Chapter 12

Carbon Cycling: The Dynamics and Formation of Organic Matter

William Horwath

Department of Land, Air, and Water Resources, University of CA, Davis, CA, USA

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I ATMOSPHERIC CO₂ SINCE THE DEVONION ERA

The atmospheric CO_2 level has fluctuated considerably over the past 400–500 million years. The variation is attributed to changes in gross primary production, volcanism, the inclination of Earth's axis and the carbonate weathering processes. Over the past 200 years, atmospheric CO_2 has risen by over 120 ppm. Overtime, plants have responded by changing their stomatal density. The relationship of CO_2 to stomatal density is a proxy measurement to reconstruct past CO_2 levels. For example, Retallack (2001) used the fossil record of the genus Ginkgo dating to the late Triassic period (229 M years ago) to the Permian period to infer CO_2 levels.

Other proxies include stable isotopes of ¹⁸O and ¹³C. Variations in the amount of stable isotopes are represented as parts per thousand or per mil and designated by the Greek letter delta (δ). The ¹⁸O in CaCO₃ on the seafloor provides a proxy measurement of changes in the amount of frozen water in ice sheets, thus making it useful as a paleothermometer. The ¹³C in CaCO₃ comes from two sources – plants and the atmosphere – with plants being



FIG. 512.1 The evolution of Earth's life forms and atmospheric CO_2 concentrations relative to the Earth's age (millions of years BP).

depleted and the atmosphere being enriched. The CO_2 concentration of the atmosphere can be estimated from sediments by determining the amount of heavier atmospheric CO_2 in CaCO₃. A larger contribution from the atmospheric source indicates higher CO_2 levels. Further discussion on stable isotopes is found in Chapter 13.

II ORIGINS OF FOSSIL FUELS

The deposition of organic matter from vascular plants, mainly trees and mosses in low lying swampy areas, are the source of today's coal deposits. The swampy areas likely limited decomposition by excluding oxygen, which was not abundant at the time. Mature coal is mostly composed of C. The enriched C coal substrate is formed in the Earth's crust at temperatures of ca. 300 °C over tens of millions of years. The hydrogen and oxygen originally associated with the organic materials was distilled away leaving a substrate with a chemical formula of C_n representing an oxidation state of zero. The less chemically reduced oil (CH₃ (CH₂) nCH₃) and natural gas (CH₄) are formed from algae deposited onto the ocean floor where it has accumulated in

sedimentary rock. The combustion of less chemically reduced coal produces less energy and more CO_2 than the combustion of other fossil fuels. Methane is the most chemically reduced form of C, and upon combustion, produces more energy per unit of C than either oil or coal.

III GREENHOUSE PROPERTIES OF CARBON DIOXIDE AND METHANE

Greenhouse gases have the ability to absorb infrared radiation (IR). The reflected visible light from the sun is emitted as IR. Greenhouse gases also emit IR at the same frequency they were adsorbed in the upper atmosphere. The net effect of greenhouse gases is a reradiation of the IR emitted from the warm surface in the colder areas of the upper atmosphere (troposphere). The change in the total IR intensity from adding a greenhouse gas is termed radiative forcing, measured in units of wattsm⁻². As the concentration of greenhouse gases increases, the radiative forcing becomes less sensitive. The radiative forcing of CO_2 is proportional (number of doublings) to its concentration. The radiative forcing function 298 times that of CO_2 .

IV UNITS OF THE GLOBAL C CYCLE

A mixing of metric and English units has often confused the units describing the global C cycle. From a science perspective, metric units are preferred and are used here to describe the numerous reservoirs of the global C cycle. The most commonly used unit is gigatons of C, or Gton C. The prefix *giga*- (G) means 10^9 , so a gigaton is a billion metric tons. A metric ton is equal to 10^6 grams, so $1 \text{ Gton} = 10^{15} \text{ g C}$. In many scientific publications, the unit *peta*- (P) meaning 10^{15} is used. A petagram (Pg) is a quadrillion grams. One Gton is equal to one Pg.

One potential source of confusion in C unit description between popular and scientific literature on climate science lies in their interpretation of the mass of C versus the mass of CO₂. The confusion is apparent in developing C in market discussions, such as cap and trade, where the cost of reducing CO₂ emissions is presented as dollars per ton of C or sometimes per ton of CO₂. These units are very different. The conversion follows:

$$1 gC = \frac{44 gCO_2}{12 gC} = 3.7 gCO_2, \qquad (S12.1)$$

where 44 g of CO_2 is a mole of CO_2 and 12 g of C is the molecular weight of C. Therefore,

One ton of
$$CO_2 = 1$$
 ton of $C \times 3.66$ (S12.2)

One ton of
$$C = 1$$
 ton of $CO_2 \times 0.27$ (S12.3)

V PHOTOSYNTHESIS

Photosynthesis is the primary biological synthetic process that creates organic matter on Earth. It is a process by which light energy is converted into chemical energy. The evolution of photosynthesis occurred about 3.5 billion years ago when CO_2 levels were much higher and the O_2 content much lower in the atmosphere. The first photosynthesizers likely used hydrogen sulfide (H₂S) and hydrogen (H) as sources of electrons (Olsen, 2006). About 3 billion years ago, cyanobacteria evolved the ability to synthesize organic C in the form of sugar directly from CO_2 and water using light energy (Buick, 2008). The overall chemical of photosynthesis is:

$$6CO_2 + 6H_2O(+light energy) \rightarrow C_6H_{12}O_6 + 6O_2$$
 (S12.4)

Plants, algae, and many species of bacteria, excluding those in archaea, are capable of photosynthesis and are termed photoautotrophs. The process of photosynthesis is the primary source of O_2 in the atmosphere.

The chemical energy is harvested in photosynthesis by running the above reaction in backwards to produce adenosine triphosphate (ATP):

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + energy(36 \text{ ATP})$$
 (S12.5)

Respiration is a combustion process that drives metabolic processes of all living things. The combustion of fossil fuels is an energy extracting process that consumes chemical energy photosynthesized millions of years ago.

VI PLANT SUGARS

The product of photosynthesis is sugars. These sugar molecules are the basis for more complex molecules, such as glucose (Fig. S12.2). The glucose molecule is a monosaccharide that serves as a main source of energy and is an important metabolic substrate. Monosaccharides consist of a minimum of 3 C sugars ranging up to 6 C sugars. Glucose is a hexose that can be interconverted into a number of different 5 C sugars or pentose monosaccharides (shown in Fig. S12.2). The diverse pentoses are used to synthesize oligosaccharides and polysaccharides are used in the production of a wide array of cell wall glycoproteins and complex pectin and hemicellulose.



FIG. S12.2 Common sugars of the plant cell wall and their interconversions to form other 5 and 6 C sugars. The modifications to convert D-glucose into other sugars are highlighted in light blue.

VII SUPPLEMENTAL REFERENCES

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