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In this final section we'll examine the cycling of carbon on geologic time scales. In the past few sections we've primarily focused on carbon in the atmosphere, and in the ocean, and in the terrestrial biosphere, and we've talked about the time scales over which the atmosphere equilibrates with the ocean. Here we look at time scales much longer than the time scale of ocean mixing, and so we can essentially treat the ocean and atmosphere as one well mixed reservoir of carbon. Here geologic reservoirs of carbon come into play. This diagram nicely shows the sources and sinks of carbon that are relevant on geologic time scales. We'll take a look at each of these in turn.

So first we'll look at sources of carbon. Over time carbon accumulates in marine sediments as organic carbon and as calcium carbonate. The slow movement of oceanic crust into subduction zones returns oceanic crust to the mantle. Sediments go down with the oceanic crust and at depth they're heated, and the carbon associated with them is released. Some of this carbon returns to the mantle, and some of it is entrained into magmas associated with subduction zone volcanoes. The carbon is then released back to the atmosphere in subduction zone volcanoes and through mid-ocean ridge volcanism.

A final point that's relevant is that the CO2 supply from volcanism is thought to relate to the rate of sea floor spreading. That is, the rate of new crust production determines both the amount of mid-ocean ridge volcanism and the rate of subduction of new sediments back to the mantle, there's some reason to believe that this slow supply of CO2 to the atmosphere and ocean from volcanism would vary on tectonic time scales of millions of years. The volcanic CO2 supply is something like a tenth of a petagram of carbon per year.

So now let's turn to removal of carbon from the ocean and atmosphere. So we've already discussed the fact that photosynthesis and respiration are involved in the cycling of carbon from the atmosphere and ocean into and out of organic carbon pools. This is a geochemist's view of photosynthesis. It's highly simplified. We have carbon dioxide combining with water, and sunlight energy to make carbohydrates and release oxygen. These carbohydrates are then combined with oxygen in respiration to reverse the process and release CO2 back to the atmosphere and ocean, releasing energy in the process.

At any given time, you can have imbalances in photosynthesis and respiration. One example would be that if you have places on earth that are accumulating organic carbon faster than it can be respired, then you can slowly draw down atmospheric CO2, and in the process build up oxygen in the atmosphere. But it turns out that only about 25% of the carbon that is removed from the ocean-atmosphere system is removed as organic carbon. The remaining 75% is primarily removed as calcium carbonate buried in ocean sediments.

So what regulates the rate of this burial over geologic time scales? The simple answer is that carbonate burial depends upon calcium supply to the oceans. This calcium is supplied by the weathering of silicate rocks on land. Shown on the left of this equation is a simplified version of a calcium-bearing silicate mineral, such as make up most metamorphic and igneous rocks. In soils, carbon dioxide from the atmosphere and from the breakdown of organic matter combines with water to make carbonic acid.

This contributes to the dissolution of these minerals, releasing calcium as an ion into soil waters, which eventually move into ground waters and rivers. It's accompanied by dissolved silica, and by dissolved inorganic carbon. This river water and groundwater eventually makes it to the ocean, bringing new calcium into the ocean, where it combines with dissolved inorganic carbon to form calcium carbonate, which is buried in the sediments. Silica also precipitates as a solid. These precipitation reactions are largely associated with plankton building shells.

Combining these two equations, the net equation is that you start with a calcium-bearing silicate mineral, you weather it with CO2, and that calcium and carbon are eventually buried as calcium carbonate along with silica.

So again, over geologic time scales we have the burial of carbon as organic carbon and as calcium carbonate in sediments. The return of those sediments to the mantle, and the release of the associated carbon through volcanoes along subduction zones in the mid-ocean ridge. Seen this way, the global carbon cycle can be approximated by a simple mass balance equation. Here we see the rate of change of the mass of carbon in the atmosphere and ocean is equal to the fluxes in and out. So the flux of carbon into the ocean and atmosphere system from volcanism, and the flux out due to silicate weathering and subsequent calcium carbonate burial, and due to the burial of organic matter.

Described this way, these fluxes each appear to be quite separate and independent. It's thus easy to imagine that they might be out of balance on million year time scales. That is, you might have a time when volcanic sea emissions are high, but burial as calcium carbonate and as organic carbon might be low. However we know that the ocean and atmosphere contain relatively little carbon compared to the amount of carbon contained in the mantle and in the continents. And these fluxes are relatively large on geologic time scales compared to the overall amount of carbon in the ocean and atmosphere.

Because we know that the ocean and atmosphere haven't ever had very, very high amounts of carbon, and neither have they ever been completely depleted of carbon, these fluxes can't be out of equilibrium for very long. That is, on longer time scales this rate of change of the amount of carbon in the atmosphere and ocean needs to be approximately zero. And so on million year time scales we can actually set the input fluxes equal to the output fluxes and assume that the size of this reservoir is not changing.

But why would this be the case? How would carbon dioxide emissions from volcanoes know what's happening in the ocean where calcium carbonate and organic carbon are buried? Similarly, how would these outputs know about changes in these inputs? In order to suggest that there is long term balance, there needs to be some sort of negative feedback linking these inputs and outputs. In order to explore this, let's take a look at the things we think control each of these fluxes.

In terms of inputs, rates of CO2 release from volcanism are thought to depend primarily upon rates of seafloor spreading. That is, upon broader scale plate tectonics. On the far right hand side, the net burial of organic matter is thought to be relatively small in the overall carbon budget of the ocean and atmosphere. It's also not thought to be strongly sensitive to climate. So it's hard to see a negative feedback in either of these fluxes.

So then we turn to the silicate weathering term, which determines the rate of carbon burial as calcium carbonate. Weathering is likely to increase with increasing atmospheric CO2 and temperature. Temperature increases reaction rates that drive silicate weathering. Precipitation on a global basis also increases with increasing temperature, further facilitating higher weathering rates. Higher atmospheric CO2 also independently increases silicate weathering rates by increasing the acidity of water penetrating into soils. Silicate weathering also depends upon the nature of exposed silicates. That is, how weatherable they are. And then the rate of supply of new unweathered silicate.

This dependence of silicate weathering on carbon dioxide and temperature represents a potential negative feedback. This negative feedback is known as the silicate weathering thermostat. And the hypothesis is that changes in global temperature due to changes in carbon inputs or outputs are balanced on million year time scales by changes in silicate weathering that regulate the removal of carbon from the ocean-atmosphere system.

Let's take a look at a couple of examples of how this might work. Let's say you have increased volcanic emissions. This would lead to rising atmospheric pCO2, which would lead to increasing silicate weathering, which would lead to increasing carbon burial as calcium carbonate, which would then stabilize pCO2. In this instance, atmosphere pCO2 rises until weathering is sufficient to balance increased volcanic inputs, and that would stabilize atmospheric pCO2.

In another example, let's say we have an increase in mountain building that increases the weatherability of Earth's continents. That is, at the same temperature you get more calcium flux to the oceans. This would increase the burial of calcium carbonate, it would lead to decreasing pCO2, this decreasing pCO2 would cause less weathering, and would lead to stabilized pCO2. In this instance, atmospheric pCO2 falls until weathering falls back into balance with volcanic inputs, stabilizing atmosphere pCO2 again.

We've seen before that most reconstructions suggest that atmosphere pCO2 has been declining for much of the last 50 million years, from levels somewhere above 1,000 ppm to levels of approximately 300 ppm in the pre-industrial atmosphere. And so one explanation for this has to do with changes in volcanic outgassing, that is perhaps declining production of new oceanic crust and mid-ocean ridges, or changes in the weatherability of continents. For example, due to the uplift of the Himalayas, increases in the amount of newly erodible material being created.

So we'll close by returning to these models in which 1,000 petagrams of carbon is instantaneously added to the world's atmosphere, and then the model computes how quickly that carbon is removed from the atmosphere. As we see, there's fast removal during the first 1,000 years, which reflects dissolution in the ocean. Over slightly longer time scales, dissolution of calcium carbonate in seafloor sediments facilitates further dissolution of atmospheric CO2 in the ocean.

Finally on still longer time scales, the increased global temperature and increased atmospheric CO2 lead to increased rates of silicate weathering, which supply new calcium to the ocean and allow increased calcium carbonate burial. This last process finally, over time scales of hundreds of thousands of years, brings atmospheric CO2 back down to its original concentrations. So we see that if we were to instantaneously stop producing CO2, that much of the CO2 that we've added to the world's atmospheres would be dissolved in the oceans over several centuries. But the long tail would persist for tens and hundreds of thousands of years.