Paleoclimate – Solar System Evolution and Snowball Earth

Let's start by looking at the past history of climate. Over the past 30 years or so we've obtained more new information about past climates than all we had prior to this time, mostly because of paleoclimatic studies - studies using various natural recording systems to provide estimates of past climate variables. There are many of these, but we are going to focus in the beginning on the ocean cores and ice cores.

Before we get into that, it's useful to look at this diagram from Crowley(1991), which shows the geologic ages. It is very difficult to read the geological literature, because times are given names; Eras, periods, and epochs. There are at least 4 systems of naming conventions. They almost never give dates. This is because most of the periods were named before dating was possible or accepted. Most of the detail is at the back end in recent times, because we have less information as we go back in time. Many of the names come from the types of life that are in evidence in sediments, or information about the climate then. Some good resources are available on the web for buffing up your knowledge of the history of life or earth or geology in general. For example the Museum of Paleontology at UC Berkeley has a great site at: http://www.ucmp.berkeley.edu/ Here you can learn about various ages in more detail than can be presented in the diagram in GPC. You can learn about the three kinds of life archeans, bacteria and eukarotes, and lots of other useful stuff.

Solar System Evolution

Earth formed out of debris in the solar nebula when the solar system formed. The atmospheres of the inner planets appear to be secondary ones, that were outgassed from volatiles trapped inside the solid earth. The solar constant has increased about 30 % since the formation of the Solar System because of the increasing density of the sun, as the lighter hydrogen fuel is gradually fused into helium. Heavier elements, gives greater density, gives higher core temperature, gives a higher burning rate. It is one of the interesting problems to explain how the Earth's climate could have stayed warm with the TSI decreased by 30%. It has been common to assume that Earth's climate has remained warm since the beginning of life, very early in Earth history. Generally, to keep Earth warm with a weaker Sun one assumes that a lot more greenhouse gases were in the atmosphere. Explanations usually involved carbon cycle.

Recently, the idea that Earth was never frozen over have been shaken by evidence that the Earth was ice covered in its past history, during the neoproterozoic (1.0 billion to 544 million years ago). This idea was first raised by Harland(1965) who noted that geological evidence indicated that ice was present near sea level at tropical latitudes on many continents apparently simultaneously. The paleolatitudes, which are based on magnetic inclinations in rocks, and the simultaneity of these events were sufficently uncertain that the proposal was not taken to seriously. Geologists have become more confident of the paleo-latitudes and the timing, as time has passed.

Another problem was to explain how the Earth could have emerged from an ice-covered state if such a state had ever existed. Once the planet is covered with ice, the albedo is sufficiently high that it gets really cold, and it takes a very large forcing to put it back into an ice-free state. The way out of the 'snowball Earth' state was suggested by Kirschvink(1992), who noted that, because Earth has active plate tectonics, carbon dioxide would continue to be put into the atmosphere, even if the Earth is ice covered. If the Earth were ice-covered weathering and photosynthesis would both cease, and the carbon dioxide released by tectonism would stay in the atmosphere and gradually build up. If carbon dioxide it built up to about 0.12 atmospheres, then that would be enough to rather suddenly melt all the ice and heat up the planet (Caldeira and Kasting 1992).

After the CO2 reached the critical level and the climate warmed again, there would be very high levels of CO2 in the atmosphere, perhaps 350 times as much as today, and it would begin to sediment out rather rapidly. Chemical weathering and the flow of carbonate into the ocean start as soon as the land ice melted, rain began to fall and weathering commenced. In the geologic records for this periods are found tropical glaciations capped with a thick layer of carbonate rock, that suggested a glaciation followed by heavy deposition of carbon into carbonate rock. Moreover, the 13C abundance varies across the layer of glacial detritus marking the glacial age (Hoffman, et al. 1998). Below the glacial sediments the 13C is higher and above the glacial sediments it is lower. We assume that stable carbon isotopes come out of volcanoes in the form of CO2 in a fixed ratio of 1% 13C and 99% 12C. We assume they are taken into inorganic carbonate rock by chemical processes in the proportion that they exist in the atmosphere. Biological processes, such as photosynthesis, prefer the lighter isotope of 12C. Because biological processes leave enriched 13C behind in the ocean water, the 13C in inorganic carbonate rock is elevated when biological uptake of carbon is active and depressed when biological uptake of carbon is reduced. One can infer that perhaps biology was inactive during the time that the carbonate layer was lain down, or more likely that CO2 in the atmosphere was so high that inorganic sedimentation dominated carbon burial, leaving lowered 13C in the inorganic sediments. The idea is that the inorganic sedimentation of carbon was so strong that biology could not make a dent in the isotope ratio.

Also of importance to this idea of the Snowball Earth is the existence of banded iron formations during the neo-Proterozoic(Kirschvink 1992, Kirschvink, et al. 2000). Many of these were lain down earlier in Earth history at the onset of large amounts of oxygen in the atmosphere. The idea is that the oceans became anoxic under the sea ice. The lack of oxygen allowed large amounts of iron cations to be held in solution in the ocean. When the ice melted and the ocean became oxygenated again, the iron sedimented out in the form of iron oxide (rust) giving rise to banded iron formations in an oxygen-rich world.

The 13C ratio declines for a short while before the ice age, which suggests a cooling period during which biological productivity decreased. So we are left with a plausible argument that an ice age ensued because of low CO2 combined with low solar irradiance and continental positions. One idea is that if the continents were largely in low latitudes, then an ice age in high latitudes could ensue without reducing the weathering that keeps CO2 levels down. With continents in high latitudes, there is a negative feedback whereby glaciation on the land reduces the rate of weathering, which then elevates atmospheric CO2, which warms the climate. Low solar constant and low latitude continents, may have allowed the ice to reach the tropics (snowball Earth), which shut down most of life, although the simple life forms extant then could have survived in refugia, such as around hot springs or volcanoes, or simply because they were incredibly tough. Lots of life exists on glaciers now. However, because weathering was also shut down by the weak hydrologic system, the CO2 in the atmosphere gradually built up over time until it was sufficient to warm the tropical temperature above the freezing point, even with an ice-covered surface. Once this happened the ice would melt and a rapid transition to a very hot climate would ensue. The snowball ice age would last for an estimated 10 million years. These huge fluctuations in global mean surface temperature could drive big changes in the evolution of life, since they are so large and last long enough to project onto the time scale for evolution, whatever that is.

Ocean Sediment Cores: Stable isotopes of oxygen and carbon

If we assume that sediment steadily builds up over time, ocean sediment in the bottom of the ocean gives a record of the ecology of the ocean when the sediment was lain down. In biologically active regions a big part of the sediment is the shells of tiny sea creatures made of calcium carbonate and preserved. One can count the relative abundance of different species, and using modern information on their ecology, make good guesses about the water temperature or other conditions in the past. Some species are planktonic, and live near the surface of the ocean, and others are benthic, or bottom dwellers Each has a particular niche in ecology, and may prefer certain temperatures, upwelling, or some other physical parameter of interest. Some species, like left –coiling N. pachyderma, live only in subarctic waters and are a marker of the equatorward extent of cold waters. Ice carries pebbles out to sea, so the extent of the ice shelf and sea ice, and the frequency of ice bergs can also be inferred from ocean sediment cores.

In addition to physical evidence, the ocean core also contains chemical evidence. One very important source of information is stable isotopes, particularly ^{18}O, ^{13}C and ^{2}H. For example, oxygen has a heavy isotope ^{18}O and a lighter, more common one ^{16}O. The lighter one is more likely to evaporate, so when the ice sheets on land grow, the ocean water gets enriched in the heavier isotope. This is called Rayleigh distillation. Thus the ^{18}O amount in an ocean core is related to the global ice volume on land. Of course the fractionation process is temperature dependent too, but this is often swept under the rug and considered a small effect in ocean cores. The temperature dependent fractionation between calcite and water works in the same direction - colder temperatures tend to concentrate the ^{18}O in the shells. So higher concentrations of ^{18}O in shells mean that the temperature of the water was lower and/or the global ice volume was higher. Often what is done is to measure the ^{18}O in the shells of only benthic organisms, those that live on the bottom. During times when maritime ice is present, the deep water of the ocean remains around 4C, while the surface waters undergo larger fluctuations. So if the benthic ^{18}O is used, then the temperature effect is smaller than the ice volume effect on ^{18}O.

In ice cores the ^{18}O concentration in the ice is used to estimate air temperature. The heavier isotope is more likely to condense out sooner, just as it is less likely to evaporate. If the ^{18}O in glacial ice is low, that means that the water vapor, which may have evaporated in the subtropics, has passed through a greater amount of cooling in its path to the ice, so the lower the 18O in the ice, the colder the temperature above the ice when the snowflake formed that resulted in the glacial ice. It is perhaps obvious that this effect is dependent on altitude, and may also depend on variations in the prevailing wind near the ice sheet and its variations over time.

In air bubbles trapped in ice, the ^{18}O abundance is thought to be dependent on the ^{18}O in the ocean water, which in turn is dependent on the mass of land ice. O2 is produced in surface waters by photosynthesis and the oxygen isotopic ratio in the ocean water gets transmitted to the molecular oxygen leaving the ocean surface. This is extremely useful, because it gives you a measure of global ice volume in the same ice core where you can measure the CO2 and CH4 trapped in the bubbles. This helps one get a good estimate of possible phase lags between atmospheric CO2 changes and global ice volume changes (Broecker and Henderson 1998, Shackleton 2000). The problem is complicated by differences between the isotopic abundance of in atmospheric o2 and seawater immediately under it. This difference is called the 'Dole effect' and is related to isotopic fractionation by biological (photosynethsis and respiration) and hydrological (evaporation and precipitation) processes (Bender, et al. 1994).

The Carbon Cycle and Stable isotopes of Carbon

The stable isotopes of carbon give slightly different information, because carbon is involved in biology in a very important way and plants do some isotopic fractionization during the process of photosynthesis. It is more efficient for enzymes to use ^{12}C rather than ^{13}C when plenty of CO2 is available for photosynthesis (Lajtha and Michener 1994). As a result organic carbon tends to be lighter in ^{13}C than inorganic carbon.

Inorganic carbon is carbon that is contained in compounds that are not formed by living organisms and that do not contain carbon-carbon or carbon-hydrogen bonds. For example, CO2 is inorganic carbon. CO2 is converted to organic carbon by photosynthesis. CO2 is taken up by plants, the 02 is detached from the C atom and the C atom is attached to some N or H to form an organic compound like, say carbohydrate CH2O, and a lot of more complex organic compounds. Photosynthesis is the core of the organic carbon cycle. Photosynthesis can be represented simply by the chemical reaction equation

$$CO2 + H2O \leftrightarrow CH20 + 02 \qquad (1)$$

When the reaction goes from left to right it is photosynthesis, when it goes from right to left it is respiration (or decay). Solar energy is required for photosynthesis, but that energy comes back out when respiration occurs. So if you eat plants, you can use the energy. The carbon goes from an oxidized state on the left to a reduced state on the right. The amount of CO2 in the atmosphere has an annual variation because of the cycle of photosynthesis and respiration/decay associated with deciduous trees that put on biomass in the spring and then drop leaves in the fall, which then decay or respire. This is the 'breathing' of the biosphere. Primary productivity is the amount of organic matter produced per unit time per unit of Earth surface area. It is often measured in units of mass of carbon per unit of time and area. The carbon in the total living biomass is about equal to the carbon in atmospheric CO2. When the organic matter decays in the absence of oxygen, as in the gut of an animal or under water, anaerobic fermentation may occur, which produces methane and CO2.

$$2CH20 \rightarrow CO2 + CH4 \qquad (2)$$

Thus if you increase the number of cows and rice paddies, one can increase the amount of CH4 produced.

Organic compounds formed on land or sea by photosynthesis can find their way to the ocean bottom where they can form sediments. These sediments eventually form sedimentary rocks. A common form of sedimentary rock formed from organic carbon is shale. The movement of carbon from the atmosphere to ocean sediments by biological processes is called the 'biological pump' by people who study the carbon cycle.

Inorganic Carbon Cycling

Biological processes are not the only way to get CO2 out of the atmosphere. Carbon dioxide is readily dissolved in water and it can then undergo chemical reactions which result in sedimentation of inorganic carbon compounds. A large reservoir of carbon is in sedimentary rocks such as limestone. Limestone consists mostly of calcium carbonate (CaCO3) in the form of the mineral calcite. Older sedimentary rocks, such as those found in cratons used to study the deep history of Earth, often contain the magnesium-rich mineral dolomite ($CaMg(CO_3)_2$). Carbon dioxide can make its way into ocean sediments without the assistance of photosynthesis (the biological pump). Inorganic carbon burial begins with the dissolution of CO_2 in water to form carbonic acid.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad (3)$$

Whether the reaction proceeds to the right or the left depends on the concentrations of reactants in the water. In general, an equilibrium is achieved fairly quickly. In water, carbonic acid becomes ionized, first by losing one hydrogen ion to form bicarbonate ion,

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad (4)$$

and then the bicarbonate may lose another hydrogen ion to become carbonate ion

$$HCO_3^- \leftrightarrow H^+ + CO_3^{--} \qquad (5)$$

The release of the hydrogen cations makes the water acidic. The pH of water is closely related to the negative of the logarithm of the concentration of hydrogen ions pH = -log[H^+]. When this happens in raindrops, it helps the rainwater dissolve rocks, an important part of the weathering process. Weathering and the formation of carbonate in seawater both reduce atmospheric CO_2.

Weathering

The rocks of Earth's crust are mostly carbonates and silicates. Carbonates are most commonly calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), mentioned previously. Silicates contain compounds of silicon and oxygen – a good simple example is wollastonite ($CaSiO_3$). When exposed to rain, carbonates weather more readily than silicates. Many monuments made of limestone lose their features to acid rain more quickly than granite. Weathering reactions for carbonate and silicate weathering are:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{++} + 2HCO_3^- \qquad (6)$$

calcium carbonate plus carbonic acid yields calcium ion plus bicarbonate ion.

$$CaSiO_3 + 2H_2CO_3 \rightarrow Ca^{++} + 2HCO_3^- + SiO_2 + H_2O \qquad (7)$$

wollastonite plus two carbonic acid yields calcium ion plus two bicarbonate ion plus silica plus water.

Note that silicate weathering consumes twice as much carbon as carbonate weathering.

The products of weathering remain dissolved in the water and are carried to the sea in rivers. Although minerals can form abiologically from these dissolved compounds, as would happen if life ceased and weathering continued, most of the minerals are formed when sea creatures take the dissolved ingredients and form mineral shells. So even though biology is involved in forming the shells, the shells are considered part of the inorganic carbon cycle. The carbon is formed into inorganic minerals in the shells of organisms but is still inorganic carbon. Some organisms such as diatoms, radiolarians and sponges use dissolved silica to form mineral (opaline silica) structures. Others, such as foraminifera, coccolithophorids, corals and shellfish produce structures of solid $CaCO_3$. Most of the solid calcium carbonate reaching the sea floor today arrives in the form of the shells of sea creatures. A reaction symbolizing carbonate formation from dissolved ions is:

$$Ca^{++} + 2HCO_3^- \rightarrow CaCO_3 + H_2CO_3. \quad (8)$$

The production of bicarbonate by mineral formation in (8) would tend to increase the rate of CO_2 formation by the reverse of reaction (3). By this mechanism shell formation would tend to drive up the CO_2. Many organisms in the surface waters produce photosynthesis but do not produce much shell growth. The ratio of organic matter to carbonate mineral production by plankton is about 4 to 1. Much of the organic matter is consumed by other biota before it reaches the sediment, so most of the carbon burial is in the form of inorganic mineral body parts of small planktonic organisms. Where the ocean depth is less than about 4km the shells make it to the bottom unaltered, since the waters are saturated with respect to $CaCO_3$. Deeper waters tend to have higher levels of dissolved carbolic acid (CO_2), produced by the decomposition of organic matter. The carbonate compensation depth is the level where the rate of dissolution of carbonate sediment equals the flux of carbonate by settling through he water. Below this depth carbonate will not accumulate..

The net effect of the carbonate cycle is to return as much CO_2 to the atmosphere as it removes, if you wait for equilibrium to be achieved(add up the calcium carbonate weathering reaction (6) and the calcium carbonate sedimentation reaction (8) . On the other hand the silicate weathering(7) and carbonate precipitation (8) reactions add up to:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \quad (9)$$

If this continued forever, all the silcate rock would go to carbonate rock and silica and CO_2 would be lost forever, so we need something else. What happens is carbonate metamorphism. Because Earth has active plate tectonics, everything involved gets recycled through subduction and uplift. As it is subducted and heated, the carbonate rock and silica react to return silicate rock and carbon dioxide, which is returned in volcanic plumes.

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2 \quad (10)$$

This metamorphosis completes the circuit of the terrestrial carbon cycle and returns CO_2 to the atmosphere. The active plate tectonics of Earth are also essential for life on earth because mountain building also brings critical trace metals and nutrients up to the surface and into mountains where they can be effectively weathered into solution and enter into the food web again. Otherwise all the available nutrients would eventually be buried in sediment and life on Earth would die, or at least be much less prolific..

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