

Introduction: Global biogeochemical cycles.

Biogeochemical and tectonic processes on the surface of the earth continuously recycle chemical elements between the atmosphere, the hydrosphere, the biosphere, and the lithosphere. The long-term geochemical cycles are driven by uplift of continents, weathering, erosion, sedimentation, and subduction. Superimposed on these large-scale cycles, there are faster loops that involve smaller reservoirs, including the biota. In the following lectures, we will concentrate on the global cycles of the elements most prominently involved in biological cycles: C, O, S, N, and P (e.g. "Global Biogeochemical Cycles" 1992 Eds. S. S. Butcher et al.).

Within the carbon cycle, one of the most important reservoirs, the atmosphere, is also one of the smallest. This reservoir is important because it influences the radiation balance and the global climate of the Earth. Because of its small size compared to the other C reservoirs, the CO₂ content of the atmosphere can be changed rapidly and is largely dictated by exchanges and biogeochemical reactions occurring within and between the other reservoirs. Exchanges between atmosphere and these different C reservoirs regulate atmospheric CO₂ on many different time scales.

The C cycle can be viewed as a series of nested loops recycling C through the atmosphere at different rates:

- Changes in atmospheric CO₂ on Ma time scales are controlled by tectonically driven exchange of C with the lithosphere. (Lecture 23)
- Changes on millennial timescales involve exchanges between the atmosphere, the entire ocean, the upper sediment layer and the upper crust. (Lecture 23-25)
- Changes on decadal to centennial time scales involve exchanges between the atmosphere, intermediate-depth ocean water, and soil organic carbon. (Lecture 24-25)
- Changes on the decadal to annual time scales involve exchanges between atmosphere, upper ocean, leaf litter, and land biomass. (Lecture 24-25)
- Changes on a seasonal timescale involve the cycle of respiration/photosynthesis of land biomass. (Lecture 24-25)

Control of atmospheric CO₂ on Ma time scales

On very long time scales (10⁶ y), atmospheric CO₂ is controlled by the carbonate-silicate geochemical cycle. The single most abundant reservoir of carbon is that which is buried in sediments and sedimentary rocks, either as carbonate or as refractory organic carbon (Total carbon buried = ca. 10⁵ times greater than C in the atmosphere).

This reservoir exchanges carbon with the atmosphere via:

- Weathering of silicate materials: a process which removes CO₂ from the atmosphere producing carbonate ions and silicic acid which are subsequently buried as CaCO₃ and opal in sediments.

- Metamorphism: a process whereby silicate minerals are formed from subducted carbonate and silica deposited on the seafloor, releasing CO₂ into the atmosphere via volcanic and hydrothermal activity.

Note that there is a negative feedback in this loop. If atmospheric CO₂ increases (e.g. due to higher rates of CO₂ outgassing), weathering rates will also increase, until the rate of CO₂ consumption matches the new rate of CO₂ outgassing, stabilizing atmospheric CO₂.

In addition to carbonate, the crustal C reservoir also contains refractory organic carbon (C_{org}), most of which is finely dispersed within sedimentary rock, with a smaller fraction present as fossil fuel. In contrast to weathering of silicate minerals, weathering of the organic matter dispersed in sedimentary rocks (and burning of fossil fuel) produces CO₂. This organic carbon pool, however, amounts to only one-fifth of the total carbon buried, and % C_{org} in crustal rocks is small. Therefore, the net effect of weathering will be CO₂ uptake. On a long time scale, weathered C_{org} is balanced by burial of refractory carbon in sediments and has little effect on the level of atmospheric CO₂, which is mainly governed on geologic time scales by weathering of silicates and volcanic outgassing.

Because of the very large size of the sedimentary and crustal carbon reservoirs, changes in the rate of weathering or CO₂ degassing by volcanic activities could produce large changes in atmospheric CO₂. When considering the rate of CO₂ uptake by weathering of silicates, we find that the turnover time of atmospheric CO₂ with respect to this process is only:

$$0.055 \times 10^{18} \text{ moles} / 11.48 \times 10^{18} \text{ moles/Ma} = 4,791 \text{ y}$$

So, at the present day rate of continental weathering, atmospheric CO₂ could potentially vary on 1,000 years time scale, due to changes in weathering or outgassing rates. However, because natural variations in these two processes are tectonically driven, they generally change very slowly. Outgassing rates are controlled mainly by rates of seafloor spreading (higher rates of seafloor generation imply higher rates of subduction and metamorphism, leading to increased rates of outgassing), while weathering rates are controlled by the following:

- Surface area covered by shallow seas: more shallow seas result in small continental surface area and lower global weathering rates.
- Atmospheric CO₂: chemical weathering increases with pCO₂ and temperature; this effect produces a negative feedback.
- Continental uplift and mountain-building: higher uplift rates promote mechanical breakdown of rocks, exposing new surfaces to chemical weathering; uplift areas are dominated by easily eroded sedimentary rocks and increased runoff due to topography.

This cycle thus controls atmospheric CO₂ on the Ma time scale. Past changes in the mantle-driven spreading rate of lithospheric plates has been used to suggest higher atmospheric CO₂ during the warm Cretaceous period (BLAG model; Berner et al., 1983, Am. J. Sci 283, 641; Volk, 1987, Am. J. Sci. 287, 763). A higher rate of seafloor generation implies a higher rate of subduction and metamorphism, leading to an increased rate of outgassing, higher CO₂, and a slightly smaller inventory of carbonate rock (because of the large inventory, however, the required decrease in carbonate rock is an infinitesimal fraction of the total). Alternatively, higher

CO₂ during that period could also be the result of widespread shallow seas, lowering the continental surface area and subsequent rates of weathering.

Mountain building in the Himalayas and the Andes and resulting enhanced weathering rates have also been suggested as a possible mechanism for lowered atmospheric CO₂ over the last 5 Ma, which would have contributed to global cooling during that period (Raymo et al., 1988, *Geology* 16, 649). Increased weathering may also explain increased carbonate burial and the deepening of the calcite compensation depth observed in the ocean during the past 10 Ma.

Superimposed on these large secular changes in atmospheric CO₂ driven by tectonic processes, we also find higher frequency variations that do not involve the large C reservoir in the lithosphere.

Changes on multi-millennial timescales

Quaternary climatic variations

Changes in atmospheric CO₂ on 10³ to 10⁵ y time scales are now well documented, at least for the late Quaternary, which is characterized by alternating cold (glacial) and warm (interglacial) periods. Changes in atmospheric CO₂ during the last 400,000 years have been observed by measuring atmospheric CO₂ from air bubbles trapped in ice that has accumulated on the Antarctic continent (Petit et al, 1999 *Nature* 399, 429). High atmospheric CO₂ coincides with warm interglacial periods, while glacial periods are associated with low atmospheric CO₂ concentrations suggesting a possible link between greenhouse warming induced by atmospheric CO₂ and global climate.

Late Quaternary climate cycles result in the waxing and waning of the polar ice caps, which are best documented by the oxygen isotopic composition of calcium carbonate shells produced by foraminifera and deposited on the seafloor (as we talked about briefly in the intro to stable isotopes lecture). As a result of evaporation, water is enriched in ¹⁸O due to the preferential loss of ¹⁶O in water vapor and its storage on continents as glacial ice. During the ice ages (glacial periods), a larger quantity of fresh water was locked in the polar ice caps, resulting in a drop in sea level of about 130 m relative to modern sea level. Seawater in the glacial ocean was thus isotopically heavier (by about 1.2‰) compared to seawater during interglacial periods. Isotopic equilibration between H₂O and CO₂ in seawater, followed by uptake of bicarbonate into foraminiferal shells allows the oxygen isotopic composition of seawater to be recorded as CaCO₃. The oxygen isotopic composition of foraminifera skeletons accumulating in sediments record these systematic changes, with heavy values reflecting glacial periods with large ice caps and light values, reflecting warmer periods with small ice caps.

Spectral analysis of the frequency of these changes reveals that these variations are not random, but occur at well-defined frequencies, with a dominant 100 ka cyclicity, superimposed by higher frequency variations with periods of 19, 23, and 41 ka. These frequencies are also characteristic of changes in the intensity and the geographic and seasonal distribution of incoming solar radiations on the Earth surface, known as Milankovitch cycles (1930), resulting from changes in the Earth's orbit around the sun. These cycles represent changes in:

- The eccentricity of the orbit varying with a 100 ka period.
- The obliquity, or tilt, of the Earth's axis of rotation, changing with a period of 41 ka.

- The precession index, reflecting the wobble of the Earth's axis, changes with periods of 23 and 19 ka.

Support for the involvement of atmospheric CO₂ in climate change on Milankovitch time scales is provided by the analysis of air bubbles trapped in ice cores, which document changes in atmospheric CO₂. The record shows low pCO₂ during ice ages and high pCO₂ during warm interglacials, with abrupt increases (i.e. within a few thousand years) during deglaciation. The ice core data support a possible active role of atmospheric CO₂ in modulating climate changes on millennial time scales (note that change in pCO₂ seems to be dominated by the 100 ka cycle), but do not prove it. The question is whether these changes in atmospheric CO₂ were simply a result of climate change and had little impact themselves on dictating the amplitude of the change, or whether they were important for amplifying the small effect induced by the changes in incoming solar radiation. At the moment, we are not sure. Nonetheless, we need to understand the causes for these changes in atmospheric CO₂ on this time scale based on a mechanistic understanding of the earth system as a whole.

Possible mechanisms for controlling atmospheric CO₂ in millennial to multi-millennial time scales

Changes in atmospheric CO₂ on these timescales must involve the entire ocean, which has a 1,000 y mixing time, and the upper layers of carbonate sediments. All told, there is 60 times more carbon in the ocean than in the atmosphere. As a first approximation, we can divide the ocean into two boxes. On average, the surface box is at equilibrium with the atmosphere and its pCO₂, which is fixed by exchange of C with the bigger deep water box, establishes the pCO₂ of the atmosphere. For a given temperature and salinity, pCO₂ in seawater depends on two variables: total CO₂ (TCO₂) and carbonate alkalinity (CA). It is easy to see how pCO₂ will respond to these variables using the following equation:

$$[\text{CO}_2] = \text{TCO}_2 - \text{CA} + [\text{CO}_3^{2-}]$$

Hence, for a constant CA, pCO₂ (and [CO₃²⁻]) increase if TCO₂ increases. For a constant TCO₂, if CA increases, [CO₃²⁻] also increases, but less than CA, hence pCO₂ decreases. Therefore, the level of atmospheric CO₂ can be lowered by decreasing TCO₂ of surface waters or by increasing its alkalinity.

Controlling atmospheric CO₂ by changing TCO₂ in surface waters:

On the 10³–10⁵ year time scale, the total amount of carbon in the atmosphere/ biosphere/ hydrosphere/ reactive sediment is virtually constant due to the large total reservoir size. Hence, if TCO₂ in the deep water reservoir increases, it must come from the other reservoirs, primarily the surface water and atmosphere (and possibly the land biomass).

To lower TCO₂ in surface waters, we must transfer TCO₂ from surface to deep waters. This can be achieved in two ways, either by increasing export production or by slowing the rate of the conveyor belt circulation.

Can the lower atmospheric pCO₂ observed during glacial periods be the result of a more active biological pump? We could increase the efficiency of the biological pump by either increasing

the nutrient load of the ocean or by increasing surface nutrient utilization in oceanic regions where today nutrients remain in excess in surface water, i.e. HNLC regions.

There is evidence for enhanced nitrogen availability due to decreased water column denitrification during the last glacial period based on the $\delta^{15}\text{N}$ of bulk sediment in upwelling regions (Altabet et al., 1995 Nature 373, 506; Ganeshram et al., 1995 Nature 376, 755). It has also been noted that denitrification in shelf sediments would have been significantly reduced during low sea level stands (Christensen et al., 1987 GBC 1, 97) and N_2 fixation might have been more pronounced due to Fe fertilization of the ocean (Falkowski, 1997 Nature 387, 506; Broecker and Henderson, 1998 Paleoceanography 13, 352). The nitrate inventory of the ocean could thus have increased during the last glacial period. However, if Redfield ratios are fixed, we cannot increase the biological pump by increasing the nitrate inventory independently of phosphate. Instead, the change in nitrate inventory is dictated by changes in the phosphate inventory by adjusting the rate of N_2 fixation. During the last glacial periods, the nitrate and phosphate sink associated with margin upwelling regions at ocean margins (off Mexico, Peru, and in the Arabian Sea) were significantly reduced or eliminated, as a result of higher O_2 concentration in the water column, less water column denitrification, and less P burial. Because water column denitrification is much more important for the seawater nitrate budget than P burial in margin sediments is for the phosphate budget, this oceanographic change tends to increase seawater N/P during glacial periods, curbing N_2 fixation despite higher Fe supply (Ganeshram, 2002 Nature 415, 156-159).

The efficiency of the oceanic biological pump could also be increasing by utilizing nitrate and phosphate present in the surface water of the HNLC's without changing the nitrate and phosphate load of the ocean. One such area is the southern ocean, where nitrate concentrations in the surface water exceed $20 \mu\text{M}$. Increased biological activity in this region, possibly as a result of added Aeolian Fe (Martin, 1990 Paleoceanography 5, 1) could significantly reduce atmospheric CO_2 (Sigman and Boyle 2000 Nature 407, 859).

Can low glacial CO_2 be due to a decrease in the rate of the conveyor belt circulation? There is evidence for an increase in nutrient concentrations in deep waters of the Atlantic during the LGM, suggesting that the renewal time of deep water was longer, which could have contributed to lowering atmospheric CO_2 . However, at the same time, there is evidence for lower nutrient concentration and higher ventilation rates in waters at depth shallower than 2500 m (Boyle 1990 Science 249, 863), where most of the organic matter remineralization occurs. Changes in deep water circulation rates and pattern must be better constrained before a clear evaluation of their impact on atmospheric CO_2 can be made.

Controlling atmospheric CO_2 by changing CA in surface waters

The other way to lower pCO_2 is to increase CA of surface waters. Carbonate alkalinity is controlled by dissolution and formation of CaCO_3 . Dissolution of CaCO_3 decreases pCO_2 , while formation of CaCO_3 increases it. Thus, decreasing surface water pCO_2 requires lowering the rate of formation of CaCO_3 . Plankton growth in surface water can affect surface and atmospheric pCO_2 in two ways. While formation of C_{org} consumes CO_2 to produce organic matter, formation of CaCO_3 shells releases CO_2 . As a result, the efficiency of the biological pump at lowering atmospheric CO_2 will depend not only on the productivity of the ocean but also on the ratio of

carbonate to organic carbon produced (the “rain ratio”), which depends on the type of plankton growing in surface waters. The higher the carbonate to organic carbon ratio, the less efficient the biological pump is in removing CO_2 from the atmosphere into the deep sea.

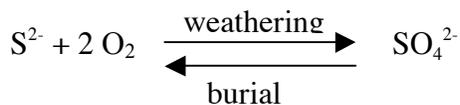
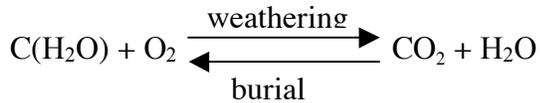
Changes in ocean alkalinity affecting atmospheric CO_2 also occur as a result of changes in the depth of the lysocline in response to changes in nutrient and metabolic CO_2 loading in deep waters due to changes in export flux of C_{org} and/or changes in the rate of deep water ventilation. A decrease in export flux of C_{org} (without changes in carbonate rain rate) or enhanced ventilation of deep waters would increase TCO_2 in surface waters, increase pCO_2 , and lower metabolic CO_2 added to deep waters, thereby increasing CO_3^{2-} in deep water. Such increase in $[\text{CO}_3^{2-}]$ would have produced a deepening of the lysocline and CCD, thereby increasing the amount of CaCO_3 accumulating on the seafloor. If the system was at steady state prior to this event, deepening of the lysocline means that the rate of output of CaCO_3 exceeds the rate of input of Ca^{2+} and CO_3^{2-} . As a result of this excess burial of CaCO_3 , the alkalinity of seawater decreases with a response time of a few thousand years, thereby further increasing pCO_2 . Since excess burial of CaCO_3 also gradually decreases $[\text{CO}_3^{2-}]$ of seawater, the lysocline shoals gradually and the carbonate alkalinity of the ocean decreases, until the lysocline and the CCD are restored to their initial position (if inputs have not changed), but in an ocean with lower CA, which further increases atmospheric pCO_2 (this is called the carbonate compensation effect; Broecker and Peng, 1987; GBC 1, 15). If that sequence of events were responsible for the deglacial increase in atmospheric CO_2 , we would expect to find in the sediment record a carbonate preservation spike associated with the deglaciation, due to the rapid decrease in metabolic CO_2 in deep water and subsequent rise of the lysocline as the system regained steady state. No clear evidence has been found yet for such a spike. Often, one finds higher % CaCO_3 in the glacial sections of cores from the Pacific while higher % CaCO_3 is found in the interglacial sections of cores from the Atlantic.

The actual mechanism controlling atmospheric CO_2 on a millennial time scale has proved difficult to pin down. Many hypotheses have been explored, all of which have fallen short in one way or another (e.g. Archer et al., 2000 Rev Geophys 38, 159). The main reason is probably that there is not one mechanism controlling atmospheric CO_2 , but the changes observed in the ice core result from a global reorganization of the C cycle between glacial and interglacial times, reflecting a complex interplay between ocean circulation, productivity, and chemistry. Most of the mechanisms proposed thus far have probably played a role. It is now for us to distinguish their relative importance and integrate them into a global C cycling model.

Interaction between the C_{org} and S biogeochemical cycles and the control of atmospheric O_2 .

The redox reactions in which the long-term biogeochemical cycles of both C and S are involved have controlled the level of atmospheric O_2 over Phanerozoic times (i.e. past 550 Ma; since recent expansion of multicellular life on the planet).

Over millions of years, the level of O_2 in the atmosphere is controlled by the burial and weathering of reduced carbon (C_{org}) and reduced sulfur (mainly sulfides and pyrite— FeS_2):



O_2 is produced and consumed by photosynthesis and respiration. The turnover rate of this loop is high, but it is not exactly balanced. The rate at which O_2 is produced by photosynthesis slightly exceeds the rate at which it is consumed by respiration, and the difference is accounted for by the burial in sediments of either organic carbon or reduced S and Fe.

Respiration proceeds not only via oxic degradation of organic carbon, but also Fe^{3+} and SO_4^{2-} reduction. Much (but not all) of the reduced S and Fe is reoxidized by O_2 , which becomes the ultimate electron sink. However, a small fraction of reduced Fe and S gets buried, along with the refractory organic matter.

O_2 is consumed during weathering of sedimentary rock due to the oxidation of refractory organic carbon, reduced S, and reduced Fe. Because it takes much more oxygen to oxidize one mole of C_{org} or reduced S than to oxidize one mole of Fe^{2+} , oxidation of refractory organic C and reduced S in sedimentary rocks accounts for 60% and 30%, respectively, of the total O_2 uptake during weathering.

The O_2 that accumulates in the atmosphere is the oxidant equivalent of the amount of reduced S, C, and Fe buried.

A simple equation that can thus describe the rate of change of $[O_2]$ in the atmosphere:
 $d[O_2]/dt = P - R - W$, where P is photosynthesis, R is respiration, and W is weathering.
 $P - R = B$, where B is buried reducing equivalents.
So, $d[O_2]/dt = B - W$. At steady state, $d[O_2]/dt = 0$ so $B=W$.

If the system is perturbed, $[O_2]$ increases when $B>W$ and $[O_2]$ decreases when $B<W$.

Changes in weathering rates and burial rates are driven by tectonics (and thus depends on land topography, depositional basins, etc) and thus are very slow, controlling $[O_2]$ in the atmosphere over millions of years.

The reason why it is the slow lithosphere cycle which controls the O_2 level of the atmosphere rather than the fast biological cycle is that the lithosphere is the only reduced C and S reservoir which is large enough to significantly affect the large amount of O_2 present in our atmosphere. The amount of carbon present in the biosphere is orders of magnitude smaller than what is buried in the lithosphere. Should the biomass be entirely oxidized, it would not significantly change the $[O_2]$ of the atmosphere.

Can past changes in atmospheric O_2 be deduced from the geologic record?

Berner (1989, *paleo3*, 75, 97) has attempted to reconstruct past changes in atmospheric O_2 using changes in the C isotopic composition of carbonates and the S isotopic composition of sulfates in evaporitic rocks of known ages.

As we've learned, there are two stable isotopes of carbon ($^{12}C = 98.89\%$ and $^{13}C = 1.11\%$) and four stable S isotopes ($^{32}S = 95\%$, $^{33}S = 0.76\%$, $^{34}S = 4.22\%$, and $^{36}S = 0.014\%$). ^{12}C is incorporated preferentially during photosynthesis, so that organic C has a lower $^{13}C/^{12}C$ ratio than the inorganic carbon pool. Likewise, ^{32}S is preferentially reduced during sulfate reduction, so that sedimentary pyrite has a lower $^{34}S/^{32}S$ ratio than sulfate.

The $\delta^{13}C$ of organic matter is negative (-10 to -30 permil), while that of carbonate is close to zero (the std used to define $\delta^{13}C$ is a marine carbonate). The $\delta^{34}S$ of pyrite is also negative (0 to -40 permil), while that of sulfate in the modern ocean is +20‰.

Because the total amount of ^{13}C , ^{12}C , ^{34}S , and ^{32}S on the Earth's surface is constant and most of it is present in the lithosphere, the higher the fraction of C buried as organic C and the higher fraction of S buried as pyrite (i.e. the higher the O_2 level in the atmosphere), the higher the $\delta^{13}C$ and $\delta^{34}S$ of DIC and sulfate present in seawater. Past changes in the $\delta^{13}C$ and the $\delta^{34}S$ of seawater are recorded in carbonate and sulfate minerals produced during evaporite formation. Thus, we can deduce how much reduced C and S were buried at certain times in the past, from which changes in the atmospheric O_2 concentration can be estimated using the isotopic composition of sulfates and carbonates in evaporates.

For example, the high $\delta^{13}C$ found in carbonates deposited during the Permian and Carboniferous suggests that a larger amount of organic carbon got buried during that period. On the other hand, the low $\delta^{34}S$ of pyrite produced during the same time period suggests that relatively little pyrite was produced and buried. While increased C_{org} burial would tend to increase atmospheric $[O_2]$, the decrease in pyrite burial would tend to decrease it. In an attempt to quantify the amount of reduced C and S buried and the level of $[O_2]$ back in time, a series of box models have been developed [Garrels and Lerman, 1984; *Am. J. Sci* 284, 989; Berner, 1987 *Am J. Sci*, 287, 177]. The results of these models indicate that, as expected, the organic C burial rate was much larger during the Permian and Carboniferous. In addition, because of the lower rate of formation and burial of pyrite, the C/S ratio of the sediment produced during that period was much higher. The increased rate of C_{org} burial has been attributed to the rise and spreading of vascular plants, which were growing and decaying in vast marshes on the Pangea supercontinent.

In the modern ocean, we find a good correlation between % C_{org} and % reduced S in sediments deposited under oxic conditions. This is because the amount of pyrite produced in sediments depends on the rate of sulfate reduction, which is primarily regulated by the rate of burial of metabolizable organic matter. In freshwater systems, the C/S ratio is much higher and % S is much less correlated to % C_{org} because pyrite formation is not limited by organic carbon input, but instead by the supply of sulfate, which is low in freshwater environments.

C/S was very low during the early Paleozoic. Low C/S ratios (and total lack of correlation with C_{org}) are characteristics of euxinic conditions, i.e. sediment deposited in anoxic water columns (e.g. modern Black Sea). In this type of environment, neither C_{org} nor sulfate is limiting pyrite formation. Instead, it appears to be limited by the availability of reactive Fe. Low C/S ratios during that period thus suggest more widespread occurrence of poorly ventilated basins. The comparatively low C_{org} burial rates during that period were probably due to the fact that marine organisms were dominating, producing much more labile organic matter than vascular terrestrial plants.

Based on this model, it would seem a simple matter to calculate changes in O_2 with time, as $d[O_2]/dt$ is simply the difference between the rate of burial of reduced C and S minus the rate of weathering. The problem with this approach, however, is that it amounts to subtracting two large and uncertain numbers, so that the calculated O_2 variations are very large and meaningless. We know that although $[O_2]$ may have changed significantly, it could not have changed by more than 50%. At very low O_2 concentrations, higher forms of life cannot survive; at high concentrations, biomass burns readily. Calculation of subtler changes in $[O_2]$, which may have occurred in the past requires more sophisticated modeling approaches.