10

Development of Carbon Dioxide in Earth's Atmosphere

Carbon Dioxide

Carbon is the fourth most abundant element in the universe and is a major component for life on the Earth. On the Earth, organisms utilize carbon for structure and/or energy. For a molecule to be organic, it must contain carbon atoms. Carbon is found in a diverse variety of forms: (1) as a gas, e.g., carbon dioxide (CO_2); (2) a liquid, e.g., petroleum hydrocarbons; and (3) as a solid, e.g., carbonates ($CaCO_3$), wood, plastics, diamonds, coal, peat and graphite.

Carbon dioxide is a colorless, odorless gas that is found (1) in the atmosphere as a trace gas, (2) as a gas dissolved in water (oceans), (3) in liquid hydrocarbon deposits as a dissolved gas and (4) in volcanic activity (CCS, 2017).

Carbon dioxide has a specific gravity of 1.555 or is ≈60% heavier than air. The carbon dioxide molecule consists of a carbon atom covalently bonded to two oxygen atoms. It occurs naturally in the atmosphere, and is soluble in water, ethanol and acetone. It is a linear covalent molecule. In the

atmosphere, it reacts readily with water droplets in clouds to form carbonic acid, which has a pH of 6.8:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad \text{(Eq. 10.1)}$$

It is a very stable molecule; few chemical processes other than photosynthesis have been found that are able to effectively reduce carbon dioxide to carbon monoxide (CCS, 2017).

Although carbon dioxide is viewed by some as a poisonous gas, life on Earth is dependent upon it. It is required for those organisms that use it in photosynthesis to harvest energy and produce carbohydrates and oxygen.

Sources of Carbon Dioxide

Archer (2010) noted that there are several different forms of carbon that one can track in the global carbon cycle:

1. Inorganic-carbon (C) in rocks, e.g., bicarbonate, carbonate, and other rocks.
2. Organic-carbon, e.g., organic plant material, hydrocarbons, etc.
3. Carbon gases (CO_2), e.g., volcanism, degassing of Earth's mantle material.
4. Solution gas, (CO_2), e.g., dissolved in the ocean water.
5. Methane gas (CH_4) of non-organic origin.
6. Carbon monoxide (CO), e.g., found in atmosphere.

The Carbon Cycle

Today's movement of carbon through the Earth's atmosphere, hydrosphere, biosphere and geosphere (which is only a portion of the total *Carbon Cycle*) is shown in Figure 10.1. This portion of the carbon cycle displays several reservoirs of carbon storage and the various processes and forms by which the carbon moves between these reservoirs. The major carbon reservoirs displayed in this figure include the atmosphere, oceans, vegetation, and soil. Also shown is the approximate quantities of carbon that flow in and out of the specific storage areas per year. The arrows indicate the direction of the carbon flow between these carbon storage reservoirs. Carbon dioxide is the primary carrier for the movement of carbon between the storage
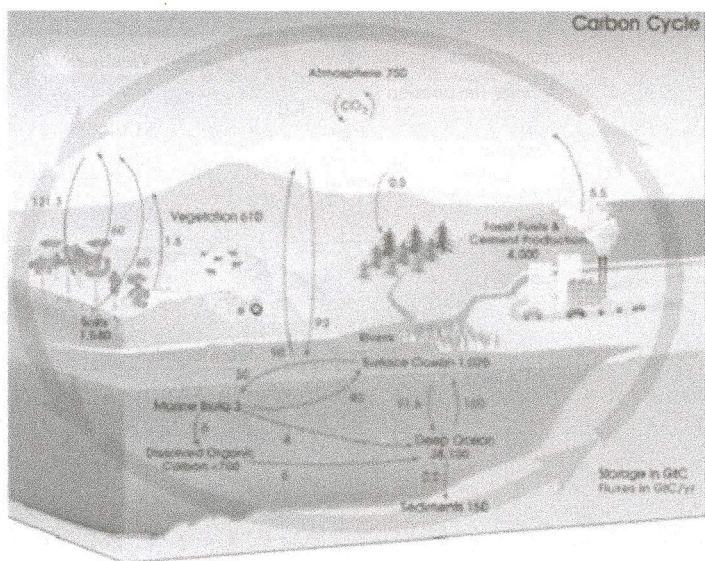
Figure 10.1 A portion of today's carbon cycle showing the carbon path through the atmosphere, oceans, and soils. (After Harrison, 2003.)

reservoirs. There are several smaller cycles or pathways of carbon flow as shown in Figure 10.1.

The ocean/atmospheric cycle is a major pathway between the two large storage reservoirs of carbon dioxide. When the water temperature increases in the oceans (which cover 72% of the surface of the Earth), the solubility of the carbon dioxide gas in the water (dissolved gas) deceases and large volumes of carbon dioxide, previously dissolved in the ocean water, are released to the atmosphere.

The *carbon rock cycle* is a description of another portion of the carbon cycle, including the movement of carbon through (1) degassing of the mantle (2) plate tectonics, (volcanism), and (3) carbonate rock formation. This is often referred to as the *Rock Cycle* (Figure 10.2). Carbon dioxide is the primary form of carbon circulating through the Earth's atmosphere, coming from outgassing of the Earth's mantle at the midocean ridges, hotspot volcanoes and subduction-related zones. Archer (2010) noted that over geologic history, there is a close relationship of the percent content of carbon dioxide in the atmospheric and volcanic activity (Figure 10.3). During high periods of volcanic activity, the percent atmospheric carbon dioxide concentration is higher; therefore, the increased percentage of carbon dioxide in the atmosphere can be partially related to volcanic activity. Volcanic activity from 1850 to 2010 is shown in Figure 10.4. Much of
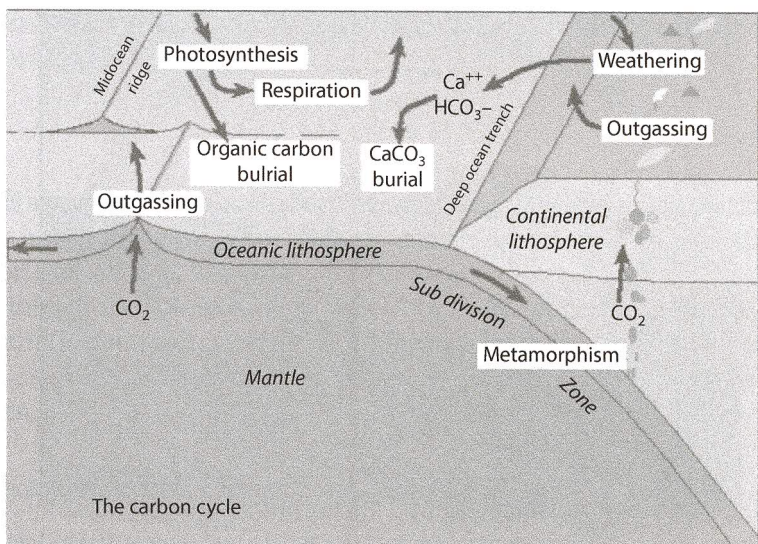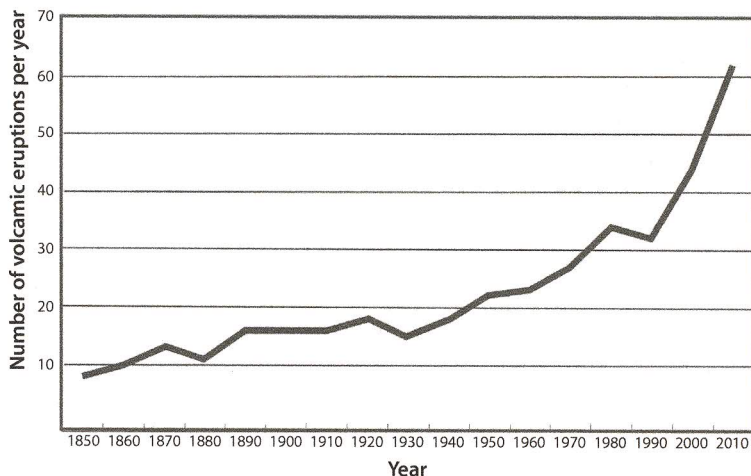
Figure 10.2 The rock cycle portion of the carbon cycle. The primary source of CO_2 is degassing from the Earth's interior. (After Columbia, 2017, http://www.columbia.edu/~vjd1/carbon.htm.)
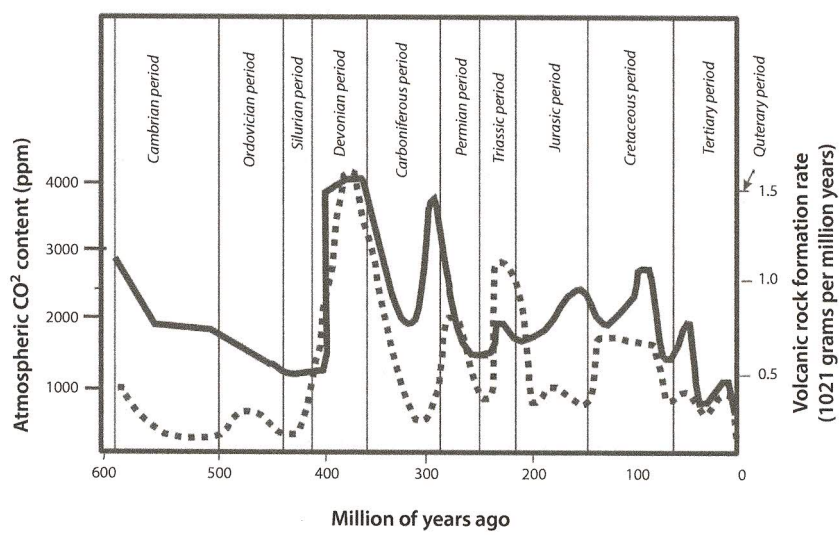
Figure 10.3 Schematic showing relationship between the CO_2 content in the atmosphere (dashed line) and the volcanic activity on Earth (solid line). (Modified after Archer, 2010.)

Figure 10.4 Global volcanism over time (1850 to 2010). There has been a general increase in volcanism over the past 100 years. (Modified after http://informacaoincorrecta. blogspot.com/2011/08/porque-nibiru-nao-existe.html.)

this carbon is abiogenic carbon (inorganic gas), derived from (1) the subduction and metamorphism of carbonate rocks and (2) degassing of the mantle. The percentage of carbon dioxide shown in Figure 5.1 in the early periods of the Earth's history, prior to bacteria, is of abiogenic origin.

Mass of Carbon in the Earth's Crust

Ronov and Yaroshevsky (1978) estimated that $\approx 3.91 \times 10^{23}$ g of CO_2 is bonded in the crustal carbonates. Cores also contain $\approx 1.95 \times 10^{23}$ g of organic carbon, C_{org}. The organic carbon, C_{org}, prior to its reduction in the biologic processes, was bonded by 5.2×10^{22} g of oxygen. Therefore, the total CO_2 mass buried in the crust is:

$$m(CO_2) \approx (3.91 + 0.72) \times 10^{23} = 4.63 \times 10^{23} g.$$

## Mass of Carbon in the Earth's Mantle

The determination of carbon content in the mantle is much more complicated than for the Earth's crust. Experimental data indicates that the high-temperature distillation fractions of volatile components in an oxygen

atmosphere of tempering glass from the tholeiitic basalts in the oceanic rift zone contain 20 to 170 g/ton of mantle-derived carbon having isotopic shifts of about −5‰ (Watanabe *et al.*, 1983; Sakai *et al.*, 1984; Exley *et al.*, 1986). Dispersed carbon is found in all igneous rocks in negligible concentrations of 10 to100 g/ton with a substantial deficit of the heavy isotope $\delta^{13}C \approx 22$ to 27‰ (Galimov, 1988a). Carbon found in the Earth's crust is isotopically heavier, with $\delta^{13}C \approx -3$ to −8‰ (average value is −5‰). Part of the mantle carbon is dispersed among the silicate crystalline grids in the atomic state (Watanabe *et al.*, 1983) and, hence, is not a volatile component of the basalt melts. Therefore, carbon content in the carbon dioxide gas phase of basalt melt-outs may be noticeably smaller than the quoted total carbon content.

The assumption here is that the mobile carbon content in the mantle is ≈30 g/ton or 110 g/ton when normalized for carbon dioxide. In this situation, the mantle carbon dioxide content is $m_{CO_2} \approx 4.48 \times 10^{23}$ g of carbon dioxide. Carbon dioxide degassing of the mantle, as well as degassing of the other mobile volatile components of the atmosphere and hydrosphere, may be described by the relationship:

$$m_i = m_{i_o}\left(1-e^{-Xz}\right) \qquad \text{(Eq. 10.2)}$$

where m_i is the mass of the degassed volatile component i; m_{i_o} is the total mass of the component i on he Earth; $\times$ is the component i's mobility exponent; z is the tectonic parameter defined by the ratio of total loss of the Earth's depth heat and its current value $Q_0 = 13.42 \times 10^{37}$ erg (Sorokhtin and Ushakov, 2002). Today's value of z is equal to 1 (see Figure 10.5).
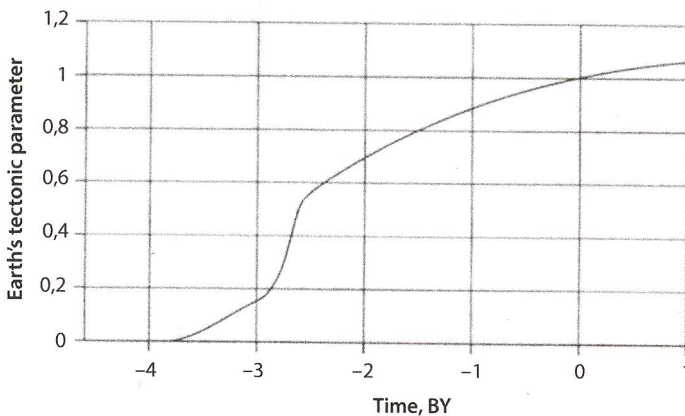
Figure 10.5 Earth's tectonic parameter defining the mantle degassing rate.

For solving Eq. 10.2, one needs to insert the marginal conditions. Assuming, as one of the marginal conditions, that $\approx 3.91 \times 10^{23}$ g of carbon dioxide are bonded within the carbonates of the Earth's crust with additional 1.95×10^{22} g of organic carbon, C_{org} (Ronov and Yaroshevsky, 1978). Prior to the reduction of the organic carbon (C_{org}) by biological processes, 5.2×10^{22} g of oxygen was bonded along with it. Therefore, the total mass of carbon dioxide degassed from the mantle is:

$$m_{CO_2} \approx (3.91 + 0.72) \times 10^{23} \approx 4.63 \times 10^{23} \, g.$$

It is harder to determine the carbon dioxide content of the Earth's mantle.

The experimental data indicates the following: (1) High-temperature distillation fractions (distillation in an oxygen atmosphere) from tempering glasses of the oceanic rift zones' tholeiite basalts usually include 20 to 170 g/ton of carbon of mantle origin carbon with an isotope shift of about −5‰ (Sakai *et al.*, 1984; Watanabe *et al.*, 1983). (2) The scatter of experimental data is too substantial for a reliable determination of average carbon and CO_2 content in the mantle. (3) The mantle carbon is in an atomic state, dispersed in silicates' crystalline grids (Watanabe *et al.*, 1983) and, therefore, not a volatile component of basalt melts. Therefore, carbon content in the CO_2 gas phase of basalt melt may be notably lower than quoted here. One can assume that the mobile carbon content in the mantle is around 30 g/ton or, recalculated for carbon dioxide, 110 g/ton. In this case the mantle contains nearly $m_{CO_2} \approx 9.11 \times 10^{23}$ g. The following relationship can be used:

$$C_{CO_2} = p_{CO_2} \cdot He^{\frac{-\Delta H}{RT}} \qquad \text{(Eq. 10.3)}$$

where p_{CO_2} is the carbon dioxide partial pressure in the atmosphere; $C_{CO_2} (\approx 0.1544 \times 10^{-3})$ is the carbon dioxide concentration in the ocean water (Kokin *et al.*, 1990) ($HCO_3^- + CO_3^{2-}$); H is the Henry's coefficient; ΔH is the entropy of the carbon dioxide dissolution in water; and T is the water temperature in deg. K.

Another aspect of Eq. 10.2 is that the Earth's degassing rate is

$$\dot{m} = m_m \chi \dot{z}. \qquad \text{(Eq. 10.4)}$$

where the derivative of the tectonic parameter $\dot{z}$ defines the Earth's tectonic activity (see Figure 10.5). For this situation, $\chi(CO_2) \approx 0.71$.

The total mass of carbon dioxide in the Earth, with C_{org} normalized for CO_2, is $m_{CO_2} \approx 9.11 \times 10^{23}$ g.

Using Eq. 10.4, one can plot the curve of carbon dioxide degassing from the mantle as shown in Figure 10.6, which indicates that the carbon dioxide degassing rate peak coincides with the period of the Earth's maximum tectonic activity about 2.7 BY ago (Figure 10.7).
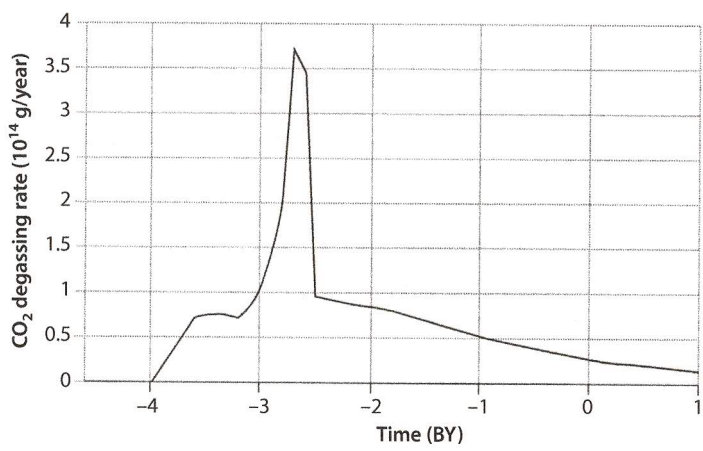
Figure 10.6 Rate of carbon dioxide degassing from mantle with time.
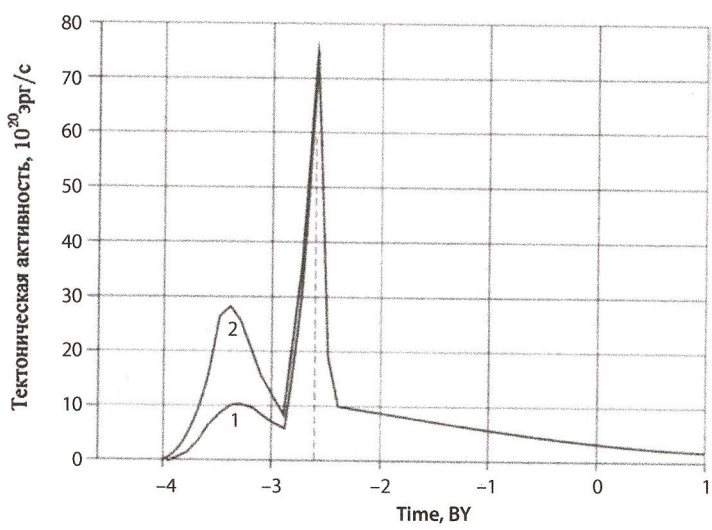
Figure 10.7 Earth's tectonic activity measured by the heat flow from the mantle, m().zQ∞: *Curve1* – Average for the Earth as a whole. *Curve 2* – Tectonic activity within a wide ring belt of the Archaean Earth crust formation above a differentiation zone of the Earth's matter. Dashed vertical line shows the time of the Earth's core separation.

Historic Content of Carbon Dioxide in the Earth's Atmosphere

The percentage of carbon dioxide in the Earth's atmosphere has changed over the geologic history of the Earth (see Figures 5.1 and 10.3). One reason the total atmospheric pressure of the Earth has varied is due to the changing composition of its various gases making up the atmosphere. When the Sun, Earth and other planets were formed, by coalescing of matter from a rotating nebula (≈4.6 BY ago), during the period of the accretion of particles forming the Earth, many volatile and nonvolatile elements from the nebular were present. Due to the centrifugal forces, the accumulation of mass at the center of this rotating planet gathered materials of heavier mass, e.g., iron, etc., whereas the lighter-gaseous elements formed the outermost layer of the Earth (atmosphere). These lighter-gaseous elements were composed of hydrogen, helium, nitrogen and other volatile-light gases of the condensing planetary nebula material.

Earth's Hadean Atmosphere (4.56 to 4.0 BY ago)

At the beginning of the Hadean time, the Earth's surface consisted of molten rock, a magma ocean and very little atmosphere. Due to the Earth's high surface temperature, water existed only in the atmosphere as vapor. Within this hot atmosphere, the lightest elements, the hydrogen and helium molecules had an average speed greater than the velocity required to escape from the Earth's gravity. Thus, they escaped from the atmosphere into space. As a result, the Earth's Hadean atmosphere lost its hydrogen and helium and all that was left in the atmosphere were the molecules of methane, ammonia, water vapor, and small percentages of nitrogen and carbon dioxide. A cataclysmic meteorite bombardment (≈3.9 BY ago) kept much of the Earth's surface in a molten state with elevated surface temperatures. The incoming impactors likely brought with them additional water, methane, ammonia, hydrogen sulfide and other gases that supplemented the Earth's earliest atmosphere as indicated in Figure 5.1.

The high surface temperature of the Earth during the Hadean time depleted the atmospheric methane through the endothermic reaction as follows:

$$CH_4 + H_2O \rightarrow CO_2 + 3H_2 \qquad \text{(Eq. 10.5)}$$

This reaction, generating carbon dioxide, requires elevated temperatures of approximately 700 °C to 1100 °C, which would have been common in

the hot crust and magma lakes of the Hadean Time. The produced carbon dioxide, readily combined with metals to form carbon compounds.

Volcanic activity began toward the end of the Hadean time, which is reflected by the increasing percentage of carbon dioxide in the atmosphere. As the Earth cooled, the surface changed from molten lava to solid rock and the Earth cooled enough for liquid-water to begin to accumulate at the higher elevations on its surface.

The major carrier of carbon in the *initial stages* of Earth's evolution during the Hadean and Archaean time, was carbon dioxide and the products of its chemical reactions. After the early depletion of methane and ammonia from the Earth's atmosphere, carbon entered the crust and the atmosphere primarily through mantle degassing.

Earth's Archaean Atmosphere (4.0 to 2.4 BY ago)

During the Archaean time, the percentage of carbon dioxide in the atmosphere increased, originating from degassing of the mantle (see Figure 5.1). The volume of volcanic carbon dioxide in the atmosphere peaked and started to decrease as the carbon dioxide was bonding with carbonate minerals. Thus, it is important, that the increase of carbon in mantle mass, M_m, at the beginning of the Archaean ($M_m = 0$) to its amount at the end of the Archean ($M_m\Sigma$) be considered. The increase of the degassing from the mantle mass is estimated in Figures 10.6 and 10.7. The total volatile component of the mantle, m_i, can be estimated as follows:

$$m_i = m_{i_0} (1 - e^{-\chi_i z}) \left\{ \frac{M_m \cdot t}{M_{m\Sigma}} \right\}, \qquad \text{(Eq. 10.6)}$$

where $M_m \cdot t$ is the mantle mass for the time $4 < t < 2.6$ BY ago. For the Proterozoic and Phanerozoic time, Eq. 10.6 can be used. It is necessary to insert the initial and boundary conditions in Eqs. 10.2 and 10.6 for the content of each component (water, nitrogen or carbon dioxide) in the Earth's external geospheres.

The rate and mass of carbon dioxide from mantle degassing is shown in Figures 10.6 and 10.7. The carbon dioxide accumulation rate in the Earth's geospheres (including the atmosphere, hydrosphere, and crust), is presented in Figure 10.8 (based on Eqs. 10.2 and 10.6).

Mantle carbon dioxide degassing is different from that of the water degassing. The reason is the lower heat of formation for water (the molecular water, $\Delta H_f^O = 57.8$, for CO_2 $\Delta H_f^O = 94.05$, and for FeO $\Delta H_f^O = 63.6$ kcal/ mol)
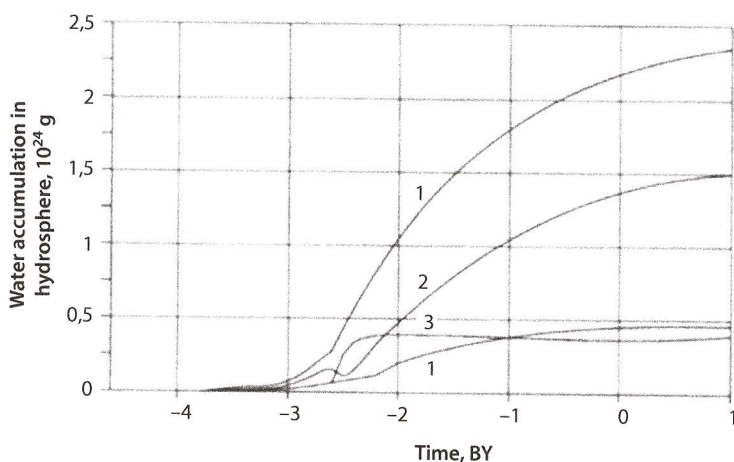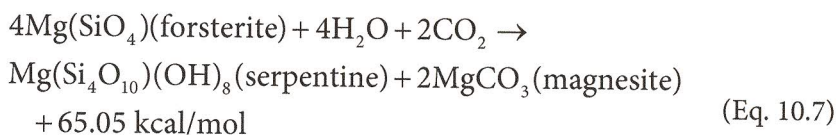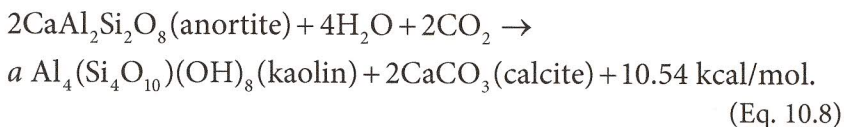
Figure 10.8 Water accumulation in the Earth's hydrosphere: *Curve 1* – Total mass of water degassed from the mantle. *Curve 2* – Water mass in the ocean. *Curve 3* – Water mass bonded in the ocean crust. *Curve 4* – Water mass bonded in the continental crust. (After Sorokhtin and Ushakov, 2002.)

and its dissociation on the metallic iron during the zonal differentiation of the Earth's matter in the Archean time. This CO_2 degassing rate peak coincides with the time of maximum tectonic activity, 2.6 BY ago (see Figure 5.2). At the same time, the water degassing was at its maximum rate ≈2.5 BY ago, that is, after the high-density Earth's core separation and after the switch in the differentiation of the Earth's matter from the zonal melting mechanism to a more quiescent barodiffusion mechanism.

If the entire volume of degassed carbon dioxide had not been bonded, but had been preserved in today's atmosphere as a gas, the Earth's partial pressure would have been ≈91 to 100 atm, which is like today's pressure on Venus, resulting in a condition where life as we know it could not exist. Life on the Earth was fortunate in that simultaneously while CO_2 was entering the atmosphere, it was being bonded into the carbonate rocks. For this reaction to occur, liquid water is required, as only then will silicate hydration be accompanied by carbon dioxide absorption with the emergence of carbonates under the following reactions:
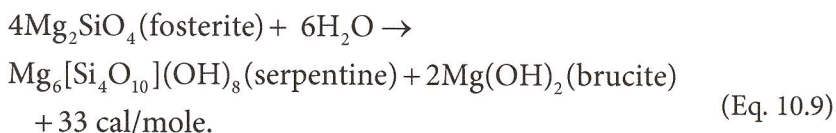
$$4Mg(SiO_4)(forsterite) + 4H_2O + 2CO_2 \rightarrow$$
$$Mg(Si_4O_{10})(OH)_8(serpentine) + 2MgCO_3(magnesite)$$
$$+ 65.05 \text{ kcal/mol} \hspace{3cm} \text{(Eq. 10.7)}$$

and

$$2CaAl_2Si_2O_8(anortite) + 4H_2O + 2CO_2 \rightarrow$$
$$a\ Al_4(Si_4O_{10})(OH)_8(kaolin) + 2CaCO_3(calcite) + 10.54\ kcal/mol.$$

(Eq. 10.8)

Therefore, the evolution of carbon dioxide in the ocean was significant in the development of the carbon dioxide partial pressure in the atmosphere (Figure 10.8).

As shown in Eqs. 10.7 and 10.8, for each two CO_2 molecules bonded in carbonates there are four water molecules used for the hydration of the rock-forming minerals of the oceanic or continental crust. Thus, when carbon dioxide is in excess within the atmosphere and hydrosphere, almost all rock hydration reactions are accompanied by CO_2 bonding in carbonates. Each unit of mass for water bonded in rocks corresponds with approximately 1.22 carbon dioxide mass units. For a carbon dioxide shortage, the hydration of portion of silicates occurs without bonding of carbon dioxide, e.g.,

$$4Mg_2SiO_4(fosterite) + 6H_2O \rightarrow$$
$$Mg_6[Si_4O_{10}](OH)_8(serpentine) + 2Mg(OH)_2(brucite)$$
$$+ 33\ cal/mole.$$

(Eq. 10.9)

The total mass of water bonded in the Earth's crustal rocks is the sum of Curves 3 and 4 in Figure 10.9. Today, this sum is equal to $(0.358 + 0.446) \times 10^{24} = 0.804 \times 10^{24}$ g. This enables the calculation of carbon dioxide mass, which could have been bonded in carbonates. This mass turns out to be equal to 9.81×10^{23} g, which is a quantity more than twice that contained within carbonates $(3.91 \times 10^{23}$ g). A significant portion of the Earth's crustal rocks were hydrated in Proterozoic and Phanerozoic time due to a substantial carbon dioxide deficit under Eq. 10.9 without forming carbonates.

Life within the ocean has always been limited by the oceans' phosphorus content. Phosphorus solubility in water is relatively low (Schopf, 1982). Therefore, the absolute mass of the organic matter in the ocean is always proportionate with its mass. The organic carbon mass, converted to carbon dioxide, in the Archaean and Proterozoic time, can be estimated considering that it is approximately proportionate to the mass of water in the global ocean (Figure 10.9, Curve 2).

Along with the CO_2 that bonded in rocks and the biomass, part of this carbon dioxide, as anions HCO_3^-, was dissolved in oceanic water. One can
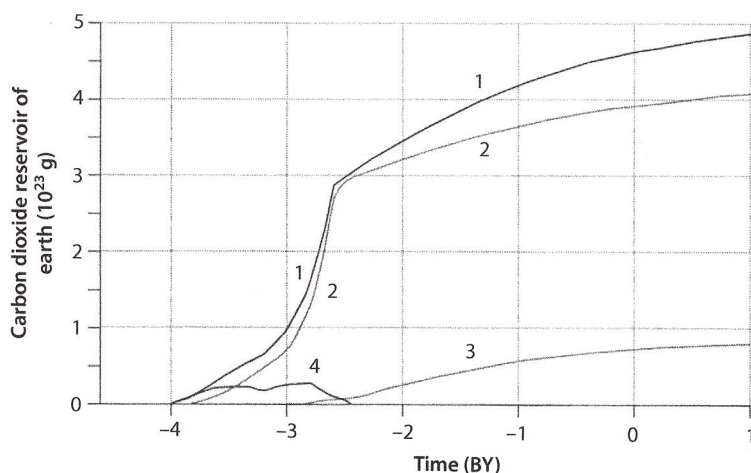
Figure 10.9 Mass of carbon dioxide bonded in the Earth's crust and present in the Archaean atmosphere: *Curve 1* – Mass of CO_2 degassed from the mantle. *Curve 2* – Mass of CO_2 in the Earth's crust carbonates. *Curve 3* – Organic carbon mass normalized for CO_2. and *Curve 4* – CO_2 mass in the Archaean atmosphere.

estimate this portion of CO_2, but it is necessary to remember that carbon dioxide solubility in water, under Henry's law (Sorokhtin and Ushakov, 2002), is directly proportionate with its partial pressure in the atmosphere. The relationship of the carbon dioxide gas solubility versus pressure and temperature in water is presented in Figure 10.10.

In Figure 10.11, the mass of carbon dioxide degassed from the mantle (*Curve 1*) is compared with the mass of carbon dioxide bonded in carbonates (*Curve 2*) and with total carbon dioxide mass in the carbonate and biogenic reservoirs (*Curve 3*). The organic carbon (in conversion to carbon dioxide mass) accumulation in the oceanic deposits is presented by *Curve 5*.

Earth's Proterozoic and Phanerozoic Atmosphere (2.4 BY ago to today)

At the beginning of the Huron Orogeny ($\approx$2.4 BY ago) the carbon dioxide partial pressure in the Early Proterozoic atmosphere drastically declined by about a factor of 10,000 to an equilibrium level of about 1.0 to 1.5 mbar (Chumakov, 1978). The total atmospheric pressure decreased from 5 to 6 bars by the end of the Archean to 1.4 bar in the Early Proterozoic (see Figure 10.12). The entire process of removal of carbon dioxide from the atmosphere during the Archaean/Proterozoic time boundary likely did

impossible to determine. During Archaean, there was a small volume of water in the Archaean oceans, and the mass of bonded carbon dioxide was substantially smaller than the mass of carbon dioxide mass degassed from the mantle. This helps explain the emergence of a carbon dioxide atmosphere during the Archaean.

The separation of Earth's core and the formation of the oceanic crust's serpentinite layer occurred between the end of the Archaean and beginning of the Proterozoic time ($\approx$2.5 BY ago) because of a drastic decline in the Earth's tectonic activity. There was a significant increase in the rate of carbon dioxide bonding in carbonates (Eqs. 10.7 and 10.8), which resulted in the accumulation of oceanic deposits (Sorokhtin and Ushakov, 2002). Therefore, in the Proterozoic and Phanerozoic time, the overwhelming portion of carbon dioxide was bonded in carbonates and organic matter, and only a small portion of carbon dioxide entered the atmosphere and hydrosphere.

As a result, in the Early Proterozoic, the atmospheric carbon dioxide partial pressure sharply declined by a factor of about 1,000 (to a few millibars). This resulted in the accumulation of massive carbonate deposits in the Early Proterozoic. However, as carbonate rocks have low resistance to weathering, most of them were redeposited in younger formations. In the Early Proterozoic there was a significant decline in the carbon dioxide partial pressure in the nitrogen-carbon-dioxide Archaean atmosphere. According to Eq. 2.25, there was a substantial temperature decline and climate cooling of the Earth during the Early Proterozoic. The average temperature of the oceanic, near-bottom water dropped from 70 °C to 30–40 °C (see Figure 1.3). Figure 10.12 displays the carbon dioxide partial pressure evolution in the Earth's atmosphere in consideration of its partial dissolution in oceanic water.

As Figure 10.12 shows, the carbon dioxide partial pressure in the Archaean reached 3 to 4 atm. because there was so little water in the Archaean oceans. The bonded carbon dioxide mass at that time was significantly lower than the mantle degassing of the carbon dioxide mass (see Figure 10.11). Therefore, in the Archaean time, the bulk of the mantle carbon dioxide degassing must have been in the ocean and stored as dissolved gas in the oceanic water. Thus, the oceans were saturated with carbon dioxide. As the average oceanic water temperature was 60–70 °C, the oceanic water was warm, acidic and an aggressive solvent for the ore elements. This resulted in the saturation of the oceanic water by many ore elements, e.g., Au, U, Cu, Pb, Zn and sulphides. When the ocean cooled down and carbon dioxide was bonded with the carbonates, in the Early Proterozoic, the oceanic water remained warm but became chemically neutral (pH $\approx$ 7). That
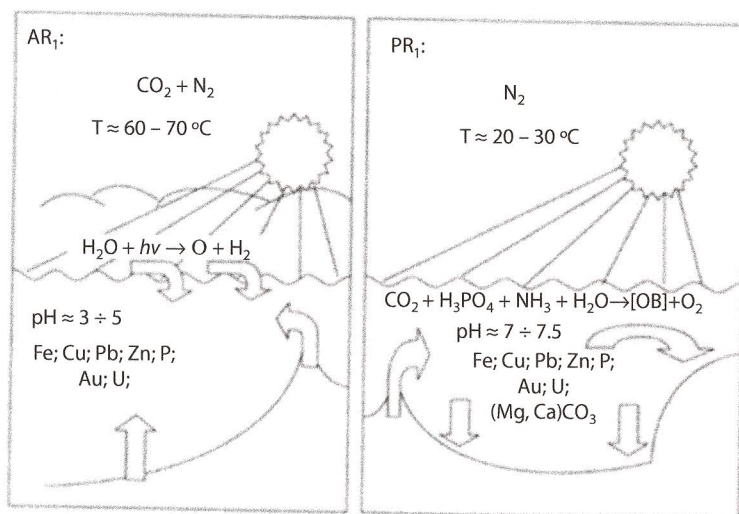
Figure 10.13 The formation of unique stratiform ore deposits in the Early Proterozoic due to the precipitation of ore elements after the bonding of Archaean atmosphere carbon dioxide in carbonates and cooling down of the oceanic water between Archaean and Proterozoic time (OB in the equation is organic matter). The arrows indicate arrival paths of ore elements in the oceans and their precipitation in Early Proterozoic (the descending arrows in Archaean show runoff from continents).

was why the ore elements precipitated (Figure 10.13) forming very rich stratiform deposits of several mineral resources (i.e., a unique gold-uranium deposit, Witwatersrand, South Africa, or copper deposit, Udokan, Siberia).

Anthropogenic Carbon Dioxide in the Atmosphere

The anthropogenic carbon's effect on the Earth's climate has often been evaluated on the assumption that greenhouse gases absorb heat of radiation in the troposphere without the understanding that most heat transfer in the troposphere is by convection. Earlier in this book, it was shown that an increase in the atmosphere's carbon dioxide content does not increase the atmosphere's absorption of energy from the Sun, resulting in an increase in temperature, but rather it decreases the absorption of energy, thus cooling the troposphere.

Various estimates of the volume of anthropogenic carbon dioxide, released by burning of natural fuels are on the order of 7 to 10 billion tons or 1.9 to 2.7 billion tons of carbon per year. This anthropogenic and natural amount of carbon dioxide is shown in the temperature chart (dashed

line) for the past 2,000 years (Figure 10.14). An examination of this figure indicates that since the seventeenth century, there may have been a natural increase in temperature of one degree. It also should be noted that the Earth's temperature is cyclic, fluctuating 1 degree over ≈ 1000-years due to natural, rather than man-made causes. In effect, it is not determinable if there is a temperature increase or decrease over short period of time. Human emissions of CO_2 in Figure 10.14 (dashed lin), show a very steep increase, but at the same time this increase has had a negligible effect on the Earth's rate of temperature increase.

As discussed earlier in this book, a significant increase in the carbon dioxide content in the atmosphere will result in cooling the troposphere, whereas a reduction in the carbon dioxide content would increase the Earth's temperature. Again, this statement is based upon the understanding of how heat is transferred in the troposphere, as most heat in the troposphere is transferred by conduction (adiabatic) and not radiation (see Eq. 2.25 and Chapters 2 and 3). To compute the temperature of a planet's
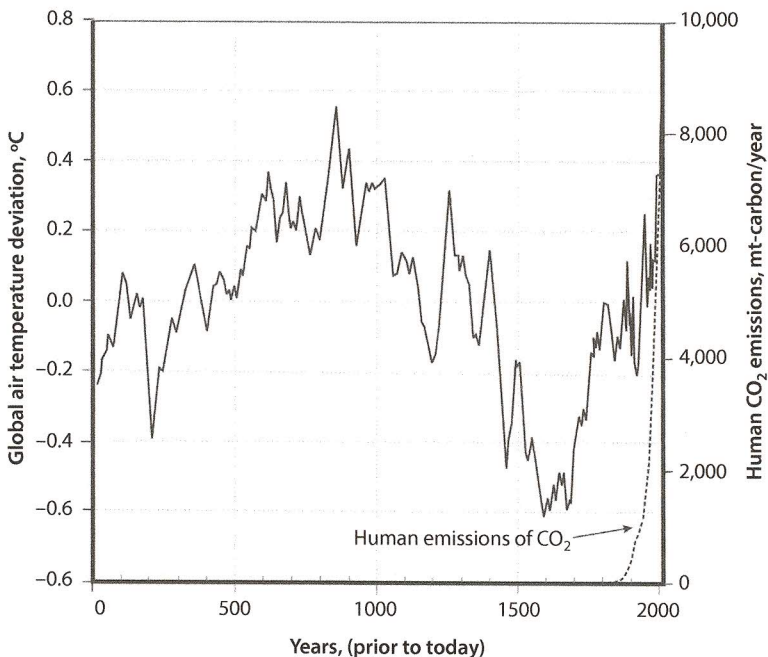
Figure 10.14 Schematic showing relationship between global air temperature and human CO_2 emissions from A.D. 16 to 2010. (Evans, 2010, states that these emission figures are not perfect because they omit some minor causes, e.g., deforestation; however, these are relatively minor). Evans also noted that the temperatures frm 1850 to 1980 are suspect because they were obtained from land-thermometers. (Modified after Evans. 2010.)

atmosphere, consisting of a variety of gases, one only needs to know the components (type gases) and their contents in the atmosphere along with total pressure of the atmosphere. The partial pressure vs time for the Earth's history is presented in Figure 10.15. The Earth's (total) atmospheric pressure is the summation of the partial pressures of all the component gases. Knowing the total atmospheric pressure of a planet, one can then use the following equation to compute the atmospheric temperature (This equation was developed in Chapter 2),

$$T = b^{\alpha} \left[\frac{S(1-A)}{\sigma \left\{ 4 \left(\frac{\frac{\pi}{2} - \psi}{\frac{\pi}{2}} \right) + 2 \left(\frac{\psi}{\frac{\pi}{2}} \right) \left(\frac{2}{1+\cos\psi} \right) \right\}} \right]^{\frac{1}{4}} \left(\frac{p_t}{p_o} \right)^{\alpha} \qquad \text{(Eq. 2.25)}$$

where S is the solar constant at the distance of Earth from the Sun, σ is the Stefan-Boltzmann constant; A is the planet's albedo (for the Earth $A \approx 0.3$); ψ is the precession angle; p_t is the atmospheric pressure; p_o is the atmospheric pressure at sea level, a is the adiabatic exponent + (for the Earth, $a = 0.1905$). and the coefficient b is defined by the following expression:

$$b = \frac{1}{(1-A)^{\frac{1}{4\pi}}} \qquad \text{(10.10)}$$
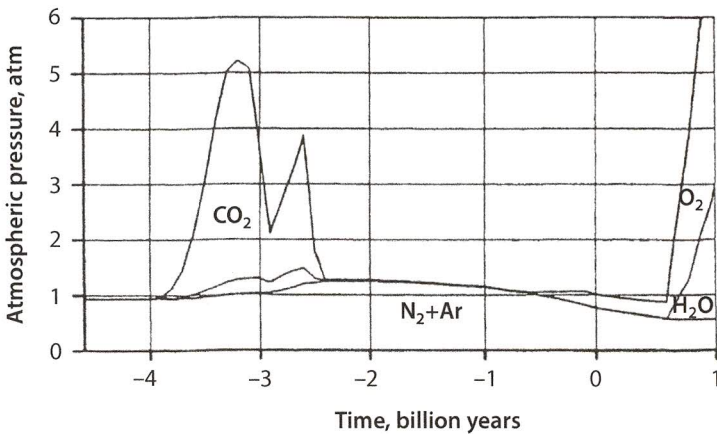
Figure 10.15 Variation of the atmospheric composition and pressure for the Earth over time. (Modified after Sorokhtin, 2005.)

The coefficient for today's atmosphere on the Earth is $ba = 1.093$. Although the value of b does not change if the composition of atmosphere changes the value of ba changes with the value of adiabatic constant a. if the composition of the planet's (Earth's) atmosphere changes.

Eq. 2.25 can be used for comparison of temperature characteristics for the same planet with various gas compositions in its atmosphere. Looking at an extreme case, if one assumes that the existing nitrogen-oxygen atmosphere of the Earth is replaced entirely by a carbon dioxide atmosphere, with the same atmospheric pressure of 1 atm and adiabatic exponent $a = 0.1428$, then the value of $ba = 1.597^{0.1428} = 1.069$ and the near-surface temperature of the Earth would decline to 281.6 K, i.e., the atmosphere would then cool by 6.4 °C. This fact again exposes the statement that *adding carbon dioxide to our atmosphere would warm the atmosphere* is false. Many who support global warming caused by man adding carbon dioxide to the atmosphere do not understand this. Scientific evidence shows that *as the content of the carbon dioxide in the atmosphere increases, the atmospheric temperature will decrease if the total atmospheric pressure remains the same.*

Another example is the hypothetical situation where the Earth's nitrogen-oxygen atmosphere is totally replaced by a carbon dioxide atmosphere and then constructing the distribution of temperature (at the same atmospheric pressure) for the corresponding elevation. The temperature will be lower than that for an equivalent nitrogen-oxygen atmosphere of the Earth.

Figure 10.16 displays the atmospheric curves showing pressure versus temperature for the Venus troposphere consisting of a carbon dioxide (*Curve 1*) and a hypothetical Venus atmosphere of nitrogen-oxygen (*Curve 2*). In Figure 10.16, *Curve 1*, the graph of temperature distribution for a 100% carbon dioxide troposphere lies below the graph of the nitrogen-oxygen, *Curve 2*, for all pressures (elevations). Correspondingly, the near-surface temperature for the carbon dioxide troposphere occurs 6.4 °C lower than that for the nitrogen--oxygen atmosphere and not considerably higher, as some scientists still, erroneously, continue to believe. These curves demonstrate that increasing the percentage of carbon dioxide in the Earth's atmosphere can only decrease (cool) the temperature of the Earth's troposphere. Insignificant changes in the partial-pressure of carbon dioxide (few hundred ppm) would not have a noteworthy influence on the ability of the troposphere to absorb energy.

By analogy, if one assumes that the existing carbon dioxide atmosphere of Venus was entirely replaced by a nitrogen-oxygen atmosphere, at the same pressure of 90.9 atm, then its surface temperature would increase from 735 to 796 K (462 to 523 °C). Thus, one can once again see, that for
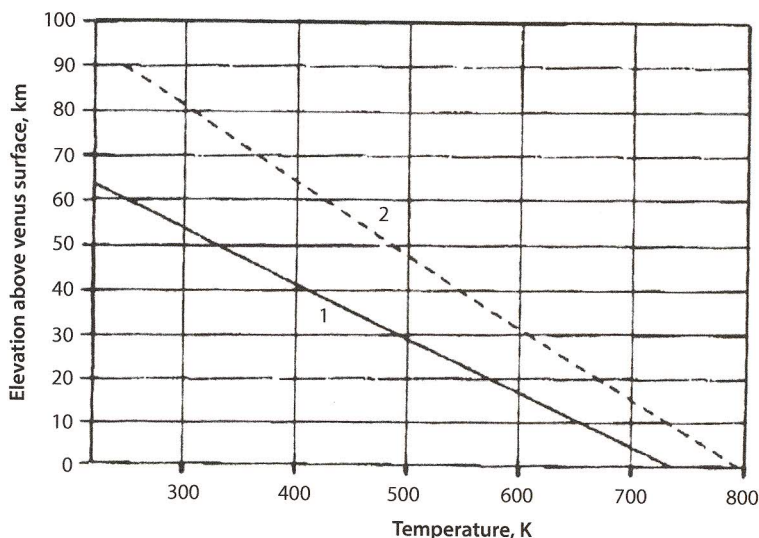
Figure 10.16 Averaged temperature distributions in the troposphere of Venus: *Curve 1 –* Today's carbon dioxide troposphere and *Curve 2 –* hypothetical model of a nitrogen-oxygen atmosphere at the same conditions. (After Sorokhtin *et al.,* 2007, figure 7.10, p. 274.)

an oxygen-nitrogen atmosphere, increasing the carbon dioxide content, under the same other conditions, would lead to cooling of the entire planet's atmosphere.

Using Eq. 10.9, after differentiation and transition to finite differences (see also Khilyuk and Chilingar 2003), and if the atmospheric pressure, $p_s \approx 1$ atm, one obtains the following equation:

$$\Delta T_s \approx T\alpha(\Delta p_s) \qquad \text{(Eq. 10.11)}$$

where ΔT_s is the change in temperature at sea level attributed to the corresponding change in atmospheric pressure Δp_s, the average Earth's temperature $T = 288$ K and the adiabatic exponent $\alpha = 0.1905$. For instance, under the doubled carbon dioxide concentration in the Earth's atmosphere from 0.046 to 0.092 mass % (as anticipated by the year 2100), the pressure increase, Δp_s, would reach 0.46 mbar. Using Eq. 10.11, $\Delta T_s \approx +0.025°C$. This temperature rise is not associated with the change in the atmosphere's composition, but due to the increase in atmospheric pressure. Thus, the anthropogenic carbon dioxide releases into the atmosphere have no practical influence on the greenhouse effect in the atmosphere.

According to Henry's law, most of the carbon dioxide released into the atmosphere is dissolved within the oceanic water, and upon hydration of the oceanic crust where it can be bound in the carbonates (some CO_2 is taken up by plants). Part of the atmospheric oxygen, together with carbon, is also fixed in carbonates.

Upon hydration of oceanic crust rocks, a portion of carbon dioxide is reduced to methane. Today, due to the formation of carbonates and methane generation, 2.3×10^8 tons/year of carbon dioxide are removed from the ocean and, therefore, removed from the atmosphere. The potential of this CO_2 removal mechanism, however, is much higher. Although the period of time for this geochemical cycle may be over 100 years, the effect is cumulative.

Together with anthropogenic carbon dioxide, some oxygen is also removed from the atmosphere. Based on the carbon dioxide molecular stoichiometry, almost 2.3 g of oxygen is removed from the atmosphere for each gram of carbon. Provided the ocean and vegetation absorbs all excess carbon dioxide after the year 2100, this will likely result in a decline of atmospheric pressure by ≈ 0.34 mbar and, therefore, results in an additional climatic cooling by $-8.2 \times 10^{-3}\,K \approx -0.008°C$. It appears that the life activity of plants could almost completely restore the equilibrium distorted by humans through an accelerated biomass growth.

Historic Effect of Anthropogenic Carbon Dioxide

Today, a major environmental concern among some is the production and burning of hydrocarbons and the subsequent release of the carbon dioxide to the atmosphere. It is thought by these individuals, without scientific evidence or understanding of the tropospheric thermal dynamic heat exchange, that humans are putting carbon (in the form of carbon dioxide or methane) into the atmosphere and that this anthropogenic carbon will be responsible for *global warming*. The prior discussion theoretically proves that changes of carbon dioxide in the Earth's atmosphere by addition of a greater amount of carbon dioxide will cool, not warm, the troposphere. Looking at the Earth's historical temperature charts for confirmation of the theoretical evidence, Figure 10.14 helps to confirm that recent minor changes in tropospheric carbon dioxide concentration has neither cooled nor warmed the atmosphere. The significant rate of increase in carbon dioxide concentration (slope of line) has not affected the temperature cycle.

As stated in Chapter 1, the concept of carbon dioxide warming the atmosphere began with Syante Arrhenius, a Swedish scientist, who was the *first* to claim that fossil fuel combustion may result in enhanced global warming

(Maslin, 2004; in: Enzler, 2015). He proposed that there was a relationship between atmospheric carbon dioxide concentrations in the atmosphere and global temperature. Since then, the concept has been taken as obvious by many without *verification* (Budyko, 1997; Global warming, 1993; Greenhouse effect, 1989).

The arguments for, against and why global warming occurs, have grown within the scientific community since Syante's proposal, possibly due to not fully understanding how heat is transferred within the troposphere. In the upper atmosphere, where there are fewer molecules and a pressure less than 0.1 atm, radiation is the primary source of heat transfer. In the troposphere (the minimum pressure is 0.3 atm), where there are many more molecules per unit volume, the primary mechanism for heat transfer is conduction (see Chapter 2 and 3). The effect of carbon dioxide concentration in the atmosphere is better understood today because of the studies of the historic-atmosphere found in ice cores drilled in the Antarctica and Greenland ice sheets. These studies show a natural cycling of the Earth's temperature, some fluctuating for periods of $\approx 100,000$ years/cycle, as ancient temperatures were directly measured in the ice-sheet-cores, for the last million years. A temperature chart from Antarctica (Figure 10.17) shows cyclic periods of temperature (*Curve a*) and percentage of carbon
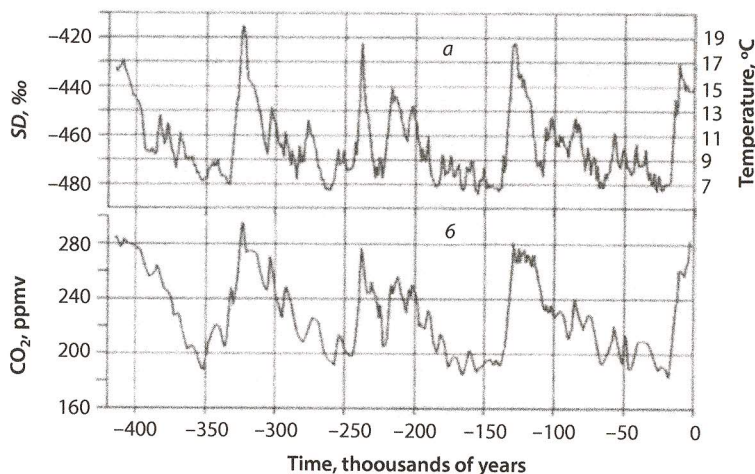
Figure 10.17 *Curve a* – Correlation between the isotopic air temperature and time. *Curve b* – Correlation between the atmospheric carbon dioxide concentration (ppmv) and time over the past 420,000 years at the Antarctic station Vostock, Antarctica. The CO_2 concentration and temperature data were derived from ice cores of a well drilled at that station to a total depth of 3,623 m. The temperature scale is the authors' interpretation of the data. (Data provided by V. M. Kotlyakov.)

dioxide content (*Curve b*) of approximately 100,000 years/cycle for the past 400,000 years. It should be further pointed out that the carbon dioxide curve peaks occur after temperature increases in the tropospheric temperature chart by 400 to 1,000 years, as determined by many historic atmosphere studies in Antarctica and Greenland.

Of importance is the fact that the atmospheric carbon dioxide content (*Curve b*), follows the temperature (*Curve a*). This relationship is common to the many ice core studies done in Greenland and Antarctica, although the period of time that the carbon dioxide curve follows the temperature cure varies between 400 and 1,000 years. The only likely conclusion is that the rise in measured temperature results in an increase of the atmospheric carbon dioxide content (see Chapter 15 for a detailed description).

It has been proposed by several investigators, including Robertson and Chilingar (2017), that this phenomenon of increasing carbon dioxide is the result of rising ocean water temperature (rising temperature reduces the carbon dioxide gas solubility in the ocean) and forcing the dissolved carbon dioxide in the ocean water (reservoir) into the atmosphere (reservoir) (see Robertson and Chilingar, 2017, Chapter 4).

Today, some investigators, ignoring the Earth's historic temperature charts, have erroneously suggested that Earth's global temperature is currently warming. However, Monctkon (2015) in a review of Earth's lower atmosphere temperature data, obtained by satellite, has noted little evidence of either warming or cooling for the past 17 years. Bastasch (2015) in a similar study, after a review of the data and collection methods from America's most advanced climate monitoring system, the National Oceanic and Atmospheric Administration (NOAA), also found that the U.S. has undergone a mild cooling trend over the last decade, despite recent statements by some scientists claiming that *global warming* has been accelerated worldwide. Figure 10.18 was prepared by the U.S. Climate Reference Network, developed by NOAA gathered over the past ten years to provide *high-quality* climate data. NOAA's network consists of 114 stations across the U.S.

A review of temperature deviation data over the past 2,000 years reveals that the Earth's temperatures have been mildly cyclic over this period and that we are currently in a *modern warm period* (Figure 10.19). An examination of this figure indicates a cycling of temperature and an overall gentle cooling period from AD 1000 to 1700 and that the temperatures are: (1) cyclic and (2) today's warm temperatures are cooler than the earlier medieval warm period.

Evans (2010) studied the relationship between global atmospheric carbon dioxide content, human generated carbon dioxide emmissions versus
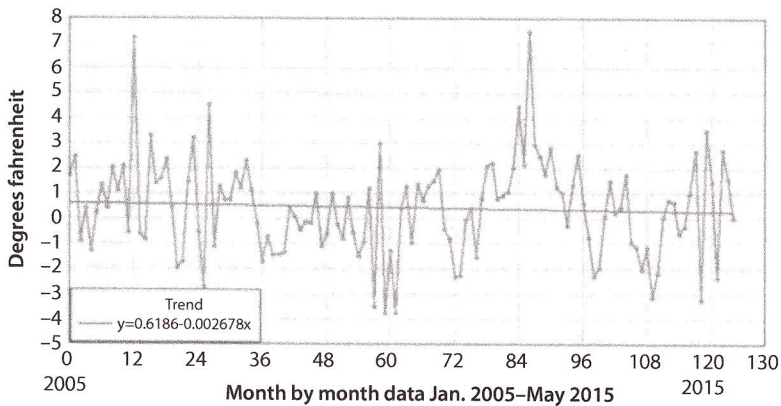
Figure 10.18 Contiguous U. S. average temperature anomaly (°F) from 2005 to 2015. (After Watts, 2015; source NOAA U.S. Climate Reference Network, USCRN.)
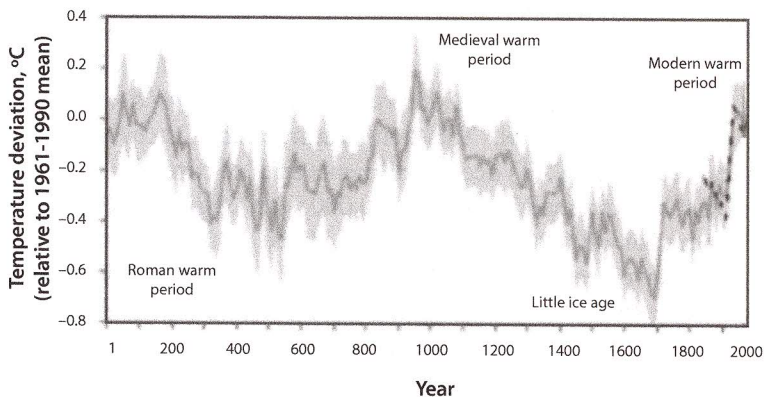
Figure 10.19 A reconstruction of temperature deviation, to the 1961 - 1900 mean temperature for the Earth's Northern Hemisphere during the last two millennia. The fact that the current warm period is not exceptional is clearly shown. (Modified after Geografiska Annaler, 2010.)

global temperature from A.D. 16 to 2010. He noted that the significant increase in human carbon dioxide emissions shown in Figure 10.14, appeared to have had little or no effect on the cyclic global temperatures over this period. In fact, there is no justification for claiming that increased carbon dioxide content due to human activity can increase the global temperature. Examining only the supposed human-generated carbon emissions and then comparing the data to the global temperature charts, there is no significant relationship between the increase of man-made

emissions of carbon content, in the atmosphere and the temperature increase (Figure 10.14). This also assumes that the increase in global temperature is due to the increased CO_2 emissions and no other factors, e.g., the Sun/Earth relationship and volcanism. Further supporting the notion that CO_2 emissions are not a factor in raising global temperatures, Evans (2010) noted that this figure shows that today's global warming trend was initiated prior to 1700; however, the additional man-made emissions had negligible effect on temperatures from 1850 to 1940, indicating that there is no possibility that humans initiated global warming. Evans (2010) data also questions if there has been any significant global warming since 1998. Since a quarter of all emissions caused by human activity have occurred in the past 12 years, why have we not seen a greater increase in temperature? Jones (2009) stated that perhaps man-made emissions of CO_2 have merely aggravated the current global warming trend. He also pointed out that 85% of all such emissions have occurred after 1945. The post-World War II industrialization greatly accelerated human emissions as shown in Figure 10.17.

Hiebe (2009) has suggested that we are currently in an ice age climate period. "However, *for the last 10,000 years we have enjoyed a warm but temporary interglacial vacation.*" This temperature record is chronicled in the geological records, e.g., (1) ocean sediments and ice cores from permanent glaciers that have formed in the last 750,000 years and (2) interglacial periods that occur at $\approx$100,000-year intervals. Hiebe (2009) also suggested that these cycles have been occurring for the past 2 to 4 MY although the overall Earth's temperature, as investigated by Robertson and Chilingar (2017) and by several other investigators utilizing many independent methods, has been continuously cooling for the past 65 MY (see Figures 1.3, 1.4, and 1.5).

The above discussion leads to only one conclusion: the theoretical effect of increasing the content of carbon dioxide emissions doesn't lead to warming of the troposphere and this theory is strongly confirmed by historical evidence.