Carbon Crib Sheet

David Archer: Global Carbon Cycle (2010)

Cooke 11/15/13

Resevoirs, units & conversions:
1gC = 3.7g CO_2

1 Gton C in atmos = 0.5ppm

Atmos now = 780 Gt C. (390 ppm)

living carbon on land = 500Gt

Soil 1 m, soil carbon pool = 1500 Gt

Oceans = 38,000 Gt C
- most C is carbonic acid H_2CO_3
- bicarbonate ion HCO_3^-
- carbonate ion $CO_3^=$
- conversions between these takes only change in PH. Most is bicarbonate, concentrations of others regulated by pH of saltwater.

Sedentary rocks contain most of Earth's carbon as limestone ($CaCO_3$, calcium carbonate) and organic (reduced) carbon as goo called Kerogen.

5000 Gt available as coal
200Gt as each of gas and oil

1 barrel oil = 100kg C, = 8000 moles
British Petrol. Inst => 125Gt oil left in ground = 1258 billion barrels
Gas, @ 1 atmos, 25deg C, 1 mole gas = 22.4 liters, 0.02245 m^3 = 0.8 cubic ft.
British Petrol inst, 185 trill cubic meters = 100Gt C as gas.
1 cubic ft gas = 1030 BTU. 1 BTU - 1.06 kilojoule

Half of CO_2 degassing is in mid-ocean ridge vent fluids. At present $CaCO_3$ is accumulating on seafloor faster than it is being subducted. $CaCO_3$ collects in shallower and mid depth oceans (Atlantic) and decomposes under higher pressure.

How much $CaCO_3$ subducted goes into mantle and how much is degassed? unknown. Stronger $CaCO_3$ subduction has occurred in the Theys Sea would release more $CaCO_2$ and warm the earth.

Pacing of hothouse and icehouse is 10's millions, determined by plate tectonics etc.

Heavy C is C^{13}, C^{14} is unstable. "$\delta^{13}C$ = -20%o in a compound" means that the ratio of C^{13} to C^{12} is 20 pro mille less than in a reference compound. Organic C is light because photosynthesis prefers C^{12}.

Oxygen has 3 stable isotopes, O^{16}, O^{17} (trace) and O^{18}. Evaporation of water favors the light isotope, and rain has δ^{18} O = -50%o. Removing water from ocean to form ice sheets makes water heavier, and looking at heavy O in $CaCO_2$ deposits during glacial max gives proxy measurement of termp...(its complicated).

Weathering

On million yr timescale, Carbon enters atmos by degassing and volcanoes, and is removed from atmos by weathering. $CaSiO_3$ is the simplest formula for igneous rock (real rocks have more stuff). The Urey reaction is the basic weathering reaction

$$CaSiO_3 + CO_2 \leftrightarrow CaCO_3 + SiO_2$$

The Urey reaction can be simplified by leaving off the SiO_2:

$$CaO_2 + CO_2 \leftrightarrow CaCO_3.$$

Carbon is recruited from the atmospheric CO_2 and ends up in limestone. The weathering thermostat works as follows: if temp rises, there is more rainfall, higher vapor pressure of water and higher rate of weathering. CO_2 is put into the atmosphere by volcanoes and hot spring de-gassing. These two processes set the earth's temperature on geologic scales. If more CO_2 were added, temp would go up, accelerating weathering, until rates of injection and removal balance - at higher temp. Mutatis mutandis if CO_2 were removed. The set point is determined by these rates of adding and removing atmospheric CO_2. Increase (decrease) degassing, the temp. rises (falls). It takes hundreds of thousands to reach equilibrium.

PETM Paleocene Eocene Thermal Maximum.

55 million yrs ago, +- 100,000 yrs duration.

Isotopically light C is from decomposition of organic carbon (set by a single enzyme, rubisco, which has changed little, makes photosynthesis prefer light C), isotopically heavy C is from weathering of $CaCO_3$. .

PETM was initiated by sudden release of isotopically light carbon, making average C lighter, $\delta^{13}C$ = - 2.5%o. How much CO_2 was added? It depends on source; it would take more biological carbon at isotopic composition of -20%o to generate -2.5$\%_o$ than it would take methane, which has isotopic signature of -60%o.

Methane hydrates in ocean sediments? 2000GtC from methane hydrates would suffice. However, a release of 2000GtC, equlibriated with ocean and $CaCO_3$ stat would raise atmos from

600ppm to 700ppm. [2000GtC => 1000GtC ppm => (after $CaCO_3$ equlibriation, few millennia, is about 10%, p.64]. Warming of 5^oC inferred from oxygen isotopes, => climate sensitivity of 30^oC???

Other option, sedimentary organic C oxidized to CO_2 as sea levels fell, or peat deposits in soils burned or decomposed?, or cs higher in the Paleocene?

PETM acidified ocean, dissolved $CaCO_3$ and left clay deposits instead of limestone, amount dissolved suggests that carbon slug was bigger than 2000Gt C. $\delta^{13}C$, O^{18} recovery was order 100,000 yrs. confirming weathering thermostat.

Snowball earth

600 million yrs ago, ice almost to equator – once ice to 30^o latitude, runaway snowball occurs. Weathering stopped removing CO_2 from atmos. degassing continued, building up CO_2. Lots of CO_2 were needed to melt ice, but then there was a rapid flip to hothouse. => lots of weathering, "cap carbonate" deposits above glacial deposits. banded iron Fe^{2+} formed as ice isolated ocean from oxygen.

Biosphere

Plants use CO_2 in 2 ways, Old photosynthesis process (400 million yr old) : C-3, needs 200ppm. New process C-4 (30 million yrs old) needs only 10ppm. (names come from 3 or 4 carbon-sugar molecules). C-4 is grasses. Biosphere will last 1 billion yrs.

Oxygen homeostat is not so well understood. Animals use O to burn organic carbon. Some bacteria can burn reduced carbon wo oxygen. In geologic times, O has reached twice current concentration. Huge dragonflies in Cretaceous testify, they get oxygen not from circulation but from diffusion. Deep ocean went anoxic in PETM and Cretaceous Tertiary (K/T) boundary (killed dinosaurs, 65 million yr ago.). Largest extinction event was 255 million yr ago, end of Permian, cause unknown.

Relation between weathering CO_2 and O,. Fossils fuels is example of organic C perturbing CO_2 thermostat. PETM another example. Organic C burial driven by accidents of continental geometry, eg shallow seas. If Earth began burying more organic C, CO_2 concentration would go down until rate of weathering slowed enough to balance.

Photosynthesis is basically $CO_2 + H_2O$ + energy -> CH_2O [form of reduced (=more electrons) carbon] + O_2. Animals run the reaction the other way when they burn organic carbon for energy. To build up O_2 in atmos, the organic carbon must be sequestered, Peat deposits preserve C for thousands of yrs, but ocean sediments is the main storage. At current rate of organic C burial, O in biosphere would double in 2 million yrs. Long term burial of organic C must balance oxidative weathering of sedimentary organic C.

Isotopic composition of organic carbon and $CaCO_3$, their ratio is quite stable 4:1. sulfur and iron undergo similar redox reactions, at times when organic (reduced) C is high, reduced sulfur tends to be low, offsetting the net O_2. This is again an atmos oceanic O regulating mechanism.

ICE AGE Carbon cycle.

Ice sheets are an anomaly in Earth's history. Current icehouse began with Antarctic ice sheet formation 35M yr ago. Ice sheets in Northern hemis began 3 M yr ago. Excess land in N hemis drives glacial climate cycles. Initiation is with Milankovich cycles, wobbles in E's orbit. Changes in insolation at solstice at 65^{o}N seems to drive. Glacial climate state is tippier than inter-glacial. Greenland flips on 1000 yr cycle with abrupt warmings calld Dansgaard-Oeschger events, punctuated by periodic collapse of Laurentide ice sheet, called Heinrich events.

Nucleation of icesheets is triggered by week insolation in N Hem in summer. Once nucleated, Ice sheets persist until big enough to melt at the base, becoming vulnerable to warm-trigger sunshine leading to collapse.

CO_2 in 1750 was 280 ppm. in last interglacial, 120,000 y ago, also 280 ppm. CO_2 rises and falls with E temp and SL. Half of glacial forcing is albedo. Orbital variations in insolaton is anti symmetric N and S, yet N seems to drive E temp, because N hem has land to make ice sheets. Natural CO_2 conc takes 1000 y to change, = how long atmos and ocean take to reach equilbrium. Ice cores suggest that CO_2 changes were driven by changes in Ocean atmos partitioning. We are now forcing CO_2 in atmos via fuel emissions. In last glacial maximum, C in atmos was 200ppm, increased in 10,000y to 260 ppm.

Gas in Antarctica ice shows that temp in Antarctica start rising about 800 y before CO_2 concentr rises. Transitions both took 10,000y. Carbon isotopes show that change in CO_2 was not driven by release and uptake of organic C. δ^{13} C of organic is about -25%o. If C drawdown in glacial times was due to Organic C, then C left behind in Atmos would be isotopically heavier. Instead δ^{13}C in CaCO3 produced in deep ocean in glacial times is LIGHTER by -0.25%o. => there was as release of organic C, not uptake. This would require release of 500Gt of -25%o (organic) carbon. This would increase C in atmos, after ocean equlibriation, by 25ppm. SO we have to explain disappearance of 80 + 25 ppm. Answer must lie in inorganic C cycle, ie ocean.

Consider explanations:
-pH chem
-biological pump
-other pumps

Gasses are more soluble in colder water than warmer. Raising water temp 1^{o}C raises partial pressure of CO_2 by 4%. When oceans warm, they push out CO_2. Heat flux in ocean drives large changes in CO_2 transfer atmos - sea.

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C and pH geochemistry

partial pressure of CO_2 (p CO_2) in atmos = pressure of atmos × fraction C. First order, ideal picture, => chemical availability (activity) is proportional to concentration. in Atmos = partial pressure, in water, moles CO_2 / liter. Henry's Law, after equilibration, conc CO_2 in solution is proportional to conc. in atmos. One also speaks of pCO_2 of surface ocean, as being the atmos pCO_2 with which it would equilibrate.

$K_H = pCO_2 / CO_2$(aqueous)

However, reactions w other chems caused by large changes in concs cause deviations => "apparent" activity constants" which hold in specified conditions, esp salinity and temp.

CO_2 combines with H_2O to form carbonic acid

$CO_2 + H_2O \leftrightarrow H_2CO_3$.

H_2CO_3 stands for the conc of CO_2 in aqueous phase. Acids release protons H^+ thereby lowering pH of solution, defined as -$\log_{10}$ (H^+ activity, ideally concentration). Carbonic acid can release 2 H^+'s:

$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

$HCO_3^- \leftrightarrow H^+ + CO_3^=$.

These reactions are fast enough that equilibrium always applies, so ([*] = conc):

$[H_2CO_3] / [H^+] [HCO_3^-] = K'_1$.

$[HCO_3^-] / [H^+] [CO_3^=] = K'_2$.

the K's are first and second dissociation coeffs for carbonic acid. these reactions form the chemical buffer that controls ocean pH and allows ocean to store more CO_2 than it would otherwise. Since H^+ reservoirs are small, neglect these and summarize reaction as

$CO_2 + CO_3^= + H_2O \leftrightarrow 2\ H_2CO_3^-$.

This reaction equilibrates in 1 min. adding one element shifts the concs. in appropriate direction: adding CO_2 lowers $CO_3^=$ and H_2O and increases HCO_3^-. the amount of CO_2 that seawater can absorb is limited by amount of $CO_3^=$. This buffer allows seawater to take up 10 times more CO_2 than under Henry's ideal law. 90% of dissolved CO_2 reacts with $CO_3^=$ to form HCO_3. $CO_3^=$ decreases with acidification, affecting marine life through the reaction

$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^=$

which dissolves sea shells.

pH of surface has decreased by 0.1 H units due to CO_2 emissions.

Total CO_2 , $\Sigma CO_2 = [CO_2] + [CO_3^{=}] + [HCO_3^{-}] + [H_2CO_3]$ (moles per liter),

this is conserved under mixing (pH is not). Also need alkalinity to consume H^+. Tabulated by adding electrical charges carried by carbonate buffer species:

$alk_c = [HCO_3^{-}] + 2\,[CO_3^{=}]$ (2 is for charge minus 2).

ΣCO_2 and alk are state vbls computed to model carbon uptake in seawater, since they are advected and mixed. To know whether the ocean is degassing, must know pCO_2 of surface ocean, which it calculates from alk and ΣCO_2.

the effect of pH buffer chemistry shows in way in which surface water pCO_2 changes as CO_2 is added. if $CO_3^{=}$ is high (depends on ΣCO_2 and alk), adding CO_2 produces small effect on pCO_2, but as more CO_2 is absorbed and $CO_3^{=}$ goes down, change in surface water pCO_2 is stronger.

Ocean carbon cycle models find that if ocean surface temp rises by 1^oC, the CO_2 conc. in atmos increases by 4%. in line with simple bucket experiments.

Average temp of deep ocean today is 2^oC, in glacial max it was about -1^oC, close to freezing point of dense salt water, -2^oC.

"It appears that the temperature effect on CO solubility is well enough understood that the largest CO_2 change, the 80ppm transition from the glacial world to the interglacial, cannot be accounted for just by the temperature effect on solubility alone. The deep ocean warmed at the end of the glacial time by about 2,3 ^oC, enough to drive 20-30 pp of CO_2 rise, but not the entire 80ppm" (p.79) (actually 80 + 25ppm).

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Biological pump

Plankton in ocean absorb CO_2 from surface water and die and sink. this lowers CO_2 in atmos. if Phytoplankton were dead, CO_2 in atmos would rise in a few centuries (ocean atmos equilib time), then go back due to weathering. Phyto take up C and nutrients in stable ratio, **Refield Ratio.** C:N:P = 125:36:1. nutrients N, P are limiting, so nutrient rich waters have more CO_2. Carbon travels with nutrients through the biological pump, @ 10% of $CO_{2.}$ this is called metabolic carbon. Net effect of bio pump is to concentrate metabolic carbon in deeper waters. Thus bio pump tends to lower pCO_2 in surface, $CaCO_3$ increases by removing $CO_3^{=}$ from surface. the bio pump is greater and net effect is to lower pCO_2.

Other pumps

Iron availability can have impact on glacial C cycle, Iron goes to surface water as wind blown dust. More in glacial times would stimulate phytoplankton. Simple C cycle (box) models of ocean initially indicated that bio pump could draw down atmos CO_2 to 200 ppm or lower. CGMs are less sensitive to changes in bio pump. Ocean is 3D and flows, temp and nutrient concs are modeled. Simple models allow phyto to capture upwelling nutrients more efficiently, in flow models, phyto is not at surface so long, less efficient. Bio pump not able to explain 80-100 ppm drop in CO_2. efficiency of bio pump is encoded in $\delta^{13}C$ in $CaCO_3$ from foraminifera. a bit stronger in glacial max, but not enough to explain drawdown.

Southern ocean silica belt : Antarctica has belt of sediments composed mostly of shells of diatoms, algae with shells made of silica (SiO_2). In glacial max, this "polar belt" moved north. Circulation of southern ocean changed in glacial max, causing diminution in exchange surface and deep ocean.

Ocean re-arrangement: some think CO_2 drawdown was due to changes in circulation. There appears to be a salty stagnant blob of water in the deepest southern ocean during glacial max. Models reproduce this if they make enough sea ice in Antarctica that winds blow them out. Can carbon go to the blob? If blob got more nutrients it could draw down more metabolic CO_2. but not enough.

If ocean stored CO_2 as bicarbonate, there would have to be a change in pH. *weathering and coral reef hypotheses*, both fail as global burial rate of $CaCO_3$ is stable. Burial of $CaCO_3$ may depend on "rain ratio" of organic C and $CaCO_3$. when organic C decomposes, it releases CO_2, an acid which dissolves $CaCO_3$. Models predict that change in rain ratio on sea floor could affect ocean pH and ultimately atmos CO_2.

"There is no single satisfactory explanation for the positive ocean carbon cycle feedback responsible for the glacial and interglacial atmos CO_2 cycles. The CO_2 that was not in the atmos during glacial times must have been in inorganic form in the ocean, the carbon isotopes tell us. ..we are to compose an explanation out of a composite of several different mechanisms."(p.101) This is unsatisfactory because the relationship between ice volume, temp and CO_2 is so strong in the data, it shouldn't depend on serendipities.

"The unfortunate implication of our ignorance is that we are unable to predict how the ocean carbon cycle will eventually respond to the provocation of our fossil fuel CO_2 release. Some of the proposed mechanisms to explain the past, such as the temperature dependence on CO_2 solubility, would extend in the warming direction, continuing to raise atmos CO_2 as the temperatures rise beyond the warmest temperatures of the natural interglacial intervals. If on the other hand the explanation were that the ocean shifted to higher pH in response to cold climate, it seems plausible but not at all certain that it could shift slowly toward the acidic in a warmer world driving CO_2 into the atmosphere....also there could be carbon cycle changes in the future, such as decomposing frozen peats or methane hydrates, which played no major role in the glacial cycles", (p.102)

Carbon cycle today

Humans emit ca 10GtC per year. 100 times larger than the natural carbon flux from the solid earth to atmos, the degassing of CO_2 etc. Atmos CO_2 is rising at 2ppm/yr. this represents about 4 GtC per yr. Where is the remaining 6GtC going?

Ocean: we make lots of measurements of surface chemistry of ocean. Flux from Ocean to atmos is the difference in the pCO_2 between the air and water. "There is considerable uncertainty, perhaps 50%, in the exchange rate, even if the chemical concentrations and the wind speed were known perfectly....there are huge variations in the pCO_2 of surface waters around the world, driven by temperatures and plankton growth. "(p113). To drive ocean uptake of 1GtC as CO_2 would require that the global average surface ocean pCO_2 be about 2ppm lower than the pCO_2 of atmos. This means the surface ocean pCO_2 has to be known with a few tenths of a ppm in order to know the global flux into the ocean. Overall back-forth exchange fluxes of CO_2 atmos-ocean are about 90GtC/yr. Current best estimate is 2GtC, in CO_2 , from atmos to ocean per yr. Plankton ecology is badly modeled currently. Not too confident about the future. Uptake in deep oceans depends on currents and mixing. Every yr the ocean takes up 2 GtC, about 1/3 all human emissions.

If that is true, we still miss 4GtC/yr....this is the land "missing sink". (NB "Long Thaw" says 2 GtC is going to land, though we dont know where, thus missing sink is only 2GtC)

Land uptake: deforestation makes up 1.5 GtC/yr of the 10GtC/yr. In early Industrial revolution, deforestation outpaced land sink, raising CO_2 in atmos. In the last 50 yrs "natural carbon sink has kicked in", balancing net emissions, In last few yrs it appears that land surface overall takes up 1 - 2 GtC/ yr. "But it has proven impossible so far to actually lay hands on this carbon. "(118). If Siberian tundra is a carbon sink because of longer growing season...then CO2 concs in air will decrease a bit as air blows over tundra ("**atmos inversions**") . This points to sink in high northern latitudes. Also measure CO_2 conc in tower as function of vertical wind gradient - "**eddy correlation method**". **CO_2 fertilization** is another possibility. best models include nitrogen limitation and predict weaker fertilization than initially thought. Other possibilities: longer growing season, reforestation, acid rain is fertilizaing the plants. Fire suppression. "Neither the mechanism nor the location of the missing carbon is known for sure"(121).

Future feedbacks

Reasons to worry: that land could turn source: Conc. of organic C in soils is a strong function of temperature: leaves etc decompose more quickly, rates double with 10^oC warming. Soil carbon could change dramatically in high latitudes where peat deposits are currently preserved in permafrost. Lakes, liquid water meets frozen peat => methane and CO_2 . Methane hydrates in Ocean also worry. They have huge potential to alter future climate on millennium timescales.

Ocean overturning carries surface water with CO_2 to deep ocean. This is driven by very dense waters in high latitudes. Temps in high latitudes will rise, rainfall will increase, leaving surface waters fresher, warmer, less dense. This could result in stagnation, lasting centuries, impeding transport of CO_2 into deep ocean. "Accelerating rise of atmos CO_2 tends to drive CO_2 invasion into the ocean more quickly. Counteracting this is depletion of the buffer chemistry of surface water. In general doubling the CO_2 halves the $CO_3^=$ in seawater, halving the ability of seawater to absorb more CO_2 . Higher atmos CO_2 , the weaker the Ocean buffer becomes.

If the unidentified positive feedback in glacial max raises its head, CO_2 airborne fraction could be higher than current models predict.

Methane

Methane CH_4 is more powerful GHG than C because of lower band saturation: as more of a chem is added to the atmosphere, its main absorption frequencies get used up and no more infrared radiation (IR) at those freqs gets through, then the lower frequencies start filling up etc. So the amount absorbed is proportional to the amount of chem already there. There's much more CO_2 than CH_4 .

Most methane in sediments comes from organic carbon, two pathways, via fresh and salt water. Biogenic methane is light -60%o. In Ocean, methane is in frozen in calthrate or hydrate. Ocean hydrates are poorly known but we guess thousands of GtonC.

"The arctic shelf of Siberia may be a special case. The water column is colder than the global average, so hydrate can be found in water as shallow as 200 meters (as opposed to 500-700 meters elsewhere). The temperature change in the arctic is amplified by the climate feedback due to melting the ice, so that the Arctic has been warming much faster than almost any place..."(161). re methane bubbles in Norway and Siberia; "the overall source of methane from this and all other "geological" sources of methane are small relative to the sources from agriculture and the fossil fuel industry, and its not certain whether the observed methane fluxes are new or have always been there"(161).

"The conclusion we come to is that the natural carbon cycle is a wild card, as large an uncertainty as that of our own CO_2 emissions." (p20)