



7. The carbon cycle

7.1. Box model of the carbon cycle

Without the greenhouse effect, our planet would experience a permanent ice age and life as we know it would not be possible. The main contributors to the greenhouse effect are the clouds and greenhouse gases. The three main greenhouse gases are water vapor, carbon dioxide (CO₂), and methane (CH₄). Human activities, particularly the burning of fossil fuels (oil, coal, natural gases), have led to a significant increase of CO₂ in the atmosphere which is warming the planet faster than would be expected without the addition of this anthropogenic CO₂. To understand the climate and predict its evolution in the future, it is essential to understand the natural mechanisms controlling the concentrations of CO₂ and CH₄ in the atmosphere. We should know where the carbon comes from and how it is removed from the atmosphere. We should also be able to quantify how much carbon flows in (**input flux**) and how much flows out (**output flux**), and how much time on average it stays in the atmosphere (**residence time**). The atmosphere is one **reservoir** of carbon but we need to identify the other reservoirs and describe how carbon moves from one to another. An obvious reservoir of carbon is the biosphere. Carbon atoms are essential for life because they form the backbones of large organic molecules. Other important reservoirs of carbon are the oceans, carbonate rocks (mainly those composed of calcium carbonate, i.e. CaCO₃), and fossil fuels (coal, oil, natural gas). In any of these reservoirs, the amount of carbon (**reservoir size**) has fluctuated over geological times. When there is a natural balance between what enters and leaves each reservoir, the system is said to be in a **steady state**. It means that for any given reservoir the input flux is equal to the output flux (often expressed in gigaton per year or Gt/yr) and the reservoir size remains constant. In this condition, the residence time is the reservoir size divided by the input flux (or the output flux). Hence, the carbon cycle can be represented in a simplified manner by various reservoirs which exchange certain amounts of carbon at certain rates. This representation of the carbon cycle is called a **box model**. The carbon cycle is one example of biogeochemical cycles that can be represented using a box model. Other examples are the water cycle, the nitrogen cycle, the sulfur cycle... Box models are particularly useful for modeling biogeochemical cycles using computer programs.



Figure 65: Reservoir in a steady state condition where the input flux is equal to the output flux and the reservoir size remains constant.

7.2. The natural carbon cycle

A simplified box model of the natural carbon cycle (without the influence of human activities) is shown in figure 66.



Figure 66: Simplified box model of the natural carbon cycle. The size of each reservoir is expressed in gigaton (Gt). Input and output fluxes are expressed in gigaton/year (Gt/yr). DOC means dissolved organic carbon and represents organic molecules present marine (oceans) and freshwater (rivers and lakes) systems. Source: partly derived from Biogeochemistry: An Analysis of Global Change (2013).

If we examine the figure above and examine the fluxes of carbon from one reservoir to another, several interesting observations can be made:

- Most carbon is stored in the reservoir “carbonate rocks”.
- The largest fluxes of carbon are between the land surface (plants and soils) and the atmosphere and between the atmosphere and the ocean (“fast domain”).
- Soils store three times as much carbon as plants.
- The smallest fluxes are related to calcium carbonate deposition in the ocean, calcium carbonate dissolution and weathering of silicate rocks, volcanism, and carbon fluxes in and out of the fossil fuel reservoir (“slow domain”).
- The residence time of carbon in the atmosphere is very short (3.5 years) whereas in carbonate rocks the residence time is very long (6×10^8 years).

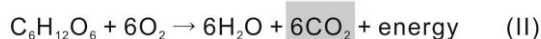
7.2.1. Land surface (plants, soils) ↔ atmosphere

The greatest flux of carbon is the exchange of carbon between the terrestrial biosphere and the atmosphere. This involves primarily **plant photosynthesis** (I), **cellular respiration** (II), and the **decomposition of organic matter** by microbes (III). During photosynthesis, plants take CO_2 from the atmosphere to build organic molecules using sunlight as a source of energy. Part of this CO_2 returns in the atmosphere during cellular respiration, a reaction producing energy. When plants die, organic matter is incorporated in soils where it is decomposed by microbes. This process releases CO_2 in the atmosphere and is one component of soil respiration. Another important component of soil respiration is cellular respiration of plant roots which also releases CO_2 in the atmosphere.

Photosynthesis

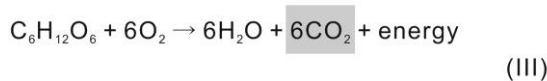


Cellular respiration

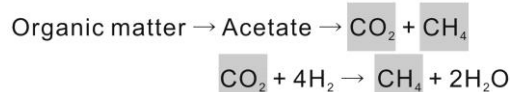


Decomposition of organic matter by microbes

a. *Aerobic*



b. *Anaerobic* Fermentation Methanogenesis





7.2.2. Atmosphere ↔ ocean

Understanding how the oceans absorb the atmospheric CO₂ is essential to predict the future of Earth's climate. The local flux of CO₂ between the atmosphere and the ocean depends on various factors including seawater composition, seawater and air temperature, and winds. Gases are less soluble at higher temperature (a soda drink becomes flat faster at room temperature than in the fridge). Increasing temperature reduces CO₂ solubility in the ocean. Stronger winds increase the exchange of CO₂ between the atmosphere and the ocean because of the formation of air bubbles in breaking waves and the production of sea spray (droplets of seawater blown from waves). Bubbles and sea spray increase the contact surface between the air and seawater and therefore enhance air-sea gas exchange.

7.2.3. Oceans ↔ marine life ↔ carbonate rocks

Marine photosynthetic organisms use the dissolved CO₂ in the ocean as a source of carbon they incorporate in their tissue. Marine organisms also perform cellular respiration which release CO₂ in the environment. Some of the organic carbon is recycled in the surface ocean and some is transferred to the deep ocean ("marine snow"). Much like on land organic matter is decomposed by microbes which releases CO₂ in the environment. In addition, many marine organisms are able to precipitate CaCO₃ (calcium carbonate) to build a hard shell or skeleton (Fig. 67). Hard parts of marine organisms made of CaCO₃ accumulate on the sea floor and enter the carbonate reservoir (but see slides for a definition of lysocline and carbonate compensation depth). The process of calcification releases CO₂ in the environment as shown by the following reaction:



The rate at which carbon enters the carbonate reservoir is very low (0.2Gt/yr). However, the carbon stored in this reservoir may remain there for millions of years. In addition, the organic matter that escaped decomposition can be buried and stored in the lithosphere for a very long time.



Figure 67: Examples of marine organisms producing a shell or skeleton made of calcium carbonate. (A) Live benthic foraminifera *Calcarina* (source: Catalogue of organisms, <http://coo.fieldofscience.com>), (B) sediment composed of *Calcarina* shells (source: Wikipedia), (C) live calcareous green algae *Halimeda* (source: www.algaebase.org), (D) sediment composed of *Halimeda* segments, (E) coral reef built primarily by corals and coralline algae (Great Barrier Reef of Australia, source: AIMS), (F) encrusting coralline algae (source: Encyclopedia of Earth, www.eoearth.org), and (G) detail of a coral skeleton.



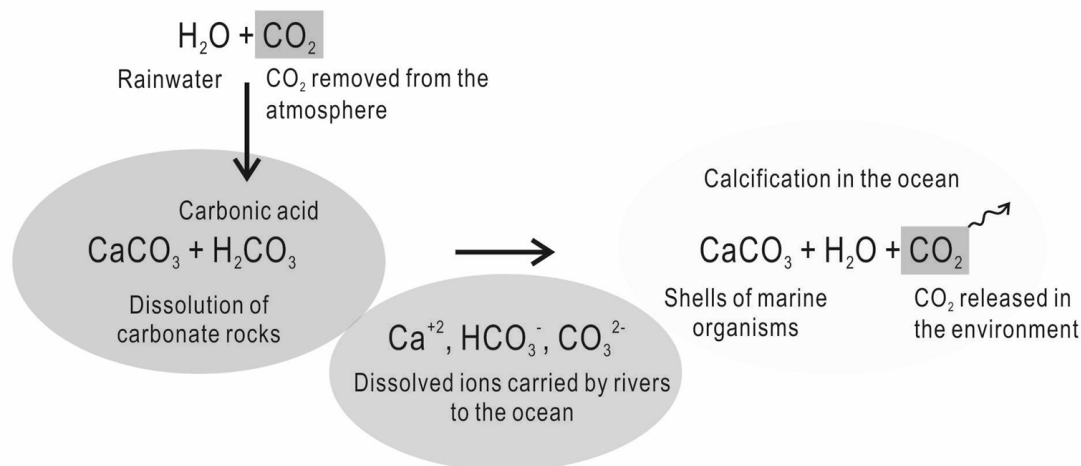
7.2.4. Lithosphere ↔ atmosphere / ocean

The lithosphere is the largest reservoir of carbon. The carbon present in the lithosphere occurs primarily in carbonate rocks, organic matter, and carbon dioxide. Some important processes behind the exchange of carbon between the lithosphere and the atmosphere (or the ocean) are explained below.

a. **Dissolution / precipitation of calcium carbonate**

Exchange of carbon between the atmosphere and the lithosphere occurs during dissolution and precipitation of CaCO_3 . Rainwater and CO_2 combine in soils to form the weak carbonic acid H_2CO_3 . In contact with carbonate rocks, the carbonic acid dissolves CaCO_3 . The products of this reaction, Ca^{2+} , HCO_3^- and CO_3^{2-} , are transported by rivers to the ocean. In the ocean, calcifying marine organisms use these ions to build their hard parts (shells, skeletons...). The process of dissolution of calcium carbonate removes CO_2 from the atmosphere. However, the same amount of CO_2 is released during calcification. Therefore, the overall process of dissolution-calcification does not result in a net loss (nor gain) of CO_2 in the atmosphere as shown by the following simplified reactions (from Ruddiman, 2001):

Dissolution-calcification of calcium carbonate



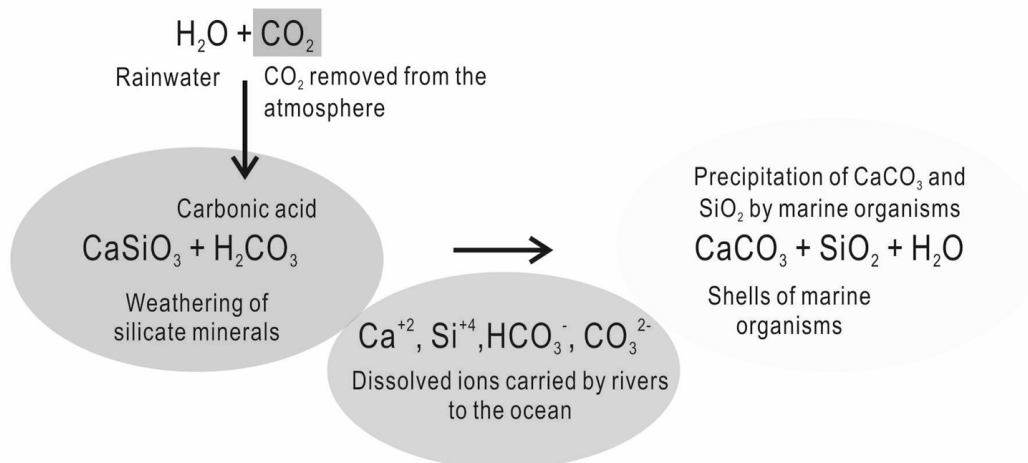
b. **Weathering of silicate rocks**

An important process controlling the long-term concentration of atmospheric CO_2 (over millions of years) is the weathering of silicate rocks. Silicate minerals are the most abundant minerals in the Earth's crust (see section 2, page 3). Here we are concerned more specifically with Ca-bearing silicate minerals. Like carbonate rocks, Ca-bearing silicate minerals react with acidic groundwater. The products of this weathering reaction include dissolved ions (e.g. Ca^{2+} , Si^{4+} , Fe^{2+} , HCO_3^- , CO_3^{2-} , H^+) and clays. These ions are transported by rivers to the ocean and some can be used by marine



organisms to build hard parts made of CaCO_3 and SiO_2^* . We can use the simple formula CaSiO_3 to represent Ca-bearing silicate minerals and the overall process of silicate weathering combined with calcification and silification in the ocean can be summarized by the following reactions (from Ruddiman, 2001):

Weathering of Ca-bearing silicate minerals



Most importantly, the above reactions show that the weathering of silicate rocks results in a net removal of CO_2 from the atmosphere! This slow removal of CO_2 must be balanced by an equally slow input of CO_2 . This input of CO_2 is provided by volcanoes and hot springs.

c. **Volcanism**

The CO_2 from Earth's interior is released by volcanoes and hot springs. The rate of CO_2 input by volcanic activity is variable and depends on the frequency and intensity of volcanic eruptions. The geological record shows evidence of past volcanic eruptions which were far more intense and lasted far longer than those recorded in human history. Such events can release a huge amount of CO_2 in the atmosphere and potentially alter the Earth's climate for an extensive period of time. An example of exceptionally intense period of volcanism is documented in the Siberian Traps, a succession of huge basaltic lava flows covering millions of km^2 and related to an eruptive event spanning one million year that happened 250-251 million years ago. This event may have been one of the factors which triggered the largest mass extinction in life history, i.e. the end-Permian mass extinction.

* Silica, i.e. SiO_2 , is with CaCO_3 a major component of mineral hard parts produced by marine organisms. Examples of organisms producing hard parts made of SiO_2 are diatoms (phytoplankton), radiolarians (zooplankton) and siliceous sponges.



d. **Fossil fuels**

Another reservoir of carbon which is part of the lithosphere is the organic matter preserved in rock strata. A common sedimentary rock composed of the accumulation of organic matter is coal. Other products of the accumulation of organic matter are oil and natural gas (mostly methane). In the natural carbon cycle (without the influence of human activities), the transfer of carbon from the reservoir of fossil organic carbon to the atmosphere is extremely slow. The organic carbon present in the lithosphere can return into the atmosphere via volcanic activity, natural fire and oxidation (biological or not).

In conclusion, unlike the exchange of carbon between the biosphere and the atmosphere, the natural rate at which carbon is exchanged between the lithosphere and the atmosphere is extremely slow. The two main processes controlling the flux of carbon between the lithosphere and the atmosphere are silicate weathering and volcanism. These very slow exchanges affect the concentration of atmospheric CO₂ (hence climate!) over the very long term (millions of years) and are controlled by plate tectonics (see slides and text of chapter 10).

7.3. Anthropogenic perturbations, global warming, and ocean acidification

In May 2013, the level of atmospheric CO₂ has reached 400 ppm (parts per million) for the first time since accurate measurements began in 1958 (Fig. 68). The rapid increase in atmospheric CO₂ is related to human activities, primarily the combustion of fossil fuels. Figure 69 shows the impact of human activities on the carbon cycle. Besides fossil fuel burning, other human-induced sources of atmospheric CO₂ are related to deforestation and cement production. The figure also indicates that natural processes removing CO₂ from the atmosphere (plant growth and ocean uptake) do not counterbalanced human emissions, leading to a net increase in atmospheric CO₂ (3.2 ± 0.1 Gt/yr for the 1990s and 4.1 ± 0.1 Gt/yr for 2000-2005, source: IPCC 2007 report).

We know with a high level of certainty that human emissions of CO₂ contributes in part to the present-day global warming. What we don't know for sure is exactly how much warming is caused by anthropogenic CO₂. As we will see in the next chapter, the Earth has experienced many cold/glacial and warm/interglacial periods over the last 2.5 million years. The last glacial period reached its coldest peak 20,000 years ago when the extent of ice sheets was maximum. Since this last ice age, the Earth is warming again and ice sheets are retreating. Warming caused by humans is accelerating this natural trend.



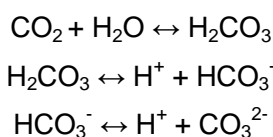
Figure 68: Evolution of the concentration of atmospheric CO₂ for the past 55 years. Source: Scripps Institution of Oceanography, CO₂ Program, Mauna Loa Observatory.



Figure 69: Impact of human activities on the carbon cycle. Carbon fluxes related to human activities are partly derived from Biogeochemistry: An Analysis of Global Change (2013).

We will discuss more about the impact of human activities on climate later in this course. Now let's briefly examine another consequence of the increase of atmospheric CO₂: **ocean acidification**.

In the ocean, CO₂ reacts with H₂O to form carbonic acid (H₂CO₃). Most of the carbonic acid dissociates to hydrogen ions (H⁺) and bicarbonate ions (HCO₃⁻). Some of the bicarbonate ions dissociate to hydrogen ions and carbonate ions (CO₃²⁻). Adding CO₂ in seawater increases the concentration of hydrogen ions and therefore decreases the pH. The chemical reactions involved can be expressed as follows:



Since these reactions involves the concentration of bicarbonate and carbonate ions in the ocean, it is clear that increasing the amount of CO₂ absorbed by the ocean has an impact on biological calcification (e.g. corals and coral reef ecosystems). One way to look at the problem is to consider that organisms combine calcium ions (Ca²⁺) and carbonate ions (CO₃²⁻) to produce their shell or skeleton made of calcium carbonate (CaCO₃). What would happen to the concentration of carbonate ions if more CO₂ was added in the ocean? As more CO₂ is added, more hydrogen ions is produced and pH would decrease. Some of these hydrogen ions would tend to bond with carbonate ions to form bicarbonate. Therefore, it would also lead to a decrease in the concentration of carbonate ions and would potentially make calcification more difficult (since carbonate ions are needed for calcification!). The relationship between pH and the concentration of dissolved CO₂, HCO₃⁻ and CO₃²⁻ is shown in figure 70. It clearly shows the decrease in concentration of CO₃²⁻ with decreasing pH. Several experiments have shown that adding CO₂ to the ocean would be detrimental to calcifying organisms. However, biological calcification is a complex process which is far from being well understood. More work is needed to predict the impact of ocean acidification on calcifying organisms and related ecosystems.



Figure 70: Concentrations of the dissolved CO₂, bicarbonate and carbonate ions as a function of pH. Source: Ridgwell and Zeebe (2005).