere and subtle changes in ocean biology or alkalinity may drive the observed variability. The recent, fossil fuel and land use change alteration of the carbon cycle may be unprecedented in the speed at which atmospheric CO_2 is being driven. Because of the fast rate of change, disequilibria are the rule rather than the exception. Although the surface ocean is at close equilibrium with the atmosphere, the terrestrial biosphere (probably) and the deep ocean (certainly) are important sinks at present.

In this lecture, we will talk about long time scale controls on CO_2 and then next lecture we will discuss the modern forcing.

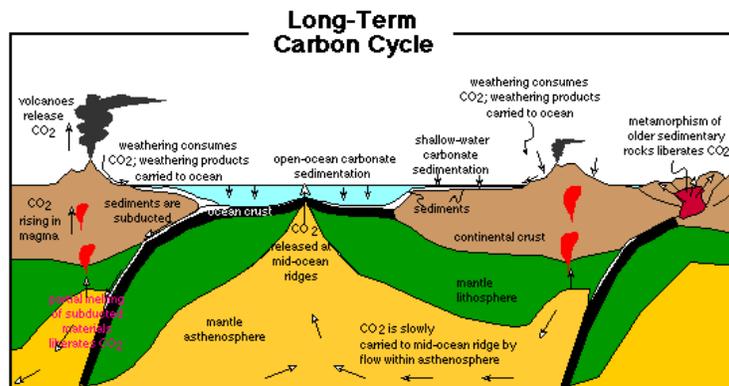


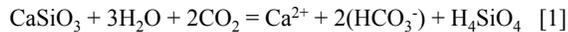
Figure 7.3. Schematic representation of the long-term global carbon cycle showing the flows (hollow arrows) of carbon that are important on timescales of more than 100 Kyr. Carbon is added to the atmosphere through metamorphic degassing and volcanic activity on land and at mid-ocean ridges. Atmospheric carbon is used in the weathering of silicate minerals in a temperature-sensitive dissolution process; the products of this weathering are carried by rivers to the oceans. Carbonate sedimentation extracts carbon from the oceans and ties it up in the form of limestones. Pelagic limestones deposited in the deep ocean can be subducted and melted. Limestones deposited on continental crust are recycled much more slowly — if they are exposed and weathered, their remains may end up as pelagic carbonates; if they get caught up in a continental collision, they can be metamorphosed, liberating their CO_2 .

http://www.carleton.edu/departments/geol/DaveSTELLA/Carbon/long_term_carbon.htm

Weathering

Chemical weathering of minerals exposed at the surface is important for setting the amount of CO₂ present in the near surface reservoirs. Although the weathering of limestones does indeed involve the transfer of carbon, it has no net effect on the amount of CO₂ in the atmosphere.

Weathering silicate minerals consumes acid (CO₂):



wollastonite + water + carbon dioxide = calcium + bicarbonate + silicic acid

The products of this reaction are all carried away in solution, ending up in the oceans. The silicic acid eventually is used by siliceous planktonic organisms; the calcium and bicarbonate ions will be combined by other organisms in the oceans, forming calcite and some dissolved carbon dioxide, which can escape back to the atmosphere:



One of the CO₂ molecules is returned to the atmosphere in this step; the other is sequestered in the form of limestone (CaCO₃).

Silicate weathering [1] thus represents an important feedback mechanism in the long-term carbon cycle (probably negative feedback). Like most chemical reactions, the process of dissolution described in equation [1] above is sensitive to the temperature; the hotter it is, the faster the dissolution. Thus, if the climate is warm (high atmospheric CO₂) then weathering will occur faster, removing CO₂ from the atmosphere, cooling the climate. This negative feedback mechanism is potentially one of the most important long-term stabilizers in Earth's climate system.

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 [BLAG Hypothesis]:

Surface area of the land or continental area - depends on sea level and extent of continents. Function of the sea floor spreading rate. Also includes estimate of exposed limestones versus that of silicate rocks

Run-off - warmer = more precipitation => weathering increases

Atmospheric CO₂ - higher => more acidic, more active biosphere

Continental elevation - physically stripping off weathered stuff exposes fresh new rocks to be weathered.

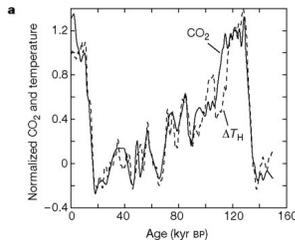
Unfortunately, it is not so simple alas

plants (high CO₂ at roots), ice (which fractures rock and thus increases surface area) are all likely important and difficult to model. Nevertheless, on long timescales, CaCO₃ sediments are recycled through the mantle or outgas during subduction.

Variation between glacial and interglacial CO₂

As we have seen, orbital forcing of climate at the 41,000 year obliquity period dominates the climate record until ~700,000 years ago when the glacial/interglacial timing appeared to become paced at ~100,000 years. This period corresponds to the changes in eccentricity of Earth's orbit, but the magnitude of the 100,000 year orbital forcing is generally considered too small to drive the climate system alone. In other words, it is hard to understand how this forcing could become so dominant and what would cause the shift to 100,000 years ~0.5 million years ago.

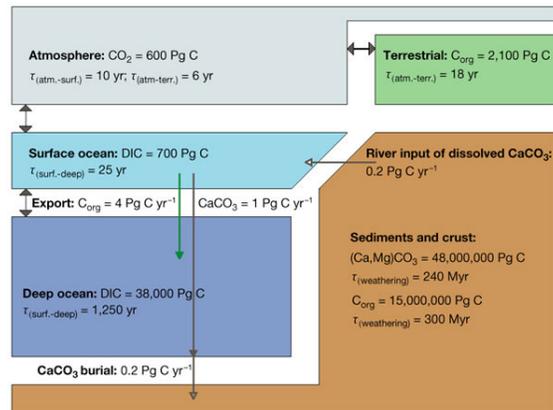
The remarkable record of atmospheric trace gas composition obtained from ice cores shows that the Earth's carbon-cycle was also paced at ~100 kyr. CO₂ rises and fall in step with the changes in temperature recorded in the isotopic composition of the ice [K. Cuffey et al., 2001, Nature]. Although association does not imply causality, it is clear that the changes in CO₂ do produce a significant radiative forcing to climate that is either a direct forcing responsible for the glacial/interglacial climate shift, or more likely acts as a powerful (and positive) feedback on some other forcing. **The glacial / interglacial changes in CO₂ alone exert a direct radiative forcing of about -2 W/m² (vs +1.5 W/m² preindustrial -> today).** In addition, the water vapor feedback will act to amplify this cooling. Most evidence suggests that the carbon signal lags the thermal signal.



In this figure from Cuffey et al., comparison of carbon dioxide and reconstructed Southern Hemisphere temperature, ΔT_H illustrate that strong covariance of CO₂ and temperature using a new proxy for temperature, excess deuterium (see paper for more detail).

Large changes in methane have also been observed, but the forcing appears more consistent with the orbital timescales (particularly 23,000 years) and less driven at 100,000 years. It has been argued that insolation driven changes in the monsoon may be responsible for the changes in methane. The strength of the monsoon, it is suggested, is determined by the instantaneous summer insolation forcing (precession). The most recent instance of summer insolation considerably higher than at present was 10,000 years ago. Much of subtropical North Africa (and indeed LA) were considerably moister at this time. Many dry lake beds of these regions were filled to overflowing [H.-J. Pachur and S. Kroplein, "Wadi Howar: Paleoclimatic Evidence from an Extinct River System in the Southwestern Sahara", *Science*, 238, 298, 1987]. Methane, which is produced biologically in soils saturated with water (and thus anaerobic methanogenesis can occur). Methane concentrations vary between ~300 and 800 ppbv producing a radiative forcing of order 0.5 W m⁻² (CH₄ is now >1500 ppb)

Sigman and Boyle, *Nature*, 2000.



A simplified view of the Holocene (pre-industrial) carbon cycle. Data includes only the reservoirs and fluxes thought to be most relevant for glacial/interglacial variations in atmospheric CO₂. Carbon that exchanges with atmospheric CO₂ on the timescale of glacial/interglacial transitions is stored in a number of reservoirs (given in units of Pg C, or 10¹⁵ g C), as dissolved inorganic carbon (DIC), calcium carbonate (CaCO₃), and organic carbon (C_{org}). For each of the carbon reservoirs, a residence time (τ , reservoir size divided by input or output) is given in relation to important exchange terms among reservoirs, which are indicated by double arrows. Relevant fluxes of C_{org} and CaCO₃ (including 'dissolved' CaCO₃) are indicated by single arrows. It is also informative to consider the fluxes that are excluded from this diagram. For instance, organic carbon burial (which occurs mostly along ocean margins), organic carbon weathering on land and volcanic/hydrothermal CO₂ release are generally thought to occur too slowly or to have the wrong sensitivities to play a major role in the consistent variation of atmospheric CO₂ over glacial/interglacial cycles.

So, how is it possible to drive 30% changes in CO₂ in such a relatively short period of time (few thousand years)? (We are not discussing at the moment the large changes in CO₂ we are forcing now by burning fossil fuels or the much slower, tectonic timescale forcing by alteration of the carbon stored in sediments and rocks). In this case, we have three carbon reservoirs to consider: the atmosphere, the oceans, and the vegetation reservoirs (soil, etc.).

Figure 11-8 from Ruddiman illustrates the various fluxes of carbon in the present climate (Gtons yr⁻¹). The ocean mixed layer is in relatively rapid communication with the atmosphere (and is to a large degree in equilibrium with the atmosphere – today within 30 ppmv despite the large temporal rate of change in atmospheric CO₂). And the atmosphere communicates (via the biosphere) relatively rapidly with the soils.

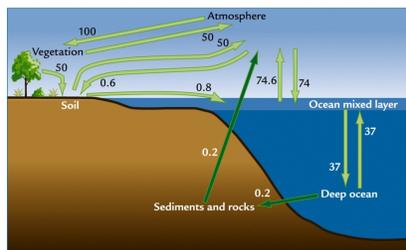
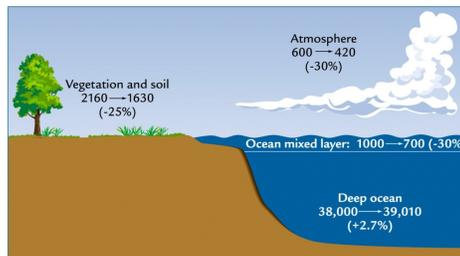
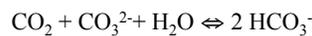


Figure 11-9 from Ruddiman (below) illustrates the estimated changes in these various carbon reservoirs between glacial and interglacial times. It is known from carbon isotopes that the carbon reservoirs on land were (like the atmosphere) depleted during the glacial periods (25 ‰). Terrestrial organic carbon reservoirs are isotopically very light (-25 ‰ $\delta^{13}\text{C}$) whereas the carbon in the oceans is so overwhelmingly inorganic with (~ 0 ‰ $\delta^{13}\text{C}$). The climate was, in general, dryer and less conducive to biosphere growth. The only place this carbon can go on the timescales of interest here are into the ocean (where carbon reservoirs are enormous by comparison - ~ 50 times more than in the atmosphere).



Atmospheric CO_2 is highly buffered by dissolved inorganic carbon ($\text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$) in the ocean. The pH of the ocean is about 8 and most (90%) of the DIC is in the form of bicarbonate, HCO_3^- . Dissolved CO_2 (and H_2CO_3) accounts for only $\sim 1\%$ of the DIC. The driving chemistry for uptake and release of CO_2 from the oceans can be written:



It is surprising difficult to alter the partial pressure of CO_2 over the oceans on timescales where the ocean/sediment system is equilibrated with the atmosphere (1000/10000 yrs). Changes in the physical properties of dissolution of CO_2 (by altering the pH) in oceans can only produce a small change in atmospheric CO_2 between glacial and interglacial times ($\sim 10\%$ of the observed change). CO_2 is more soluble in cold water and with the estimated decrease in the average ocean temperature of 2.5°C during glacial times, atmospheric CO_2 would be driven down by 22 ppmv – (though some more recent estimates suggest perhaps a somewhat larger cooling). Some of this is change is offset by the increasing salinity due to the 125 m decrease in sea level [mean depth is 3600 m]. The 3% change in salinity drives the thermodynamics of CO_2 uptake down 6.5 ppmv – atmospheric CO_2 increases).

Table 1 Atmospheric CO_2 effects of known changes

Condition during the last ice age (as different from Holocene)	CO_2 change (p.p.m.v.)
Terrestrial carbon decrease (500 Pg C)	15
Ocean cooling (5° low latitude, 2.5° high latitude)	-30
Ocean salinity increase (3%)	6.5
Total CO_2 change	-8.5

Sigman and Boyle, 2000

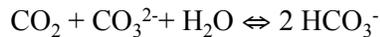
It is somewhat anti-intuitive that low atmospheric CO₂ corresponds with low carbon storage in the terrestrial biosphere. But the key thing to remember is that the atmospheric CO₂ on glacial/ interglacial timescales is overwhelmingly driven by the DIC in the oceans. The CO₂ driven into the atmosphere upon mowing down all the trees will quickly (on geological timescales) be re-equilibrated with the ocean DIC.

Nevertheless, the evidence shows that CO₂ in the atmosphere dropped ~30% (180 G tons C) and the surface ocean, which is in equilibrium with atmospheric CO₂, would be similarly depleted (300 G tons C). With a loss of 180 Gtons of carbon from the atmosphere, ~500 Gtons from the land, 300 Gtons from the surface mixed layer, the conclusion is that ~1000 Gtons carbon was sequestered. Because of the large amount of carbon stored in the deep ocean, this additional carbon corresponds to only a few percent increase.

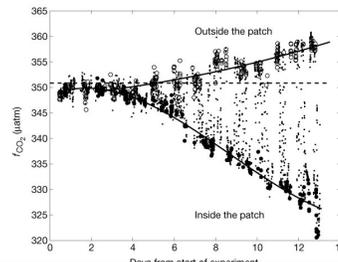
What mechanism could be responsible for driving the carbon into the deep ocean? Wally Broecker has argued that this reflects higher ocean productivity during glacial times. Photosynthesis and organic productivity occur in the surface ocean where both sunlight and nutrients are available. Photosynthesis, written stoichiometrically as $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$, drives inorganic CO₂ into organic carbon that can settle into the deep ocean.

In the modern ocean, photosynthesis is often limited by nutrients, particularly nitrogen and phosphorus. In general, waters in the deep ocean contain high concentrations of nutrients that are released during the decay of detritus organic matter. Thus, it would seem that one mechanism for increased pumping of carbon into the deep ocean would be if increased upwelling of nutrients occurred during glacial times (stronger winds?). On the timescale of interest here, however, the forcing of atmospheric CO₂ by simply increasing the rate of upwelling is very inefficient. Increased upwelling also brings up the carbon that was rained down as organic matter and to first order there is no net change in atmospheric CO₂. In most regions of upwelling, the nutrients (nitrogen and phosphate) are used with perfect efficiency and so increased upwelling simply cycles the carbon (and nutrients) between the deep and the surface more quickly but with little influence on the atmospheric CO₂ on these timescales.

In addition to organic carbon formed in photosynthesis, many organisms build calcium carbonate shells, CaCO_3 (e.g. corals). Cocaliths (primary) and foraminifera (heterotrophs) produce large amounts of calcium carbonate and this carbon often drops to the bottom of the oceans. It is perhaps tempting to think that in forming these shells carbon is being driven out of the ocean system and that this would in turn draw down CO_2 . This is not the case, however. If we look at the expression for the interaction of atmospheric CO_2 and DIC, we see that CO_3^{2-} and CO_2 are on the left of the expression. Le Chatelier's principle tells us that if we remove CO_3^{2-} (decrease alkalinity) we will drive CO_2 out of the ocean. Growing corals increases atmospheric CO_2 . Growing cocaliths and foraminifera can pump carbon into the deep ocean depending on the ratio of organic carbon to CaCO_3 in the falling matter. This ratio is known as the "rain ratio" and in the modern ocean is thought to be ~ 4 .



So, how could the "biological pump" pump faster? One possibility focuses on a few areas of the ocean where upwelled nutrients are not being used efficiently dubbed "high nutrient low chlorophyll" HNLC. Such regions are found in the subarctic pacific, in the equatorial pacific, and perhaps most importantly in the southern oceans. In these regions other factors limit the efficiency of nutrient utilization. John Martin proposed that iron was often a limiting nutrient. Unlike the other nutrients, for use in metabolism, the iron must be either brought into the ocean by rivers or deposited from the atmosphere in aerosol/dust form (see <http://www.whoi.edu/media/iron.html>). Tests of Martin's proposal have been quite spectacular - large ships dumped iron into the HNLC regions and satellite imagery recorded the subsequent bloom. In situ observations show pCO_2 being drawn down. These measurements shown below were taken during an expedition in the Southern Ocean in February, 1999 after iron was added (<http://www-personal.umich.edu/~rstey/Site%20files/science.html>).



If during glacial times, iron was more efficiently transported to the southern ocean (by higher winds and reduced hydrological cycle), increased productivity could occur. Unlike where nutrients are efficiently being used this would draw down CO_2 . The focus here is on the southern ocean because (at least in the modern ocean) this water is in rapid (1000 yr) communication with a huge ocean mass (Antarctic deep water).

A second means of increasing the speed of the biological pump is to globally increase the nutrients in the ocean, possibly by transfer of soil nutrients to the ocean and/or by weathering of the sediments exposed with the decrease in mean sea level. This latter mechanism would also increase the alkalinity and is known as the "Alkalinity pump". If large amounts of coral and other CaCO_3 sediments dissolve, atmospheric CO_2 would be driven down.