3. Atmosphere: Composition, Origin, Evolution and Climate

This Chapter will show you that

(a) our atmosphere changed over geological time scales drastically,
(b) the chemical composition of the atmosphere is mainly a result of life processes,
(c) the chemical composition has been about constant over the last 10000 years despite of cyclic variations, and
(d) climate is being described as the long-term physico-chemical status (including its statistics) of our earth's system.

Content

Note: This version will be processed from time to time – look on the following date of edition: May 2004 (2ⁿᵈ edition, 1ˢᵗ in October 2003)

3.1   Chemical composition of air

3.1.1 Concentration measures

As mentioned in the introduction of this script series (part 1), *natural air*, i.e. air uninfluenced by humans, consists of a large number of chemicals. The main constituents of natural air are shown in Table 3.1. A lot of components not listed there, escaped from natural sources into air, are within very small concentrations (below 1 ppb). Table 3.2 shows the ranges of magnitude between different groups of constituents, which we now distinguish in major, minor and trace species as well as condensed phases (liquid and solid). The range of concentration makes it clear how sensitive analytical methods need to work for air chemical monitoring. Also, this is the reason that many trace gases have been found in the recent past, e.g. CS_2 and COS in 1976.

Table 3.1 Present chemical composition of dry[a] remote air

species	concentration
nitrogen	78.084 %
oxygen	20.946 %
argon	0.934 %
carbon dioxide	360 ppm (variable and increasing)
neon	18.18 ppm
helium	5.24 ppm
methane	1.6 ppm (increasing)
krypton	1.14 ppm
hydrogen	0.5 ppm
nitrogen dioxide	0.3 ppm (increasing)
xenon	0.087 ppm

[a] Note: water vapour may be in the range up to 3 % and must be included in the chemical composition of (wet) air

Table 3.2   Ranges of concentration of air constituents (in Vol-% if not otherwise marked, based on dry air; presence of water vapor will change the numbers slightly); number concentration in cm^{-3}

constituent	species/phase	concentration	
main components	nitrogen	78 %	
	oxygen	21 %	
	noble gases	0.09 %	
by-components	water vapor	0.001-0.02 % based on humid air	
	carbon dioxide	0.035 %	
cloud water	liquid water	10^{-4} %	$(n \approx 300)$
	dissolved species	$\geq 10^{-4}$ mass-% related to cloud water	
rainwater	dissolved species	$(\leq 10^{-4}$ mass-% related to rainwater	
trace gases	methane	$1{,}6 \cdot 10^{-4}$ %	
	SO_2, NO_x	$10^{-9} - 10^{-5}$ %	
	VOC (NMHC)	$10^{-8} - 10^{-6}$ %	
atmospheric aerosol	continental	10^{-8} % (50 µg m^{-3})	$(n \geq 500)$
$(r < 1$ µm)	maritime	10^{-10} % (< 10 µg m^{-3})	$(n \geq 100)$
radicals	OH, HO_2, NO_3	$\leq 10^{-13}$ %	$(n \leq 10^7)$

You see that the range of concentrations covers more than 15 orders of magnitude. In Tables 3.1 and 3.2 different measures for concentrations have been used. According to the SI units (Système International d'unités), the modern metric system of measurements, physical quantities should espressed only by these base units; for the purpose of concentration we need the quantities mass, amount of substance and length with the units kilogramm (kg), mole (mol) and meter (m). Area (m^2) and volume (m^3) are so-called derived units, defined in terms

of the seven base quantities via a system of quantity equations. Thus, a concentration is defined as the ratio of an *extensive* quantity[1] (mass, volume, amount, number) to the volume:

$$c_i = Q_i/V. \tag{1}$$

It also can be related to a surface (surface concentration in contrast to volume concentration). An *intensive* quantity (e.g. amount of substance, volume) is related to an amount in space. When putting together or separating two identical physical systems, extensive quantities increases or reduces whereas intensive quantities (e.g. pressure and temperature) do not change.

Consequently, one has to differentiate between concentration, molality, fractions and ratios despite the last three figures are also expression for "concentrations". *Fractions*, normaly named to as *mixing ratios* are widely used in atmospheric sciences because they are independent from pressure and temperature. They are given as ratios between masses, volumes and moles and named by units like percent, % (10^{-2}), promille, ‰ (10^{-3}), part per million, ppm (10^{-6}), part per billion, ppb (10^{-9}) und part per trillion, ppt (10^{-12}). To distinguish among mass and volume ratios, the affixes (m) or (V) are used but mostly leaved out. The ratios are defined according

$$x(m)_i = m_i/\Sigma m_j \qquad\qquad x(V)_i = V_i/\Sigma V_j \qquad\qquad x(n)_i = n_i/\Sigma n_j;$$

where total mass $\Sigma m_j = m$, total volume $\Sigma V_j = V_g$ ($\equiv V$) and total mole $\Sigma n_j = n$. Only volume related ratios are common in the gase phase; for condensed (liquid and solid) phase often the mass ratio is used.

The recalculation between concentration and ratios is based on the general (ideal) gas equation:

$$pV = n\,\mathbf{R}T, \tag{2}$$

where p pressure, $\mathbf{R}$ gas constant and T temperature. In a mixture of gases like air this equation can be used for each gas (i):

$$p_iV = n_i\,\mathbf{R}T \qquad\qquad pV_i = n_i\,\mathbf{R}T$$

and it follows

$$n_i/n = V_i/V = m_i/m = p_i/p = x_i(n,V,p).$$

Now resubstituing n by Eq. (2) and taking into account that $n_i = m_i/M_i$ (M mole mass) and $c(m)_i = m_i/V$, it follows

$$x_i = n_i/n = \frac{n_i}{pV}\mathbf{R}T = \frac{m_i}{V}\frac{\mathbf{R}T}{p} = c_i(m)\frac{\mathbf{R}T}{M_ip}. \tag{3}$$

Thus, the molar and volume mixing ratio is identical with the ratio between the partial pressure and the total pressure, where $\Sigma p_i = p$. However, because air also contains small amounts of condensed matter (aqueous droplets called *hydrometeors* and solid particles called

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[1] Physical quantity (or property) whose magnitude is additive for subsystems (vice versa: intensive property). *Intensive* quantity: Any property of a system that is not altered by removal of mass from the system, for example, temperature.

aerosol particles), more exactly one has to consider that

$$V_{air} = V_g + V_{aq} + V_s \approx \Sigma V_j + V_{aq} \approx V_g.$$

The volume of the solid compartments generally can be neglected (cf. Table 3.2) and only in presence of clouds and describing not very water soluble gases (e.g. CO_2, SO_2, NH_3) the *reservoir distribution* $q = n_{aq}/n_g$ must be considered taking into account the ratio V_{aq}/V_g:

$$q = n_{aq}/n_g = H_{eff} (V_{aq}/V_g) \mathbf{R}T; \tag{4}$$

where $V_{air} = V_{aq} + V_g$; $H_{eff} = c_g/c_{aq}$ is the effective *Henry* constant, i.e. c_{aq} represents to sum of the overall physically and chemically dissolved substance (i).

Many measurements (esp. from Governmental Environmental Agencies) are given as mass concentration (e.g. in µg m^{-3}). To express it in a mixing ratio (e.g. in ppb), simultaneous measured pressure and temperature must be known (see Eq. 3). The following Table 3.3 shows conversion factors for some trace gases (at 1 atm, 298 K)[2].

Table 3.3 Recalculation factors between mass concentration and fraction

trace species		$x(v)_i$ in ppb	$c(m)_i$ in µg m^{-3}
ozone	O_3	1	1.96
hydrogen peroxide	H_2O_2	1	1.39
sulphur dioxide	SO_2	1	2.63
nitrogen monoxide	NO	1	1.22
nitrogen dioxide	NO_2	1	1.89
nitrous acid	HNO_2	1	1.92
nitric acid	HNO_3	1	2.56
ammonia	NH_3	1	0.69
benzene	C_6H_6	1	3.23

In case of very small concentration as found for radicals (sub-ppt), is is useful to use *number concentrations* as a measure:

$$c(N)_i = N_i/V,$$

where N denotes the number of particles (molecules, atoms etc.).

This measure also frequently is use for the condensed phase to express the number of droplets or aerosol particles in a volume of air (note the comments above according to the definition of air volume); as unit is (particle)·m^{-3} (for the condensed phase) and (particle)·cm^{-3} (for molecular substances) in use[3]. Another important concentration measure for atmospheric aerosol is the mass concentration c(m), mostly given in µg m^{-3}. It is meant also TSP (*total suspended matter*). Chemical content within atmospheric aerosol particles can be related to TSP (in ppm or µm g^{-1}) but also to the air volume (e.g. in amount of Pb in m^{-3}). The last figure follows from

$$c_i(m) = x_p(m)_i \cdot TSP.$$

Because chemical composition of particles is (characteristically) changing with diameter, it has been defined aerosol fractions, presently PM_1, $PM_{2,5}$ und PM_{10} (particulate matter

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[2] More exactly 1.01325 bar (= 1.01325·10^5 Pa) and 298.15 K.
[3] LWC, however, will be given in literature mostly as mass concentration c(m) in g m^{-3}. Assuming the density of 1 kg m^{-3}, often it is written only [Volume^{-1}]; both measures are identicall.

according to its effective separation diameter in μm). To characterize atmospheric aerosol from optical and surface chemical points of views, frequently the total surface is measured:

$$c(s) = s/V; \quad s = \Sigma s_j.$$

Similar characteristics are used for *hydrometeors* (cloud, fog, rain droplets), number concentration (droplets/volume), which mostly is given as volume mixing ratio $x(V)$, the LWC (*liquid water content*)[4]. Chemical composition of atmospheric droplets is given in different measures: mass, molar and equivalent concentration. Because aqueous phase concentration depends (beside other parameters) strong from LWC (due to microphysical processes), it is extremely useful (esp. for comparing measurements among different sites) to relate the aqueous phase concnetration of the air volume:

$$c_i(m) = c_{aq}(m)_i \cdot LWC \qquad c_i(n) = c_{aq}(n)_i \cdot LWC.$$

Considering ionic species, it is useful to take equivalent concentrations, derived from molar figures taking into account the ionic charge number ($e = 1$ für univalent and $e = 2$ for bivalent ions etc.):

$$c_i(eq) = c_i(n) \cdot e.$$

3.1.2 Residence time

An useful measure for atmospheric trace species is the *residence time*[5] which is defined to be the mean time of a species existing in the atmosphere, i.e. between its emission into the air and its removal by chemical transformation or deposition. Regarding not the global atmosphere but an atmospheric box, also the transport time (between importation and exportation) determines the box residence time. Mathematically, we can define the residence time as the arithmetic mean of individual life time of all particles of a trace species[6]:

$$\tau = \frac{1}{N_0} \int_{N_0}^{0} t \, dN \,. \tag{5}$$

Thus, different processes (reactions, transportation, phase transfer and deposition) determine the overall residence time. Each process must be described by a specific *kinetic law*, characterized by the process-related residence time τ_i (see Eq. 7). In this sense, one also can define a residence time for aerosol particles and hydrometeors.

Assuming a first-order process ($dN/dt = kN$) for the kinetics of atmospheric removal (often being the case) it follows due to $dN = -kN_o \exp(-kt)dt$,

$$\tau = \frac{1}{k} \,. \tag{6}$$

As mentioned, the overall removal kinetics is determined by all chemical transformation

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[5] Also named as *turnover* time and *life* time.
[6] With the general term „particle" we will denote atoms, molecules and radicals (gases), solid particles (atmospheric aerosol) as well hydrometeors (liquid drops, ice particles, snow cristalls etc.). More specific, "particles" denote particulate matter (aerosol particles).

and deposition processes. For each individual process we define the residence time $\tau_i = 1/k_i$ and because of $k = \Sigma k_i$ it follows

$$\frac{1}{\tau} = \sum \frac{1}{\tau_i} \,. \tag{7}$$

Concerning wet events (cloud processes, rain, i.e. wet deposition) which happen only occassionally, Rodhe (1978) defined a residence time which represents the mean time (starting from an arbitrary time step) untill chemical transformation in cloud water (liquid phase chemistry) and/or removal by precipitation:

$$\tau = \tau_a \frac{\tau_a}{\tau_a + \tau_b} + \frac{\tau_a + \tau_b}{\tau_b} \tau' \,. \tag{6}$$

The indices *a* and *b* denote the duration of the dry periode (*not* rainy, *no* cloud) and wet periode (cloud, rain), respectively; τ' is the residence time during the wet event (e.g. characteristic aqueous phase chemical transformation).

Table 3.4 Squares, volumens and masses of the atmosphere and its interfaces with earth surface, after Holland (1984)

masse atmosphere	$5.2 \cdot 10^{21}$ g	
masse troposphere (untill 11 km altitude)	$4.0 \cdot 10^{21}$ g	
volume troposphere (untill 11 km altitude)	$5.75 \cdot 10^{18}$ m^3	
volume ocean[a]	$1.37 \cdot 10^{18}$ m^3	
surfaces	(in 10^{14} m^2)	(in % land surface without antarctis)
square ocean[b]	3.64	-
square continents[c]	1.49	-
antarctis	0.23	-
forests	0.48	38
tundra, bush land	0.08	6
deserts	0.24	19
gras land (steppes, savanna)	0.24	19
misc. (marshy soils, halfdeserts, ice etc.)	0.06	5
cultivated land	0.16	13

[a] density 1.036 g cm^{-3}
[b] Northern hemisphere: 1.54   Southern hemisphere: 2.10
[c] Northern hemisphere: 1.03   Southern hemisphere: 0.46, includes Antarktis: 0.23

The residence time depends from time and space, i.e. is not being constant in the atmosphere due to varying conditions for chemical reactions and deposition processes. For example, the residence time of ozone (O_3) amounts 2-3 months in the upper troposphere but only a few days in the planetry boundary layer (PBL) and even a few hours in the soil-near layer.

The residence time is an important quantity for describing the amount of a trace substance in the atmosphere in sense of a reservoir (Fig. 3.1; cf. Table 3.4). In case of *stationary state*, i.e. within a fixed time interval the input Q into the atmospheric box (emission) is equal to the output flux F (removal rate), the residence time is also defined according to

$$Q = F = M/\tau. \tag{7a}$$

Note that τ is averaged over the space and time (e.g. year) regarded. Assessing and comparing different residence times therefore need the reference in time and space. The condition Q = F

is unvalid, more exactly, and only an approximation. Based on a year, the system is quasi-stationary, when τ < 1 a, i.e. the whole emitted amount of the substance is removed also in this year. When the residence time becomes larger than the time periode regarded (Fig. 3.1), the reservoir mass (burden) is increasing and Eq. (7a) is invalid. The removal rate F, however, will allways determined by

$$F = M/\tau \qquad\qquad (7b)$$

because $F = dN/dt = kN = N/\tau$ and $M = Nm_i$, where m_i mass of single particle. Generally the mass of different atmospheric trace species will be determined by measurements to establish a (3-dimensional) concentration distribution:

$$M = \iiint c\,dx\,dy\,dz \ .$$

Assessing τ from kinetic measurements, it is possible to determine (roughly) the unkwon quantity F by use of Eq. (7), and in case of stationarity, to assess independently the emission figure Q (which mainly will determined locally by direct flux measurements and "upscaled" to large-scale averages).
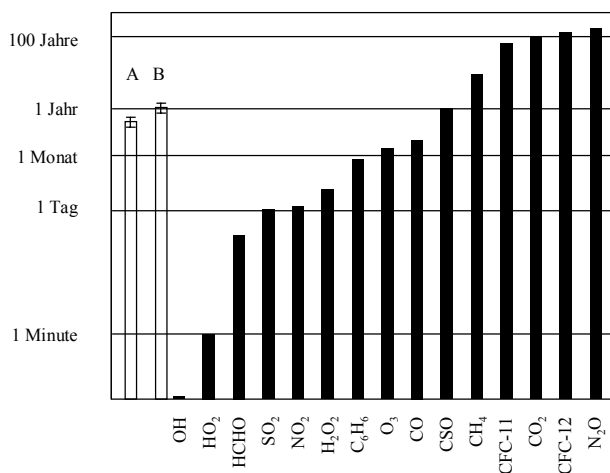
Fig. 3.1

Residence time of atmospheric trace species (A interhemispherice transport time, B troposphere-stratosphere-exchange time)

In Chapter 4 (sources of trace species) you will learn different emission sources (and processes) which determine together with the residence time (*remember*: it only depends from the characteristics of removal processes) the atmospheric concentration (burden). Consequently, a substance with small emission rate but high residence time will lead to high air concentrations (e.g. carbonyl sulfide COS). Moreover, a substance will be accumulated in the atmosphere when its emission rate is larger then the removal rate (e.g. CO_2, CH_4, N_2O). This non-equilibrium state, however, is only found for man-made sources. Natural processes are within a dynamic equilibrium as a result of evolutionary development. On geological time-scale, however, also natural source and removal processes are instationary and result in climate variations and even changes (see subchapter 3.4.2).

3.2 Evolution of the earth system

3.2.1 Origin of the solar system

For understanding the origin, evolution and fate of our earths atmosphere it is necessary to make a short excursion to the roots of our planet and even to the solar system. Our Galaxy is probably 18 billion years (18 Ga) old and was formed by the hot *Big Bang*, assuming that the whole mass of the Galaxy was concentrated in a primordial core. The initial products of the Big Bang were neutrons which, when released from dense confinement (quarks), began a decay into protons and electrons: $n^o = e^- + p^+$. As the half-life for this reaction is 12.8 minutes, we can assume that soon later after the Big Bang, all matter in the universe was ½ protons and ½ electrons. Temperatures and pressures were still high and nuclear reactions were possibly leading to the production of He (helium) via the interaction of neutrons and protons (remember that the proton already represents hydrogen), see Fig. 3.2. Recall that it is the number of protons in the nucleus that defines an element, not the number of protons plus neutrons (which determines its weight). Elements with different numbers of neutrons are called *isotopes*, and different elements with the same number of neutrons plus protons are called *isobars*.

Fig. 3.2 Scheme of thermonuclear formation of chemical elements
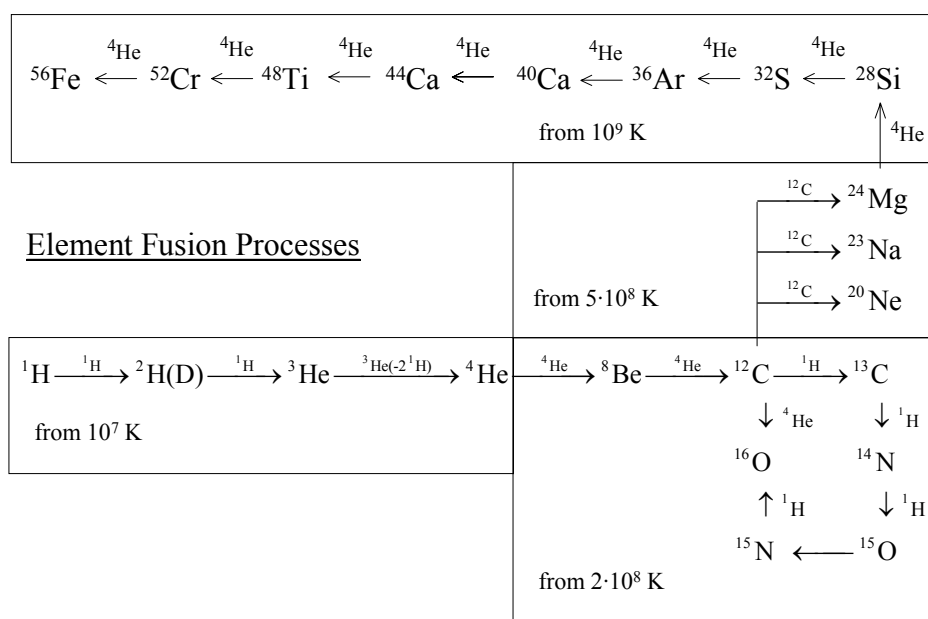
Nowadays, one assumes that the sun and its planetary system were formed from heterogeneous debris of a supernova that exploded 5 Ga ago. The sun formed from the collapsed supernova core, a neutron star with radiant energy and protons in the solar wind. Other debris from the supernova remain as gases and particulate matter, called *solar nebula*. This system cooled, particles rose by condensation growth and the sun growth by gravitational settlement about 4.6 Ga ago. Cooling and subsequent condensation happened with distance from the protosun, resulting in an enlargement of heavier elements (e.g. Fe) at the inner circle (Fig. 3.3). Mercury formed closest to the sun, mostly from iron and other materials in solar nebula that condense at high temperatures (above 1400 K). It also shows the highest density (5.4 g cm^{-3}) of all earth-like planets, and in contrast, Jupiter contains more hydrogen and helium with an average density of only 1.25 g cm^{-3}.

Fig. 3.3 Types of planets and its density
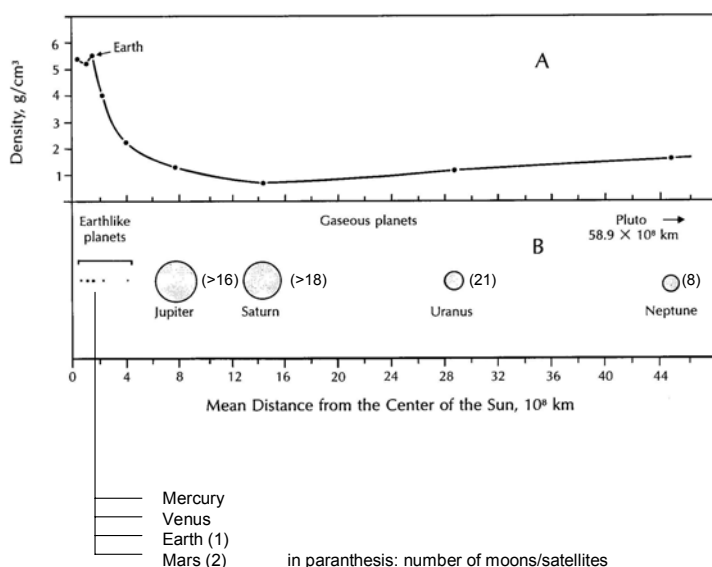
The abundance of elements in space (Fig. 3.4) is a result of the temperature-pressure depending fusion processes shown in Fig. 2.
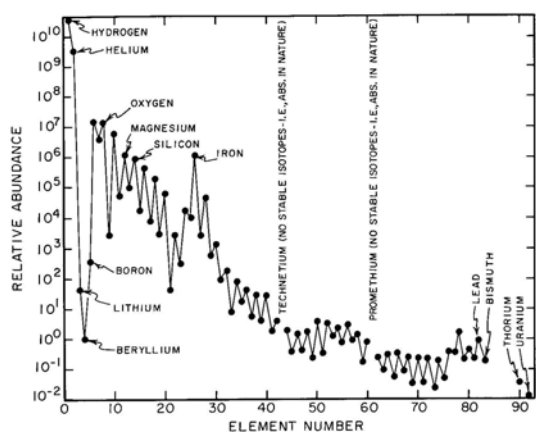
Fig. 3.4 Abundance of chemical elements

It is now quite clear that the earth, like the other solid planetary bodies, formed by the accrecation of solid objects, probably largely in the form of small grains, but interspersed with occasional major pieces. The largest particles (protoplanets) developed a gravitational field and attracted further material to growth. We assume that all this primary material was cold (10 K) first. With increasing appearance of protoplanets a partial melting process took place, causing materials of lower density to make their way to the surface, while presumably melts of high density sank down towards the center. The heat of this melting process was the result of radioactive decay processes in the material, as well as the heat from the planetary body being compressed. We now have to take into account that the material distribution was heterogeneous due to different chemical composition of the particulate matter within solar nebula. From meteorites we have our knowledge how these chemical composition could have been. The molten materials also have been inhomogeneously distributed over the protoplanet. The theory of *heterogeneous earth formation* would simply explain the structure of our earth with a liquid core, a hot mantle and the crust. Another theory, called *homogeneous*, assumes that earth was also cold at the beginning, but with concerning elements being homogeneously distributed. Increasing heating, originating by the same processes as explained above, lead to

melting and rapid settling. It is likely that the segregation of the core must have been a catastrophic event, melting the earth entirely and destroying all surface rocks. The time scale of evolution of solar nebula and accrecation of inner planets was geologically very short – less than 10 Ma (Walker, 1977).

Harkins[7] showed in 1917 that 99% of the material in ordinary meteorites consists of seven, even-numbered elements - iron (Fe), oxygen (O), nickel (Ni), silicon (Si), magnesium (Mg), sulfur (S) and calcium (Ca). However, in the 1920s, *Payne*[8] and *Russell*[2] showed that the solar atmosphere is mostly hydrogen (H) and helium (He). Today there are theories[9] that the suns chemical composition (at least in the core) is similar to that one of meteorites, i.e. Fe is the most abundant element.

There exists the hypothesis that most of the earths mass is likely to have been received during heavy meteor bombardment in the first billion years, supported by the finding that oldest rocks have been aged to be 3,6 Ga old (Schlesinger, 1997). However, such a massive infall would have left much other evidence in the geologic record, and this is absent (Gold, 1997).

During formation of the earth by the accumulation of cold solids, very little gaseous material was incorporated. The knowledge of this comes from the extremely low level of the non-radiogenic noble gases in the atmosphere of the earth. Among those, only helium could have escaped into space, and only xenon could have been significantly removed by absorption into rocks. Neon, argon, krypton would have been maintained as an atmospheric component. Most of helium found on earth is ^{4}He, the result of the radioactive decay of uranium and thorium; primordial Helium is ^{3}He.

3.2.2 Degassing the earth

We call the present earth's atmosphere "secondary". But the discussion is still open whether there was a primordial and what was the composition of the primary one. The so-called *primitive* atmosphere could be given by the remaining gas phase (solar wind) from solar nebula (H_2, He). However, it is still not clear whether earth had a primitive atmosphere or not. There are several assumptions (e.g. the collision of earth with another celestial body, by which we assume today the formation of moon) by which this primitive atmosphere must have quickly eroded to space. Hydrogen from such an atmosphere will also outgas quickly to space.

The key question for all gases forming an atmosphere is the one asking for its origin. As discussed in the previous chapter, it is forced to conclude that the acquisition of gases, or substances that would be gaseous at the pressures and temperatures that ruled in the region of formation of the earth, was limited to the small value implied by the low noble gas values. Assuming that gaseous material despite noble gases was absent or of less importance in the mass budget of the initial earth, all gases believed in the primordial or primitive atmosphere must be a result of volatilization of materials from the inner part of earth.

Earlier hypothesis suggested that the primitive (or better called: *primary*) atmosphere consisted from NH_3 and CH_4. This idea was supported by the finding of both species being in some meteorites and the believing that the solar nebula consists to a small amount also from ammonia and methane (Schlesinger, 1997). The existence of a NH_3-CH_4-atmosphere was

[7] Harkins W.D. (1917) *J. Am. Chem. Soc.* **39**, 856-879

[8] Payne, C.H. (1925) *Stellar Atmospheres* (Harvard Observatory Monograph No.1, Cambridge, MA, USA) pp. 177-189; Russell, H.N. (1929) *Ap. J.* **70**, 11-82

[9] O. Manuel, J. T. Lee, D. E. Ragland, J. M. D. MacElroy, B. Lee and W. K. Brown (1998) Origin of the solar system and its elements, *J. Radioanal. Nucl. Chem.* **238**, 213-225

believed to be a precondition for the origin of life. The well-known *Miller-Urey* experiment[10] in 1953 showed that under UV radiation organic molecules can be formed in such an atmosphere. However, even the intensive UV radiation at earth beginning would have destroyed NH_3 and CH_4 soon and no processes are known to chemically form both species in air. Nowadays, most scientists agree (see next subchapter) that the primitive atmosphere consists mainly of CO_2 and H_2O (and N_2). A small percentage of oxygen also would destroy all organic molecules[11] into CO_2 and H_2O. In the following, we will explain where carbon dioxide and water (vapor) were coming from. There are, however several reasons to assume at least intermediary a first NH_3-CH_4-atmosphere.

A basic question not yet answered is the origin of nitrogen (N_2) in the pre-biological atmosphere. Assuming first ammonia in the atmosphere, even its radiative decay

$$2\,NH_3 \rightarrow N_2 + 3\,H_2 \uparrow$$

would explain the origin of nitrogen. Hydrogen quickly (even when assuming a hot atmosphere with 600 K) escaped into space. Thus, it is unlikely that H_2 was available at high concentrations for hydrogenations, e.g.

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O.$$
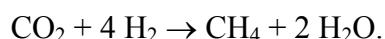
To answer the question where ammonia is coming from, we simply assume that in the earth crustal ammonium chloride (NH_4Cl) was present, which with increasing temperature quickly and completely dissociated into NH_3 and HCl. HCl (and Cl_2, which is easy formed via HCl photolysis) were also comparts of the primitive atmosphere. HCl/Cl_2 were also found in volcanic gases (see Table 3.7). Today there are no indications that NH_3 is found in volcanoes[12], however, it is not unlikely that a large share of them have undergone extensive recycling, so that they should not be considered juvenile degassing products. There is no argue not to believe that all salmiac (NH_4Cl) was destroyed in an early state of the earth and that HCl in present volcanoes is a product from other mineralic chlorides and N_2 from gaseous deposits, even due to recycling of sediments. Igneous rocks contain 25 mg kg^{-1} nitrogen as ammonium and 3 mg kg^{-1} as N_2 (Schlesinger, 1997).

The fact that oxygen has not been observed in volcanic gases (Warneck, 2000), should not be taken into account for the volcanic activities in the early earth's (see also the later discussion on oxygen budget)

Walker (1977), who preferred an initially hot earth with strong tectonic activities, volcanisms and cross-mantle interchange, indicated that the rate of degassing must have declined over time. Degassing introduced water and carbon dioxide to the primitive atmosphere, he wrote. But, where did the huge amounts of CO_2 and H_2O – oxidized species – come from? The fractions of H_2 and CO found in volcanic exhalations agree approximately with those expected from the thermo-chemical equilibria with their precursors H_2O and CO_2, provided oxygen pressures of 10 mPa or less (Warneck, 2000).

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[10] Miller, S. (1953) A production of amino acids under possible primitive earth conditions. *Science* 117,528-529; Miller, S. and H. Urey (1959) Organic compound synthesis on the primitive earth. *Science* 130, 245-251.

[11] Nitrogen, the principal constituent in the atmosphere of Titan, is believed to have been formed by the photolysis of an early Titan atmosphere which contained ammonia. The second most abundant atmospheric compound in Titan's atmosphere, methane, is currently undergoing photolysis to form more complex hydrocarbons. CH_4 photolysis occurs at α-Lyman wavelength (121,6 nm) into H, H_2, CH, CH_2 and CH_3. A small presence of O_2 and /or OH radicals as a result of H_2O photolysis, however, would inhibit the formation of more complexe organic molecules due to CO formation (and subsequent CO_2).

[12] NH_4Cl is found nearby some volcanoes.

We now will combine this question with that of the origin of carbon on the earth. The carbon we have on the surface or in the sediment of the earth is estimated to be 80% in the form of carbonate rocks, and 20% in unoxidized form, frequently referred to as *organic* carbon. The carbon supply the earth received initially could not have been in the form of hydrocarbon gases, high volatile hydrocarbon liquids, or CO or CO_2. What it shows is a reasonably continuous process of laying down carbonate rocks; no epoch having enormously more per unit time, nor enormously less. If outgassing from depth is responsible, then one has to discuss what the source material in the earth might have been, what liquids or gases might have come from them, and what their fate would have been as they made their way up through the crust. Warneck (2000) argued that the amount of oxygen needed for formation of carbonate sediments is twice of that produced by photosynthesis in earth history. This led us to conclude that

(a)   oxygen was initially released by inorganic processes (remember: we do not assume primordial CO_2 on earth) and

(b)   that carbonates also have been formed directly (i.e. not via atmospheric CO_2 after its dissolution in ocean and subsequent carbonate formation) from CO_2 and oxides in the mantle and crust.

This also means that CO_2 was a product of inner earth's processes (not only atmospheric CH_4 oxidation), thermic dissociation of primordial carbonates – which is not very likely due to its spare finding in meteorites – or other carbon species, already formed within the solar nebula.

I will follow the ideas of *Thomas Gold*[13] who proposed that some of the particulate matter within the solar nebula, still found as meteorites, called *carbonaceous chondrites*, contain significant amounts of carbon, and they contain it mainly in unoxidized form, a substantial fraction in the form of solid, heavy hydrocarbons. This material, when heated under pressure as it would be in the interior of the earth, would indeed release hydrocarbon fluids, leaving behind deposits of solid carbon. The quantitative information on carbonaceous chondrites is difficult to evaluate. They are much more friable than most other meteorites, and therefore survive the fall through the atmosphere less often than the others. Carbonaceous chondrites also are destroyed by erosion on the ground much more rapidly.

Table 3.5 Water soluble organic compounds (WSOC)[a] in the Tagish Lake meteorite, fell in January 2000 in Canada, after Pizzarello et al. (2001)- the first pristine carbonaceous chondrite found on earth.

substance class	concentration (ppm)	Number of identified species
aliphatic hydrocarbons	5	12
aromatic hydrocarbons	≥ 1	13
dicarboxylic acids	17.5	18
carboxylic acids	40	7
pyridine carboxylic acids	7.5	7
dicarboximides	5.5	4
sulfonic acids	≥ 20	1
amino acids	< 0.1	4
amines	< 0.1	3
amides	< 0.1	1

[a] formula of insoluble fraction: $C_{100}H_{46}N_{10}O_{15}$

Recently (January 2000) the *Tagish Lake* meteorite fell on a frozen lake in Canada and may provide the most pristine material of its kind (Pizzarello et al., 2001). Analysis have

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[13]   Thomas Gold,. Professor Emeritus of Astronomy at Cornell University; founder and for 20 years director of Cornell Center for Radiophysics and Space Research.

shown this carbonaceous chondrite to contain a suite of soluble organic compounds (~ 100 ppm) that includes mono- and dicarbonyl acids, dicarboximides, pyridine carboxylic acids, a sulfonic acid, and both aliphatic and aromatic hydrocarbons[14], see Table 3.5. The insoluble carbon (total 2.4%) exhibits exclusively aromatic character, deuterium enrichment, and fullerenes containing "planetary" helium and argon. These findings provide insight to an outcome of early solar chemical evolution which differs from any seen so far in meteorites.

If the carbonaceous chondrite material is the principal source of the surface carbon we have, then the initial material that could be mobilized in the earth at elevated temperatures and pressure would be a mix of carbon and hydrogen. What would be the fate of such a mix? Would it all be oxidized with oxygen from the rocks, as some chemical equilibrium calculations have suggested? Evidently not, for we have clear evidence that unoxidized carbon exists at depths between 150 km and 300 km in diamonds. We know they come from there, because it is only in this depth range that the pressures would be adequate for their formation. Diamonds are known to have high-pressure inclusions that contain CH_4 and heavier hydrocarbons, as well as CO_2 and nitrogen (Melton and Giardini, 1974). The presence of at least centimeter-sized pieces of very pure carbon implies that carbon-bearing fluids exist there, and that they must be able to move through pore-spaces at that depth, so that a dissociation process may deposit selectively the pure carbon; a process akin to mineralization processes as we know them at shallower levels. The fluid responsible cannot be CO_2, since this has a higher dissociation temperature than the hydrocarbons that co-exist in the diamonds; it must therefore have been a hydrocarbon that laid down the diamonds.

One assumes that the original carbon on earth from carbonaceous chondrites was bitumeous and tar (40% of the reduced carbon *Tagish Lake* meteorite are carboxylic acids). It is supposed that between 100 and 300 km depth we have a patchwork in which the carbonaceous chondrite material comprises 20% on an average. With the carbonaceous chondrite type of material as the prime source of the surface carbon, the question arises as to the fate of this material under heat and pressure, and in the conditions it would encounter as buoyancy forces drove some of it towards the surface. The detailed mix of molecules will depend on pressure and temperature, and on the carbon-hydrogen ratio present. Other atoms that may be present also, such as oxygen (from dissociation of metal oxides) and nitrogen (ammonia from ammonium salts), will form a variety of complex molecules with the carbon and hydrogen. Thus it is easy to understand that reduced carbon in form of CH_4 as well as in oxidized form (CO_2) and H_2O will be produced. At depth, methane will chemically behave like a liquid, and it will dissolve the heavier hydrocarbons that may be present, and therefore greatly reduce the viscosity of the entire fluid[15].

The deposition of carbonate rocks has been an ongoing process throughout the times of the geologic record. Most, but not all of this carbonate has been an oceanic deposit, deriving the necessary CO_2 from the atmospheric-oceanic CO_2 store. The amount that is at present in this store is, however, only a very small fraction of the amount required to lay down the carbonates present in the geologic record. The atmospheric-oceanic reservoir holds at present only about 0.05% of earth's carbon (cf. Table 3.9).

In earlier times there was the belief that earth had formed as a hot, molten body. In that case no hydrocarbons or hydrogen would have survived against oxidation, nor would any of these substances have been maintained in the interior after solidification. With that belief, there seemed no other possibility of accounting for the hydrocarbons embedded in the crust than by the outgassing of carbon in the form of CO_2, produced by materials that could have survived in a hot earth, and subsequent photosynthesis by plants that converted this CO_2 into

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[14] in small concentrations (< 0.1 ppm) amino acids, amines and amides also have been found.
[15] The continuing upward stream would acquire more and more of such unchangeable molecules, and the final product that may be caught in the reservoirs we tap for oil and gas, is the end product of this process. This is abiotic theory of formation of "fossil" fuels like oils, gas and coal.

unoxidized carbon compounds. This consideration is irrelevant, now that we know that a cold formation process assembled the earth and that hydrocarbons could have been maintained, and could be here for the same reasons as they are on the other planetary bodies.

Destruction of hydrocarbons under pressure and higher temperatures produced CH_4 as well elemental C (oxygen poor conditions) and CO_2 as well H_2O (oxygen rich conditions). At the very beginning of the earth, where inner temperature still were limited, it is likely that first NH_3 (from ammonium salts) and CH_4 as well volatile organic compounds escaped from the earth's body. Later − with increasing temperatures − oxidation of carbon materials was dominating and CO_2 and H_2O was the major product of degassing.

3.2.3 Evolution of the atmosphere

Today we assume that our earth had no *primordial* atmosphere. Our knowledge on the past atmosphere (*paleoatmosphere*) , which is to a large extend still speculative, is based on many geological date sets and element distributions concerning also redox state and isotopic ratios in all reservoirs. Chemical composition of other planets atmospheres is quite different (Table 3.6).

The terrestrial (*inner*) planets have an air composition with oxidized compounds (H_2O, CO_2) whereas (*outer*) Jove, Saturn, Uranus und Neptune have an H_2/He atmosphere. Mercury and Pluto basically have no atmosphere and Titan (a moon of Saturn) an N_2 atmosphere. Only earth has produced free oxygen in its evolution (see next chapter) which has enriched in air. Neighboring planets Mars and Venus differ from earth's atmosphere due to the absence of O_2 and dominating CO_2, whereas N_2 plays a minor role. This differences in planets atmospheres suggest a different evolution with diverse processes. The giant outer planets show a comparable composition with that of the solar nebula.

Table 3.6 Composition of atmospheres of the inner terrestrial planets (concentrations in ppm, if not otherwise marked), after Brimblecombe (1996)

species	Venus		earth		Mars	
carbon dioxide	96	%	0.03	%	95	%
nitrogen	3.5	%	77	%	2.7	%
oxygen	< 0.001	%	21	%	0.13	%
water vapor	< 0,5	%	0.01	%	0.03	%
helium	10		5.24		< 100	
argon	70		9340		16000	
argon-36	35		31		5	
neon	5-13		18		2.5	
krypton	0.5		1.1		0.3	
xenon	< 0.04		0.08		0.08	
carbon monoxide	50		0.1		700	
sulfur dioxide	150		0.01-0.1			
hydrogen chloride	1		0.001			
D/H ratio	0.022		0.00015		0.0009	

Most scientists assume that our atmosphere about 4.5 billion years ago consisted mainly of CO_2 under high pressure, with N_2 and H_2O being two minor important species. Those volatile elements[16] and compounds, as discussed in the previous chapter, were degassed from the inner earth (see also Walker 1977, Holland 1978, Brimblecombe 1996, Wayne 1996, Warneck 2000).

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[16] Formation of elements begun 15 billion years ago with formation of space in thermonuclear reactions long time before our Solar System has been established; see solar nebula (dust and grain particles) formed stars and planets according to the special temperature conditions, see subsection 3.1.1.

Table 3.7 Mean composition of Hawaiian volcanoes gases (in %), after Walker (1977)

species	concentration
H_2O	79.31
CO_2	11.61
SO_2	6.48
N_2	1.29
H_2	0.58
CO	0.37
S_2	0.24
HCl/Cl_2	0.05

Table 3.8 Mean composition of sea water (in %), after Walker (1977)

species	concentration
H_2O	96.5
Cl^-	1.935
Na^+	1.076
SO_4^{2-}	0.271
Mg^{2+}	0.129
Ca^{2+}	0.041
K^+	0.039
HCO_3^-	0.014

The composition of volcanic gases (Table 3.7) is assumed to be relevant to this secondary atmosphere[17]. This air was slightly reducing. However, due to intensive UV radiation one has to assume that practical all substances could be photolytically dissociated and a huge variety of radicals were present: H, O, OH etc. Thus, also small amounts of oxygen and ozone had been formed.

The presence of oxygen in a hypothetical primitive atmosphere poses a difficult problem for notions of self-assembling molecules. If oxygen is present, there would be no amino acids, sugars, purines, etc. because they all react with OH and subsequent with oxygen to form carbon dioxide (CO_2) and water.

With cooling of the atmosphere, water vapor condensed and oceans formed. Parallel all soluble gases (CO_2, SO_2, HCl, Cl_2) were washed out. At first, sea water became acidic and minerals (Na, Mg, etc.) were released from the earth's crust by erosion. This is simply the explanation for the chemical composition of sea water (Table 3.8).

Contrary, the air enriched with insoluble N_2. We assume that air just before beginning of life (about 4 Ga ago) consisted of N_2 (10^5 Pa), CO_2 (10^4 Pa) and H_2 (10^2 Pa) and small amounts of O_2 (10^{-8} Pa). These small amounts of oxygen remained by inorganic photolytical processes and could be up to 1% in the upper atmosphere.

Further trace gases are assumed to come from different geogenic sources: NO (lightning), HCl (sea salt), CO (volcanoes), HCHO (photochemistry). Because O_2 was not yet produced by water dissociation via *photosynthesis* (see Appendix 1), the earth surface was a strong oxygen sink by reduced metals (e.g. Fe and U).

Table 3.9 shows in a simplified scheme of the evolution of the atmosphere. I distinguish between five atmospheres, taking into account a primordial from gases within the solar nebula. The only remains from this first atmosphere might be a few percentages of the noble gases. Than it seems likely to separate the earth's degassing phase into two periods, differ in temperature. In the first phase (we call it now *primitive* atmosphere) major components were ammonia and methane which, however, were quickly converted into N_2 and possibly simple hydrocarbons. From this time nitrogen remained in the atmosphere. As soon as water was present in this atmosphere (probably by outgassing), an oxidation process of carbon species into carbon dioxide aroused. In its second phase of earth's degassing (higher temperatures), CO_2 and H_2O were major products (N_2 already was in atmosphere from previous phase). During later cooling of this atmosphere, water condensed to oceans and all soluble gases were washed out. Much later (~ 2 Ga ago) significant levels of oxygen arose in atmosphere due to photosynthesis (see next subsection) establishing the present (fourth) atmosphere.

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[17] However, compare remarks in previous chapter concerning re-cycling of rocky materials through volcanoes, i.e., the *present* composition of volcanic exhalations may *not* absolutely represent the former one.

Table 3.9 Evolution of the earth's atmosphere

atmosphere	composition	origin	fate
primordial[a]	H_2, He	solar nebula	erosion to space
primitive (first)	NH_3, CH_4 (CO_2, H_2O)	degassing (cold process)	photolysis (oxidation)
secondary	N_2, CO_2, H_2O,	degassing (hot process)	condensation and washout
intermediate (third)	N_2	secondary phase	remaining
present (fourth)	N_2, O_2	photosynthesis	biosphere-atmosphere equilibrium

[a] speculative

Beside those major components it is sure that at all times there were minor components and even many trace species (halogen compounds, NO_x-NO_y, organics, sulfur species)

3.3   Biosphere-atmosphere relationship

3.3.1 Origin of life

The English scientist *James Lovelock*[18] proposed with the GAIA hypothesis (Lovelock und Margulis, 1974) that our present atmosphere is far away from a chemical equilibrium as it is assumed for other planets (see also Appendix 2). One expression is the difference in the redox potentials between biosphere (reducing medium) and atmosphere (oxidizing medium). It is believed that living organisms are responsible (to a large extent) for the chemical composition of the present atmosphere and from a vice versa point of view the chemical composition of the atmosphere determines the biota. Remarkably, the composition of the biosphere is similar to that of the present atmosphere.

Table 3.10 Abundance of vital elements in different reservoirs (based on mass); in parenthesis other elements in ranking order

order	biosphere	atmosphere	hydrosphere	terrestrial crust	meteorites	sun[a]
1	O	N	O	O	Fe	H
2	C	O	H	Si	O	(He)
3	H	H	(Cl)	Al	(Ni)	O
4	N	(Ar)	(Na)	Fe	Si	C
5	Ca	C	Mg	Ca	Mg	N
6	K	(Ne)	S	Mg	S	Si
7	Si	(He)	Ca	Na	Ca	Mg
8	Mg	(Kr)	K	H		(Ne)
9	S		(Br)	C		Fe
10	Al	S	C	(Ti)		S

[a] New ideas (Manuel and Katragada, 2003) suggest a similar composition like in meteorites, i.e. the given figures represent only the outer gaseous layer of sun. In some publications this list is given as "cosmic" composition, what is not true.

The four principal elements of living materials (C, O, H, N) are found among the first five main constituents in air (N, O, H, Ar, C). Being a buffer or interface, the hydrosphere had an important role in the biological evolution with the elements H and O.

The so-called vital elements, without them plant and animal life is impossible to our present knowledge, are in an abundance order: O, C, H, N, Ca, K, Si, Mg, S, Al, P, Cl, Fe,

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[18] James Lovelock (born 1919) in England, atmosphere and Earth system researcher, Harvard University and NASA (USA) developed together with Lynn Margulis (US microbiologist) the hypothesis that the Earth is s self-controlling system; *Gaia*: the Earth goddess (greek)

Mn, Na (after Butcher et al., 1994). Table 3.10 shows the mass abundance in different reservoirs.

It is generally believed that life on earth was based on abiotic formation of "organic carbon" in an early atmosphere (*Miller-Urey* experiment, which has been repeated in many laboratories, and with many combinations of conditions. Belong them, some organic molecules will self-replicate, metabolizing, and membrane bound form that we might call life. A traditional view holds that life arose in the sea, and that biogeochemistry preferentially incorporated constituents that were abundant in seawater (Schlesinger, 1997). One circumstance to assume this way is the even smaller oxidizing capacity of the paleoatmosphere. However, what would be the possible fate of more complex organic molecules in this atmosphere, because photolysis would destroy it fast. For example formaldehyde, the primary oxidation product of CH_4 oxidation will quickly photolysed into inorganic molecules (CO and H_2O). Without any doubt, organic molecules could be produced in this way and washed out into the ocean. Another way could be the pre-biological existence of organic molecules, found in chondrites (see Table 3.5) and here believed in the earth's crust. Due to conversion processes and outgassing beside CH_4 and CO_2 many other hydrocarbons could be released into the atmosphere or direct into the ocean.

However, there appears a dilemma. As mentioned, the presence of oxygen in the early atmosphere would destroy organic molecules. On the other hand, the presence of oxygen is the precondition for production of ozone (O_3) which protects the earth's from UV radiation. Without this layer, organic molecules would break down and life would soon be eliminated. We also know that first form of life must have existed under anaerobic conditions.

Thus, it seems more likely that organic basic molecules primordially were abundant within the crust and, consequently, in the ocean, where "life" had been formed. The existence of bacteria even in deep crustal layers (up to 7 km) may suggest that life also could developed in the crust. Moreover, a new basic idea (Gold, 1997) is that a large amount of microbial life exists in the pore spaces of the rocks down to depths of between 6 and 10 kilometers, which arose in the following way: natural petroleum almost always contains elevated levels of the chemically inert gas helium and at the same time it contains molecules that are unquestionably of biological origin. How these two different substances met up in oil has long been a puzzle. If there exists microbial life, down to all levels that can be reached by the drill, then the biological molecules can be explained. The association with helium can then be explained adequately if the hydrocarbons have come up from much deeper levels and thereby swept up the diffusely distributed helium that exists in the rocks. A flow of hydrocarbon fluids through the crust will have affected much of its chemical development. The concentration of many types of mineral deposits, especially of metal ores, has not had adequate explanations. The leaching out of particular components from the rocks requires fluids that can dissolve these components, and it requires large pressure differentials to drive these fluids through the pores of a sufficient quantity of rock to gain access to the materials. Hydrocarbons ascending from depth may provide these requirements.

Consequently, "organic" molecules existed in the whole vertical crust of earth from the very beginning, providing self-organizing mechanisms we regard now as simple forms of life. In the background of the evolution of the atmosphere it seems to be more likely that such molecules and bacteria were penetrating into seawater from the crust and that even the water body provided more conditions for its development and distribution.

This simple life (bacteria) existed under anaerobic conditions. By *fermentation*, a very non-efficient process, they produced ethanol and carbon dioxide from fructose (and other organic material), but many other products (e.g. acids) and methane may have been produced:

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2 \tag{8}$$

An important success was given by first *autotrophic*[19] forms of life which transfers carbon from its oxidized form (CO_2) to the reduced (organic) forms that results in plant growth. This process is called *photosynthesis* (see also Appendix 1):
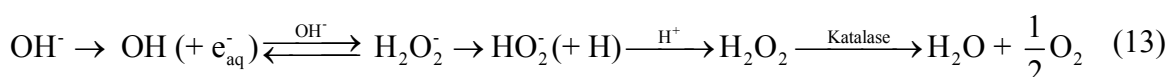
$$2\ CO_2 + 4\ H_2 \rightarrow CH_3COOH + 2\ H_2O, \tag{9}$$

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O. \tag{10}$$

Source of hydrogen could be H_2S where metal sulfides were formed and sedimentated (e.g. FeS_2). Possibly free hydrogen was available as a result of primordial hydrocarbon destruction (remember the presence of H_2 in volcanic exhalations). More developed organisms have used H_2O as electron donator:

$$2\ H_2O + h\nu \rightarrow 4\ H^+ + 4\ e^- + O_2 \uparrow. \tag{11}$$
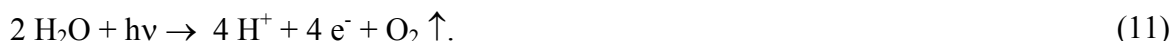
This process (water photolysis) is the primary reaction of the photosynthesis of algae, higher plants and some bacteria where coloring matter (like chlorophyll) first produce hydrated electrons while radiated within the visible spectrum of sun light; the electron transfer proceeds via special cellular substances:

$$H_2O \rightleftarrows H^+ \left(+ OH^- \right) \xrightarrow{e^-_{aq}} H\ . \tag{12}$$

The free hydrogen is used for carbon reduction according Eq. (9) and (10). Under oxic conditions, however, it will oxidized: $H \xrightarrow{O_2} HO_2 \rightleftarrows O_2^-(+H^+)$; finally back to water. Free oxygen is produced via the following reactions chain:

$$OH^- \rightarrow OH\ (+ e^-_{aq}) \underset{\xleftarrow{\hspace{1cm}}}{\xrightarrow{OH^-}} H_2O_2^- \rightarrow HO_2^-(+ H) \xrightarrow{H^+} H_2O_2 \xrightarrow{Katalase} H_2O + \frac{1}{2}O_2 \tag{13}$$

This reaction is the origin of O_2 on the earth's atmosphere. The overall reaction for photosynthesis is

$$6\ CO_2 + 6\ H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6\ O_2, \tag{14a}$$
$$n\ CO_2 + n\ H_2O + h\nu \rightarrow (CH_2O)_n + n\ O_2. \tag{14b}$$

Remarkable that in this way a stochiometric ratio 1:1 between fixed carbon and released oxygen is established. The oxygen was not yet used by the biosphere and destruction of biomass was only realized via abiotic mineralisation (back reaction 14b):

$$(CH_2O)_n + n\ O_2 \rightarrow n\ CO_2 + n\ H_2O. \tag{15}$$
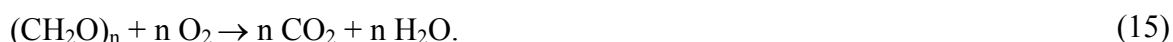
This was the first closed *biogeochemical cycle*. However, with the accumulation of biomass (and later buried carbon within sediments) an accumulation of equivalent mass of oxygen arose. Oxygen was first accumulated in seawater and used for oxidizing reduced species ($HSO_3^- \rightarrow SO_4^{2-}$, $Fe^{2+} \rightarrow Fe^{3+}$ etc.). Only by getting a redox equilibrium the seawater became saturated with O_2 and oxygen may have escaped to the atmosphere (about 2 Ga ago). This

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[19] Meaning for organisms (plants and bacteria) who takes carbon for its biomass from CO_2 dissolved in water or from atmosphere. In contrast, heterotrophic organisms can use carbon only from living or dead biomass (higher plants, animals, mushrooms, most bacteria).

certainly had quite an impact on further evolution. Small amounts of oxygen, abiotically produced in the atmosphere (see also next chapter) have been tolerated for the first 2.5 Ga. Beside, free oxygen in the lower atmosphere were deposited due to oxidation of reduced materials on the crustal surface of continents.

With increasing oxygen levels in the atmosphere the ozone concentration rose – and what we learned from photochemical modeling – faster than that of O_2. O_3 and O_2 are linked within a photo-stationary equilibrium. With increasing oxygen (and subsequent O_3) the absorption of UV(B) becames more complete. Before oxygen levels in atmosphere were significant, about 10 m water column was sufficient to protect the layers below against UV. Only with reducing the UV water organisms were able to life near the surface and finally they were able to cover the continents. Thus it is necessary to state out that neither missing nor present O_2 prevents land settlement but the presence of hard UV radiation.

The toxic O_2 and the oxygen containing radicals also caused different biological problems, now called *oxidative stress* (see for details Chapter 6). The organisms answered this stress by developing mechanisms to protect them against oxidants (*antioxidants*). The organisms available at around 2 Ga ago had two ways: first go back to anaerobic regions and live without oxygen or secondly to live in tolerance with oxygen. Choosing the second variant, the evolution created with the *respiration* by heterotrophic organisms (biotic back reaction 14b) an unique, biogenic controlled equilibrium between atmosphere and biosphere, between reducing and oxidizing regions of the earth's (Fig. 3.5).
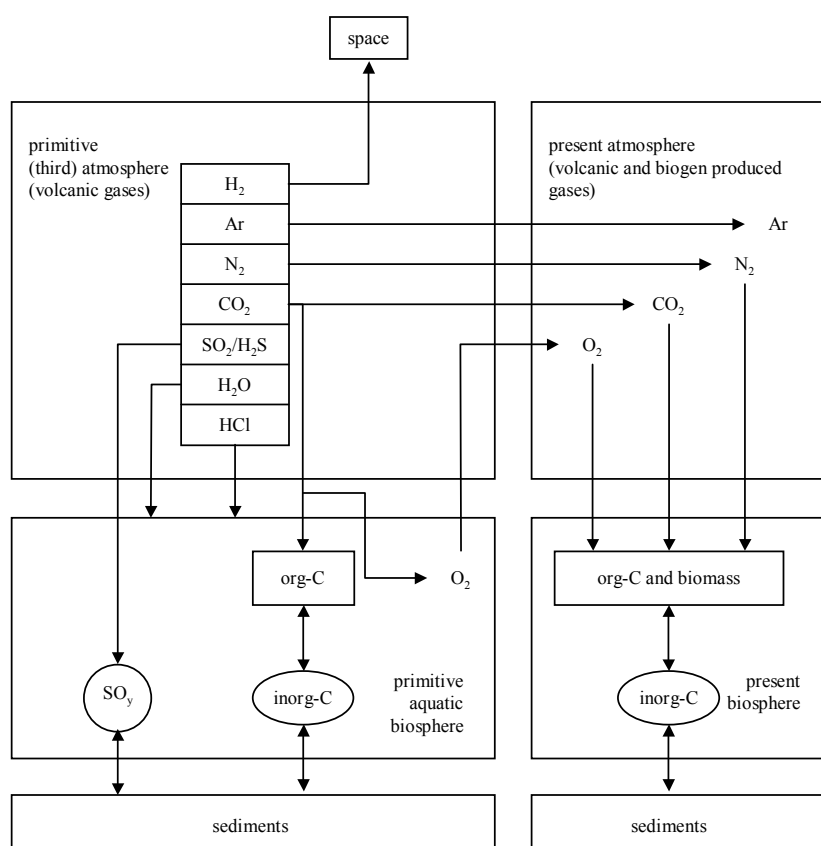
Fig. 3.5 Evolution of the chemical composition of the atmosphere (biosphere-atmosphere interaction)

Assuming an O_2 level of 10^{-8} or less before 4 Ga, with biological life it is believed a concentration of 10^{-5} which increased with beginning of Kambrium (0.6 Ga ago) to about 2%. This O_2 level would absorb 100% of solar light with wavelength < 250 nm and 89% < 302 nm (today 97% of the fraction < 302 nm will absorb). The water column necessary for protection

reduced at this time to about 1 m and it is assumed that just after this time (0.5 Ga ago) an erratic biological development on land begun. Thus, after short time land plant photosynthesis increased O_2 in the atmosphere and we assume that with the beginning of the Silur (0.4 Ga ago) the ozone layer was completed to protect all life.

Accepting that biological life (it remains a hypothesis) is causative related with the changing air composition we also have to take into account the feedback mechanisms, principally suggested by the GAIA hypothesis (Appendix 2). It is not important for our understanding to believe that the continental life was a result of the protecting ozone layer or whether the beginning land plants first created the protecting ozone layer via O_2 production. Important remains that there exists a close relationship between biota and air. *Evolution of one reservoir is the history of the evolution of the other*.

3.3.2 The budget of carbon and oxygen

Today an oxygen turnover in the atmosphere of 300 Tg a^{-1} is assumed, resulting in an average residence (or turnover) time of $4 \cdot 10^6$ years. Due to the low solubility of O_2 in seawater the atmosphere is being a buffer and reservoir for free O_2.

It is well accepted that there are imbalances between carbon and oxygen budgets on earth. For example, if the vast amounts of present carbonate sediments had originally been exhaled in reduced forms (CH_4 or CO) it would have required oxygen from the atmosphere for oxidation. The mass of carbonate is so large that the oxygen required would be roughly twice the present atmospheric content, not counting the oxygen needed to oxidize reduced sulfur and iron. Thus, the earth's present carbonate reservoir was probably initially exhaled from the earth as CO_2. The present reservoir distribution (Table 3.11) of elements/compounds is the result of the evolutionary processes described in the previous subsections.

Table 3.11 Reservoir distribution (in 10^{19} g element, despite for the water molecule)

reservoir	C[j]	O[j]	H₂O[c]	S[k]
atmosphere	0.075[a]	119	1.7	negl.
ocean	3.8[b]	12500[d]	14000	128[h]
continental living biomass	0.061	negl.	negl.	negl.
soils	0.16	? (negl.)	? (negl.)	negl.
fossil fuels	0.5	negl.	negl.	0.0013
oceanic clathrates[f]	1.0	negl.	negl.	-
lithosphere (sediments)	~10000[b]	4745[h]	1500	247[h]
lithosphere (rocks)[g]	~130000	~2000000	?	1200[i]

[a] CO_2
[b] carbonaceous (CO_3^{2-})
[c] after Walker (1977)
[d] in water molecules
[e] in oxides
[f] methane hydrates, after Kvenvolden and Lorenson (1998)
[g] estimated by using mean element abundance and assuming a mass of crust being $0,4 \cdot 10^{26}$ g (density 2.7 g cm^{-3})
[h] as sulfate (SO_4^{2-})
[I] as sulfide (S^{2-})
[j] after Schlesinger (1997)
[k] after Möller (1982)

In the carbon cycling we have to consider a long-term cycling including *rock weathering* and *volcanism*. Over much longer time scales (million of years) atmospheric CO_2 concentrations have varied tremendously due to changes in the balance between the supply of CO_2 from volcanismm and the consumption of CO_2 by rock weathering. Over geological timescales, large (but very gradual) changes in atmospheric CO_2 result from changes in this balance between rock weathering and volcanism. CO_2 in the atmosphere is consumed in the *weathering* of rocks (CO_2 combines with H_2O to make carbonic acid, which slowly dissolves rocks). This weathering produces bicarbonate (HCO_3^-), a form of inorganic carbon, and

calcium (Ca^{2+}) that is then transported in river water to the oceans. Once in the oceans the calcium and bicarbonate are combined by organisms to form solid calcium carbonate, the mineral that is found in shells. This calcium carbonate mineral is buried in the sediments, where eventually it comes under great temperature and pressure and is melted during the process of "subduction". The melted rock rises to the surface in the form of magma and is released back to the surface of the earth at volcanoes. This high-temperature process also converts some of the calcium carbonate back to CO_2, which is released during volcanic eruptions to the atmosphere to begin the cycle over again.

This inorganic (no photosynthesis) but biotic (mineral production) carbon cycle is not linked with the oxygen cycle but with water (H_2O) and acidity (H^+). Simply said, unsoluble rock carbonate is transformed into more soluble bicarbonate where atmospheric CO_2 is fixed as dissolved bicarbonate:

$$CO_2 \xrightarrow{H_2O} H_2CO_3 \left[H^+ + HCO_3^- \right] \xrightarrow{CaCO_3} Ca\left(HCO_3\right)_2 \left[Ca^{2+} + 2\, HCO_3^- \right].$$
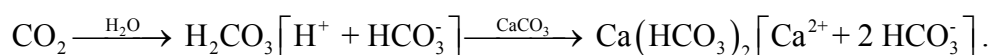
Additional one have to include in the budget still permanent CO_2 degassing (unknown figure) from the crust (adopting the deep carbon hypothesis, see 3.2.2).

Total amount of volatile oxygen consumed over the earth's history has been estimated by Warneck (2000) to be $3.1 \cdot 10^{22}$ g. In this figure are included:

- H_2S oxidation into sulfate,
- FeO oxidation into Fe_2O_3,
- CO oxidation into CO_2 (from volcanic exhalations),
- H_2 oxidation into H_2O.

This amount is balanced with the production of O_2 via photosynthesis according to

$$CO_2 + H_2O + h\nu \rightarrow CH_2O + O_2.$$
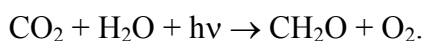
In the last equation it should not forgotten that O_2 is coming from the water molecule and not from CO_2. Neglecting the minor masses in living biomass reservoirs, this oxygen figure corresponds to $1.2 \cdot 10^{22}$ g buried carbon, which is much less than found in sediments (Table 3.11).

Obviously there is a conflict between carbon and oxygen in Table 3.11; $10 \cdot 10^{22}$ g carbonaceous C in sediments need $40 \cdot 10^{22}$ g O, i.e. several times more than it was produced as free oxygen on earth. Thus carbonates has to be assumed to be formed by weathering of oxides via direct attack of CO_2. The missing carbonate fraction in meteorites led us conclude that they were no primordial on earth and they could not be the source of CO_2 on the other hand. The total reduced carbon on earth, based on biological origin[20] is about $1.7 \cdot 10^{19}$ g being a maximum figure (derived from the data in Table 3.11). This corresponds to only $3.9 \cdot 10^{19}$ g oxygen, i.e. only 3% of oxygen present in atmosphere. Consequently, over the whole earth history, there must have been an oxygen production in excess, only possible by linking photosynthesis with fermentation (NPP – net primary production remains zero):

$$CO_2 + H_2O \xrightarrow{photosynthesis} C_{ORG} + O_2 \qquad\qquad (15)$$

$$C_{ORG} \xrightarrow{fermentation} CO_2 \qquad\qquad (8)$$

The residence time of O_2, based on the rapid exchange of carbon between the biosphere

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[20] However, assuming biological origin of fossil fuels.

and CO_2 in the ocean-atmosphere system, amounts 5000 years[21] (Warneck, 2000), corresponding to 24000 Tg O a^{-1} (240 Gt a^{-1}) due to photosynthesis and respiration. The exchange rate of oxygen due to weathering and net emission from buried carbon is only $0.3 \cdot 10^{19}$ g (corresponds to 6 Ma turnover time).

On the other hand, assuming the oxygen figure in sediments only in form of carbonates (what is wrong, as large amounts are stored as oxides of iron, sulfur and other elements), the carbonate figure would be only $12 \cdot 10^{22}$ g C. Thus, a dominant part of carbon must be in different chemical forms what is now believed in primordial hydrocarbons (see discussion in chapter 1.2.2).

Another imbalance exists between oxygen in water and carbon in sediments. In chapter 1.2.3 we discussed the formation of water from oxidative destruction of hydrocarbons, degassing into the primitive atmosphere and subsequent forming the ocean by cooling the atmosphere. The molar ratio between the sum of carbon, hydrogen and oxygen taking the figures from Table 3.9 results in a formula CH_3O_2. Biomass may be reduced to a sum formula of CH_2O. It let us conclude that there is an excess of oxygen over biological production via photosynthesis. From the formula of primordial carbon in carbonaceous chondrite material (Table 3.3), $C_{100}H_{46}O_{15}$ or simplified into about C_6H_2O it follows that these material were either to a large extent unsaturated or even a mixture with elemental carbon (graphite).

Carbon and oxygen were formed during the fusion process from He within the first steps (cf. Fig. 3.2):

$$^4He + {}^4He \rightarrow {}^8Be,$$
$$^8Be + {}^4He \rightarrow {}^{12}C \text{ and}$$
$$^{12}C + {}^4He \rightarrow {}^{16}O.$$
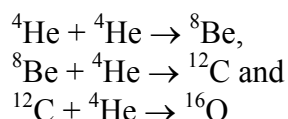
It is likely that most of oxygen (and other volatile elements) in particulate matter of the solar nebula was chemically bonded with metals forming oxides.

The initial production of free oxygen in Eaerth mantle can be explained by the thermal decomposition of metal oxides, transported to hotter regions: for example iron oxides, giving oxygen and metallic iron; the heavy iron moving toward earth's core, leaving the oxygen to escape. It is likely that no water was present in earth at its initial status. The free oxygen, however, could have oxidized the reduced carbon existing in heavy hydrocarbons into carbon dioxide and water:

$$(CH_2O)_n + n\ O_2 \rightarrow n\ CO_2 + n\ H_2O)$$
$$C_6H_2O + 6\ O_2 \rightarrow 6\ CO_2 + H_2O.$$
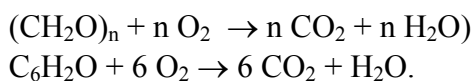
It is remarkable that the formula of the carbonaceous material is equivalent to

$$C_6H_2O = CH_2O + 5\ C,$$

explaining the huge excess of C (or oxidized into CO_2) comparing to "biomass" carbon (C_{ORG}).

The amount of CO_2 removed from the atmosphere each year by oxygenic photosynthetic organisms is massive (Fig. 3.6). It is estimated that photosynthetic organisms remove about $120 \cdot 10^{15}$ g C per year. This is equivalent to $4 \cdot 10^{18}$ kJ of free energy stored in reduced carbon, which is roughly 0.1% of the incident visible radiant energy incident on the earth/year (see also Chapter/Script 6). Each year the photosynthetically reduced carbon is oxidized, either by

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[21] It represents a partly process in determining the overall residence time mentioned at the very beginning of this subchapter to be 40000 years.

living organisms for their survival, or by combustion. The result is that more CO_2 is released into the atmosphere from the biota than is taken up by photosynthesis. The amount of carbon released by the biota is estimated to be $(1\text{-}2)\cdot10^{15}$ g C a^{-1}. Added to this is carbon released by the burning of fossil fuels, which amounts to $6\cdot10^{15}$ g C a^{-1}. The oceans mitigate this increase by acting as a sink for atmospheric CO_2. It is estimated that the oceans remove about $2\cdot10^{15}$ g C a^{-1} from the atmosphere. This carbon is eventually stored on the ocean floor. Although these estimates of sources and sinks are uncertain, the net global CO_2 concentration is increasing. Direct measurements show that each year the atmospheric carbon content is currently increasing by about $3\cdot10^{15}$ g. Over the past two hundred years, CO_2 in the atmosphere has increased from about 280 parts per million (ppm) to its current level of 360 ppm. Based on predicted fossil fuel use and land management, it is estimated that the amount of CO_2 in the atmosphere will reach 700 ppm untill end of this century. The consequences of this rapid change in our atmosphere are unknown. Because CO_2 acts as a greenhouse gas, some climate models predict that the temperature of the earth's atmosphere may increase by 2-8 °C. Such a large temperature increase would lead to significant changes in rainfall patterns. Little is known about the impact of such drastic atmospheric and climatic changes on plant communities and crops. Current research is directed at understanding the interaction between global climate change and photosynthetic organisms.

Fig. 3.6 Global Carbon cycle (fluxes in 10^{15} g a^{-1} and pools in 10^{15} g); data after Schlesinger (1997)
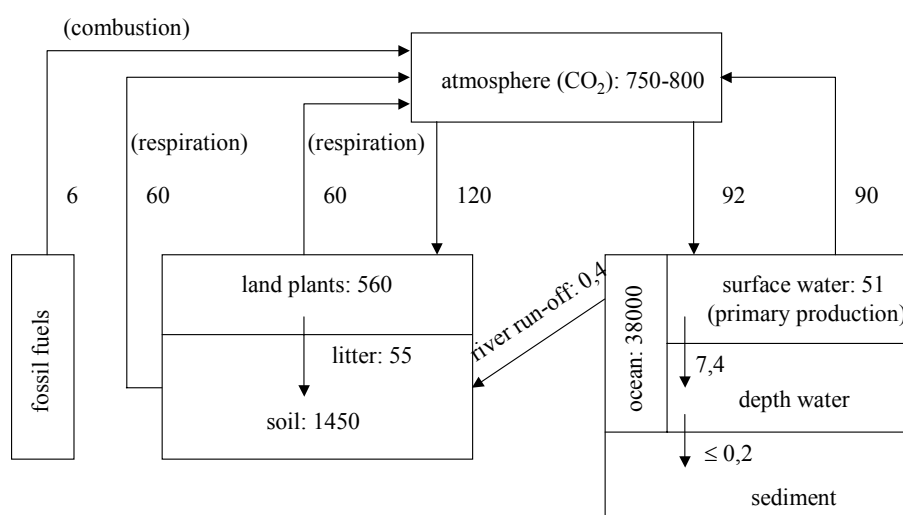

3.3.3 Water budget

Most minerals of Earth's upper mantle contain small amounts of hydrogen, structurally bound as hydroxyl (OH). The OH concentration in each mineral species is variable, in some cases reflecting the geological environment of mineral formation. Of the major mantle minerals, pyroxenes are the most hydrous, typically containing ~200 to 500 parts per million H_2O by weight, and probably dominate the water budget and hydrogen geochemistry of mantle rocks that do not contain a hydrous phase. Garnets and olivines commonly contain ~1 to 50 parts per million. Nominally anhydrous minerals constitute a significant reservoir for mantle hydrogen, possibly accommodating all water[22] in the depleted mantle and providing a possible mechanism to recycle water from Earth's surface into the deep mantle. As explained

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[22] This is not in contradiction with the hypothesis (see page 13) that primary water was formed by thermic dissociation and oxidation (by oxygen from metal oxides) of *primordial* hydrocarbon in deep earth crust.

in subsection 3.2.2, we assume that all "free" water (hydrospheric and atmospheric) was released in past earth history by degassing from the mantle. Consequently, the total amount of water (cf. Table 3.11) have to be assumed constant.
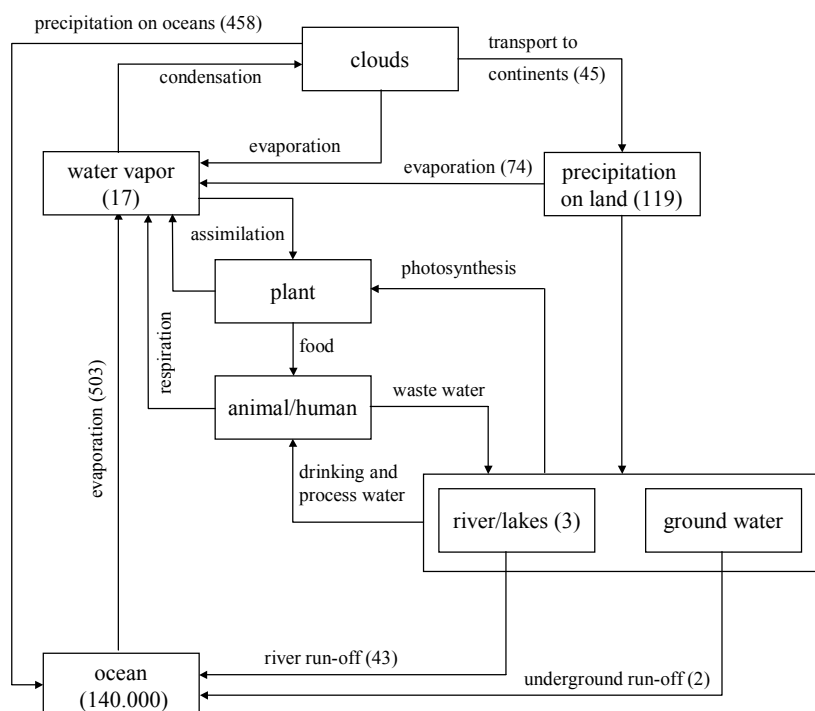
Fig. 3.7

Global water cycle (pools in 10^3 km^3 and fluxes in 10^3 km^3 a^{-1}), data after Hendl u.a. (1983) and Schlesinger (1997)

As discussed in subsection 3.1.2, the water fluxes can bee characterized by a *turnover time*, see following Table[23]:

reservoir	turnover time
Ground ice of the permafrost zone	10.000 yr
polar ice	9.700 yr
world ocean	2.500 yr
mountain glciers	1.600 yr
ground water	1.400 yr
lakes	17 yr
bogs	8 yr
soil moisture	1 yr
atmospheric moisture	16 d
biological water	few hours

The global water cycle as pictured in Fig. 3.6 is by far the largest transfer of a chemical substance on earth (the global atmosphere-ocean transfer amounts to an annual $4 \cdot 10^5$ Gt). It is run by evaporation and precipitation formation. The tropics are the major producer of water vapor, which is transported to the poles, together with the latent heat. Precipitation as a result of clouds are significantly controlled by atmospheric aerosol (cloud condensation nuclei) and by temperature. We see that a large number of feedbacks occur, which negatively or positively determine the whole system. Accounting for the most important elements are the

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[23] Data from http://www.unesco.org/science/waterday2000/Cycle.htm. The *International Hydrological Programme* (IHP), UNESCO's intergovernmental scientific co-operative programme in water resources, is a vehicle through which Member States can upgrade their knowledge of the water cycle and thereby increase their capacity to better manage and develop their water resources.

albedo of the atmosphere (clouds) and the surface (land use) as well as the content of absorbing matter (gases, clouds) and scattering/reflecting matter (aerosol particles, clouds). The composition of air, temperature and biomass activity are interdependent values. The stability of the system within the suggested ranges is the expression of a global biogeochemical cycle in "equilibrium" state.

3.4   Climate

3.4.1 The climate conception

The term *climate* has been used over the time in different sense. The word "climate" is derived from the Greek word "clima-ata,"[24] defined as "the slope of the earth from equator to pole" (Barnhardt, 1957). The concept of a spherical world is attributed to the Greek philosopher *Pythagoras* in the sixth century BC (see also Chapter 2). Based on this mathematical-astronomical definition[25], the ancient geographers, namely *Ptolemäos*, introduced 24 *climata*, being zones between two parallel circles, for which the "length of longest day" increases from the equator until polar circle by half a hour stepwise. It is easy to see that theses zones correspond to different "climate"[26]. The ideas of Greek philosophers have been not changed and even not be improved (also not be Romanians) by new observations until end of the Middle Age. Only after introduction of measurement instruments to detect atmospheric properties (temperature, humidity, pressure) and the beginning of continuous monitoring[27] in 18th century, *Alexander von Humboldt* was the first who introduced the term "Klima" in sense of an averaged status of the atmosphere (Fig. 3.8).

Fig. 3.8

Kosmos. Design of a physical world description.
First Volume. 1846. Stuttgart und Tübingen, 493 pp.
By Alexander von Humboldt. Front page (left),
page 340: climate (Klima) definition (right)
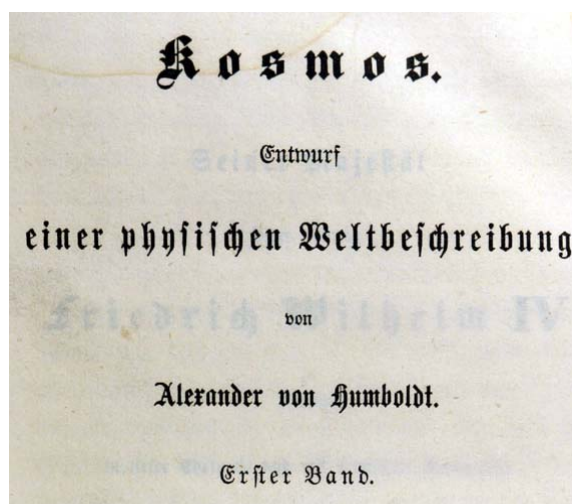
340

Die Einsicht in die Wärme-Vertheilung im Luftkreise hat einigermaßen an Klarheit gewonnen, seitdem man versucht hat die Punkte, in welchen die mittleren Temperaturen des Jahres, des Sommers und des Winters genau ergründet worden sind, durch Linien mit einander zu verbinden. Das System der Isothermen, Isotheren und Isochimenen, welches ich zuerst im Jahr 1817 aufgestellt, kann vielleicht, wenn es durch vereinte Bemühungen der Physiker allmälig vervollkommnet wird, eine der Hauptgrundlagen der vergleichenden Klimatologie abgeben. Auch die Ergründung des Erd-Magnetismus hat eine wissenschaftliche Form erst dadurch erlangt, daß man die zerstreuten partiellen Resultate in Linien gleicher Abweichung, gleicher Neigung und gleicher Kraft-Intensität mit einander graphisch verband.

Wenn die Oberfläche der Erde aus einer und derselben homogenen flüssigen Masse; oder aus Gesteinschichten zusam-

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[24]   greek: κλίμα; latin: clima.

[25]   In same sense: slope at a given site against rotations axis of earth (depends from each geographic latitude).

[26]   The astronomer *Hipparchus* in 140 B.C. stated that countries lying beyond the clima with a longest day of 17 h were uninhabitable on account of the cold and, thus, were of no interest.

[27]   Only at selected sites and for some time. Uninterrupted measurements started only middle of 19th century.

However, *Hippokrates of Kos* (appr. 460-377 BC) was the first who wrote a book on the relationship between air (climate), water and soil properties and its impacts on psychological and physiological constitutions of inhabitants[28]:

Kōou Peri aerōn, hydatōn, topōn. Peri physōn -
Coi De aëre, aquis, & locis libellus. Eiusdem de flatibus. (greek and latin)[29]
On the air, the localities and water (often simple entitled: *On the environment*)

Johann Gottfried von Herder (1744-1803) noted in his book series „Ideen zur Philosophie" (ideas on philosophy), 7th book „Geschichte der Menschheit" (on the histrory of mankind) in footnote 123:

*S. Hippokrates, »De aëre, locis et aqius«, vorzüglich den zweiten Teil der Abhandlung. Für mich der Hauptschriftsteller über das Klima. (...*excellent the second part of treatment. For me the main writer on climate*).*

The *Humboldt* definition with his focus on biosphere-atmosphere interaction (we will see some later that nowaday we accept this defintion again in sense of earth system research) was to broad and soon has been – with the fast development of the *meteorology* as a physical discipline – related to only atmospheric properties. Until now we understand behind climate

the sum of meteorological factors (elements) / or
the summary of weather / or
the mean (averaged) weather,

describing the mean status of the atmosphere at a given site of the earth surface, represented by the statistical total properties (mean values, frequencies, durations etc.) of a long enough time period (Julius v. Hann, 1883; W. Köppen, 1923; E. S. Rubinstein, 1956; K. Schneider-Carius, 1961; J. Blüthgen, 1964; WMO, 1979). Note that it is essential to include the *statistics* into the climate term, i.e., climate means not simple the "mean weather". It follows that

- climate is a function of space and time;
- climate can not be described as a single unit.

With our increasing understanding of global environmental processes it has been conducted that the mean atmospheric status (over several years) not only depends from processes occurring in the atmosphere itself but also from the oceanic circulation, the glacier movement, the spread of vegetation, etc…. Consequently, Gates (1974) defined climate with three categories, namely the *climate system*, the *climate states* and the *climate change*. The climate systems consists from the atmosphere, hydrosphere, kryosphere, lithosphere and biosphere. A climate state is determined by the full description of the statistics of the inner climate system. A climate change is the difference between two climate states of same kind.
The term *climate system* often is named (or synonymous used) by following terms:

- natural earth system, ecosphere, nature (*Alexander von Humboldt*),

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[28] *Poseidonius* (135–51 B.C.) was the first geographer to relate climate to man, saying that the people in the torrid zone, as a consequence of the heat and lack of rain, were born with woolly hair and protruding lips, their extremities being, as it were, gnarled (Brown, 1949).

[29] Hippocratis: Graece & Latine Iano Cornario Zviccaviense Interprete. Basel: Hieronymus Froben und Johannes Herwagen August 1529.

- biosphere (*Vladimir Iwanowitsch Vernadsky*) or
- GAIA (*James Lovelock* and *Lynn Margulis*).

By the stepwise loosing of the human society from only natural conditions (in terms of energy and matter) it has created a new „anthropogenic (*man-made*) system" the *anthroposphere*[30] which, however, is linked with the "nature", i.e. the natural system (which, however, is man-made modified), which nowadays often is called
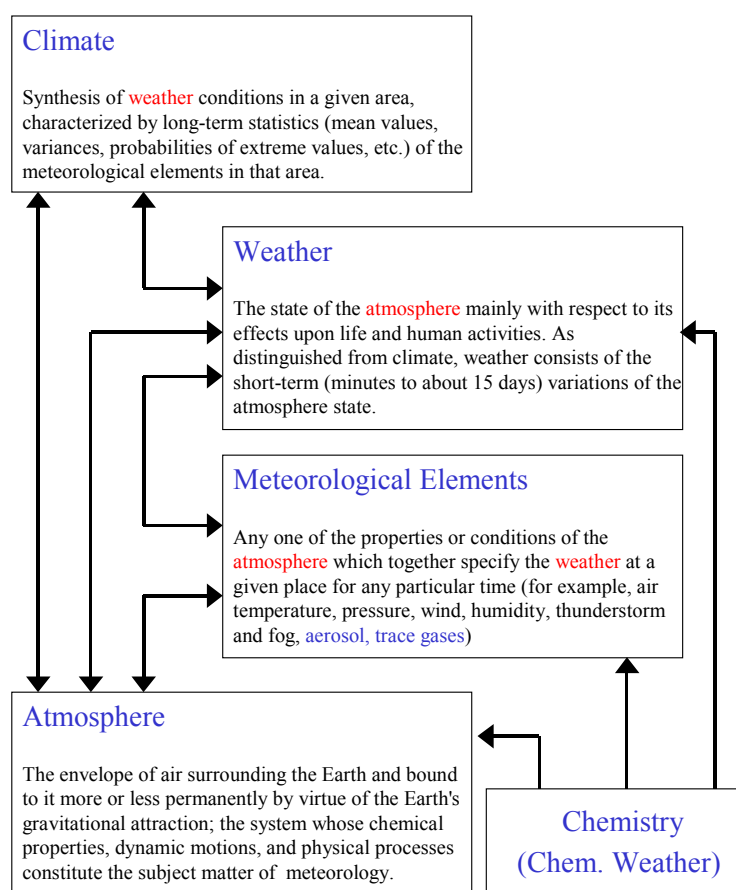
- Noosphere (*Vladimir Iwanowitsch Vernadskij*)[31].

We now can state that an earth system modified by humans has been developed. Thus, we define among climate system the *earth system*:

earth system (= noosphere) = nature + anthroposphere

nature = climate system / natural earth system

anthroposphere = human life sphere (= culture)

Climate

Synthesis of weather conditions in a given area, characterized by long-term statistics (mean values, variances, probabilities of extreme values, etc.) of the meteorological elements in that area.

Weather

The state of the atmosphere mainly with respect to its effects upon life and human activities. As distinguished from climate, weather consists of the short-term (minutes to about 15 days) variations of the atmosphere state.

Meteorological Elements

Any one of the properties or conditions of the atmosphere which together specify the weather at a given place for any particular time (for example, air temperature, pressure, wind, humidity, thunderstorm and fog, aerosol, trace gases)

Atmosphere

The envelope of air surrounding the Earth and bound to it more or less permanently by virtue of the Earth's gravitational attraction; the system whose chemical properties, dynamic motions, and physical processes constitute the subject matter of meteorology.

Chemistry
(Chem. Weather)

Fig. 3.9

Definition of climate, weather, atmosphere and meteorological elements according the the *World Weather Organisation* WMO, Geneve). For meteorological elements, the examples "aerosol, trace gase" is added by D. Möller

Coming back to the more atmospheric definition of climate (Fig. 3.9), the so-called *meteorological elements* (temperature, pressure, humidity, precipitation, wind etc.) – when they are related to a long time period[32] also called *climate elements* (in contrast we may state that weather is the momentum state of the climate elements) play a central role in describing the status of the atmosphere. The WMO definition – and this is trivial now with our present understanding of atmospheric processes – includes (Fig. 3.9) beside physical also chemical properties (Fig. 3.10). Thus, it is unintelligible why no chemical properties have been included in the WMO

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[30] *Paul J. Crutzen* proposed, to subdived the present epoch *Holozän* by *Anthropozän.*.

[31] This term the great Russian geochemist *Vernadsky* got from the french priest and philosopher *Pierre Teilhard de Chardin* (they met in Paris end of 1920s). Vernadsky understood with noosphere a new dimension of the biosphere, developing under the evolutionary influence of humans on natural processes.

[32] The duration of the period is not fixed. The weather service calculates climate data on a basis of 30 years.

definition of meteorological elements (Fig. 3.9).

Fig. 3.10

Physical and chemical properties of the atmosphere being climate (and weather) element

Changes of temperature are only one aspect of a changing climate! Accepting this universal definition describing the status of the earth system (or at least a significant part of it) it is easy to accept that beside atmospheric physical elements there are also chemical and other parameters determining the system, which have to be included into *climate elements* (Fig. 3.10). Moreover, with this background we better understand *climate change*, because it means that one or more of the earth system determining climate

Climate Elements

meteorological:

- temperature
- precipitation
- wind
- cloudiness
- humidity
- sun shine duration
- air pressure
- radiation

physico-chemical:

- deposition (dry, wet)
- trace gas concentration (ozone, greenhouse gase etc.)
- aerosol (number, mass, surface, properties)
- climate forcing
- acidifying potential
- oxidation potential

elements are changing to a qualitative transfer[33]. Despite the linguistic simplification we should not forget the complexity of the system: even the most advanced mathematical models running on the biggest (and network linked) computers are still unable to produce a true picture of the climate system to draw *reliable* conclusions. Experimental validation of the model outputs, however, is only possible *after* climate change – that is the dilemma! Parts of the model (or the system) can be validated with related experimental approach, e.g. cooling the atmosphere by particulate matter after large volcanic eruptions.

In recent time the term *chemical weather* came in use. Using the definitions above, the meaning is limited on selected "weather elements", e.g. the chemical composition of even selected species, e.g. ozone concentration. Some institutions prepare the forecast of "chemical weather". I do not see much sense in doing it, as trace gas concentrations presently (when there is not an accident) are almost below acute impact levels and there is neither no way nor no need to response on chemical weather. In contrast, a long-term forecast of the *chemical climate*, however, is extremely important due to the close interaction between the physical and chemical system (climate change) and due to the fact that any feedback response to establish abatement strategies needs many years and even decades.

It is remarkable that 130 years ago, just in the periode of defining climate being a meteorological quantity, the idea of a *chemical climatology* was born:.

"Acid Rain – the Beginning of a Chemical Climatology" by R. A. Smith, published in

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[15] In nature there is no jump, as nature itself composes of jumps. The idea of interactive changes from quality to quantity and vice versa is a main principle of dialectics. The fact that our subjective thinking and the objective world underlies the same laws and therefore can not contradict in their results, but correspond, rules our complete theoretical thinking. It is an unconscious and unconditional premise. The materialism of the 18th century studied this premise according to its vitally metaphysic character on its content only. It limited itself on the proof, that the content of all thinking and knowledge descends from sensual experience, and reconstructed the sentence: *Nihil est in intellectu, quod non fuerit in sensu* (Nothing is in the mind, which has not before been in the senses). Dialectics as the science of the common laws of all movement has first scientifically been founded by Friedrich Engels (s. Karl Marx/ Friedrich Engels - Werke. (Karl) Dietz Verlag, Berlin. Band 20. Berlin/DDR. 1962."Dialektik der Natur")

London 1872 (Longmans, Green, & Co)

Robert Angus Smith (1817-1884) was a Scottish chemist who investigated numerous environmental issues. He published his findings of different kinds of rain first in 1852 in the Memoirs and Proceedings of the Manchester Literary and Philosophical Society "On the air and rain of Manchester". Since that time the term "*acid rain*" is used (newly introduced in the 1960s as synonym for acidifying the environment). To me, more noteworthy is the thinking of *Smith´*s concerns climate.

3.4.2 Past climate (paleoclimate)

With land settlement the rate of photosynthesis quickly increased and induced in *Karbon* a decrease of atmospheric carbon dioxide due to carbon storage in biomass. On the other hand, CO_2 regeneration via oxidation of organic carbon were unable to balance the atmospheric CO_2 pool. As a consequence, due to smaller absorption of terrestrial radiation by atmospheric CO_2, the earth surface was cooling. Smaller temperatures reduced the photosynthesis and lowered the O_2 content. We explain the ice era in *Perm* (280 Ma back) by this controlling mechanisms. Oxygen and carbon dioxide did oscillate anticorrelated but very smoothed and within a period of about 100 Ma (Budyko et al., 1987). Probably not the changing CO_2-O_2 ratio is a consequence but the cause of the *Pleistocene* ice eras. Photosynthetic assimilation works as a "regulator". Ice eras lasted over a few ten thousand years. With the beginning of an ice era CO_2 concentration fell to 200 ppm and at the end (the beginning of a warm period) rose to 270 ppm. The last *Würm* ice era ended 11.000 years ago with a reduced mean temperature of 3° C.

The global climate – or *earth climate* – is also influenced by outer factors (variations of solar radiation and orbit), which are probably responsible for the 10000-50000 year oscillation of ice eras within the last 2 Ma. Inner factors concern changes in surface albedo or solar scattering due to volcanic eruptions, variation of oceanic circulation and changes of atmospheric chemical composition.

Solar models show us that at beginning of the earth evolution (4,5 Ga back) solar radiation must have been 25-30% reduced compared to present time. The subsequent reduced earth surface temperature (8%) would freeze all oceans for 2 Ga. However, total freezing never happens and it is assumed that temperature compensation was made by increasing greenhouse effect (Wayne, 1996).

Natural climate variation in periods between decades and some hundred years have been found; the causes are not yet clear. Variations of the earth rotation – caused by core dynamics or shifts in mass at the surface – may be mechanisms. sunspot cycles (11 and 22 a) as well as cycles (208 a) of orbits of the outer planets (Uranus, Neptune, Pluto) are other causes.

Despite alternating ice and warm eras our climate has to be considered as quite stable over the last 3,5 Ga. Ice eras affected the surface in areas above 45° N and below 45° S - about 30 % of the surface, partially permanently frozen. All biogeochemical findings suggest, that the ocean had never been completely frozen nor boiling. Very likely the mean surface temperature ranged between 5° and 50° C. If there were not any infrared absorbing gases in our atmosphere and if the surface had an albedo – just as Mars – the mean near surface temperature would measure about 23° lower (at present at about 5°C). These components, called greenhouse gases are mainly H_2O, CO_2 und CH_4. The radiation budget (and therefore the heat budget) is modified by atmospheric aerosol and clouds. The presence of H_2O and CO_2 in the secondary atmosphere lies more than 4 Ga back in time and was a requirement for the oceans not to freeze.

The disturbances caused by anthropogenic activities ever since the industrial revolution of 1860 to the biogeochemical cycles, which in part already heavily exceeded the natural matter

flow, may still be within the natural variation of the air composition. The periods of natural variations and changes, however, are far beyond dimensions of the last 150 years. Our atmospheric environmental problem is therefore a matter of adaptation in time of various subsystems with the global system in the first place.
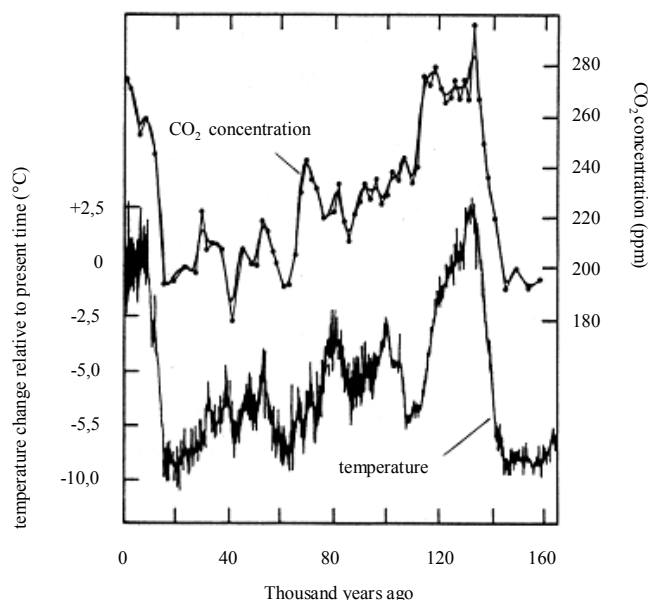
Fig. 3.11

CO_2 concentration (in ppm) compared to the local temperature change, as deducted from Vostok ice core (Antarctica) by Schneider (1991)

Ice core studies are one of the best methods to find out something about the paleo climate (up to 0,2 Ma back). From chemical analysis and isotope relations of the ice core composition as well as the embedded air bubbles the composition of the atmospheric air at that specific time can be concluded (Fig. 3.11).

Present as the steady border in time between past and future gives us a drastic acceleration in change of air composition (Tab. 3.11).

Table 3.11 Atmospheric concentration of climate relevant trace gases, by Lelieveld et al. (1998)

year	CO_2 (ppm)	CH_4 (ppb)	N_2O (ppt)	CFC-11 (ppt)	CFC-12 (ppt)
before 11000 a[a]	195	350	244	0	0
1850	280	750	260	0	0
1900	296	970	292	0	0
1960	316	1270	296	18	30
1970	325	1420	299	70	121
1980	337	1570	303	158	273
1990	354	1720	310	258	484
1995	360	1730	312	258	532

[a] last ice era

According to the report of the IPCC[34] (2001) the following statements concerning the climate change can be made:

- The global mean surface temperature rose during the 20th century by 0,6±0,2 K, where the strongest warming occurred in the periods of 1910-1945 and 1997-2000.
- The 1990s were the warmest decade and 1998 the warmest year since 1861.
- The rise in temperature over a hundred years was the biggest over the last 1,000 years.
- Snow coverage was reduced by 10% since the end of the 1960s (satellite observed), the freezing duration of lakes and rivers sank in middle and higher latitudes of the northern hemisphere in the 20th century by 2 weeks (surface observations)
- The global mean sea level rose by 0.1-0.2 m in the 20th century.
- Precipitation in the 20th century rose in most areas of the middle and higher latitudes of

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[34] Intergovernmental Panel of Climate Change

the northern hemisphere by 0.5 - 1% a decade, while it sank over tropical areas (10° N - 10° S) by 0.2 – 0.3%.
- The frequency of heavy rains in middle and higher latitudes of the northern hemisphere rose by 2-4% in the last 20 - 30 years
- Cloud coverage in middle and higher latitudes of the northern hemisphere likely rose by 2%.
- Since 1978 no changes of the ocean ice have been observed.
- In some areas of the southern hemisphere, especially in antarctica and over oceans, no warming has been registered
- The atmospheric content of CO_2 rose from 1750 by 31%; the current concentration has very likely never been exceeded within the last 420,000 years – maybe not even in the last 20 million years. Since 1980 it rises by 1.5 (0.9-2.8) ppm a year. Three quarters of the CO_2 emissions originate from fossil fuel burning, another quarter from changes in land use.
- The atmospheric concentration of CH_4 (1060 ppb) rose from 1750 by 151%; the current concentration has never been exceeded over the last 420,000 years.
- The atmospheric concentration of N_2O (46 ppb) rose from 1750 by 17%.

Appendix 1: The photosynthesis (history)[35]

The observation that a willow that has been cultivated in a container for five years with enough watering gained more than half a centner weight although only two ounces of the container's soil were lost goes back to *J. B. van Helmont* (1577-1644)[36]. The British natural scientist *S. Hales* (1677-1761) understood that air and light are necessary for the nutrition of green plants. But it was not before the composition of air out of different gases became known that their significance for plant nutrition was studies. In 1771 observed *J. Priestley* (1733-1804), one of the discoverers of oxygen (beside the Swedish *C. W. Scheele*), that green plants give off oxygen and thus improve the air.

The priest *J. Senebier* (1742-1809) from Geneva discovered that the regeneration of the air is based on the use of "ixed air" (carbon dioxide). These observations were confirmed and broadened by studies of the Dutch doctor *J. Ingenhousz* (1730-1799) who recognized both the meaning of light and the fact that the whole carbon contained in plants is of atmospheric origin. He, too, conceived that plants take up small amounts of oxygen at night or in the shadow and give off carbon dioxide. In 1804 discovered *Th. des Saussure* (1767-1845) from Geneva that the plants' increase in weight cannot solely be caused by the uptake of carbon and minerals, but is based on the binding of the water components, too.

In 1894 constructed *Engelmann*[37] a gadget out of a modified microscope condenser that allowed him to expose parts of photosynthetically active cells (of the green alga *Spirogyra*) to a thin ray of light. His aim was to discover which components of the cell functioned as light receptors. To measure the oxygen production, he dispersed the thread-like *Spirogyra* in a

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[35] See also Chapter (Script) 2. This Appendix has been taken (and slightly changed) from the homepage of Professor *Paul von Sengbusch* (University Hamburg); The project "Botany *online* - The Internet Hypertextbook" inclusive of all its parts is copyrighted. Each utilization exceeding the limits of the copyright is inhibited unless the copyright owner has agreed to it. This holds especially for duplications, translations and the feeding into and processing in data processing systems with the aim of commercial use. This copyright note has to be added to all non-commercial copies. See http://www.biologie.uni-hamburg.de/b-online.

[36] Biographic information is only given for persons not yet mentioned in Chapter 2 (Historical overview on discovering the atmosphere).

[37] Theodore Wilhelm Engelmann (1843–1909) German botanist. 1897 succeeded *Emil du Bois-Reymond* at University of Berlin (1818-1876; 1858 professor of physiology at the Physiological Institute)

bacteria-containing suspension. Whenever parts of the chloroplast were illuminated, did the bacteria concentrate in this area (where oxygen was available). The illumination of other parts of the cell resulted in no such aggregations.

In an earlier study did he split white light into its spectral components using a prism. He then illuminated a green alga, *Chladophora*, with this spectrum. In contrast to *Spirogyra* are the *Chladophora* cells completely and evenly filled by the chloroplast. He observed that the bacteria accumulated mainly in the blue and red light. A first spectrum of photosynthesis was thus yielded. It resembles roughly the absorption spectra of chlorophyll a and b.

Sachs[38] could finally prove that chlorophyll is involved in photosynthesis. These results are in accord with the first law of thermodynamics, whose discoverer *Mayer*[39] postulated already in 1842 that plants take up energy in the form of light and that they transform it into another, a chemical state of energy. Based on this assumption was the reaction equation

$$6\ CO2 + 6\ H_2O > (chlorophyll) > C_6H_{12}O_6\ (glucose) + 6\ O_2$$
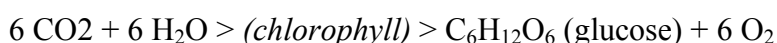
formulated. *Justus von Liebig* assumed that the oxygen stems from the breakdown of the carbon dioxide. This idea was uncritically accepted by the plant physiologists of the late 19th and the early 20th century (*Sachs*, *Pfeffer*, *Jost* and others) although *M. J. Schleiden*[40] had as soon as 1842 realized that (a) glucose is produced as a result of photosynthesis (and he was closer to reality than SACHS was later) and (b) that it is very likely that it is water that is broken down. He wrote:

"It is well-known that CO_2 is among the most stabile compounds and that no chemical way of breaking it down is known while H_2O is very easily broken down.... and it does therefore seem likely that the 24 H_2 of the 24 H_2O are combined with the 12 CO_2."

(from: *Grundzüge der wissenschaftlichen Botanik*). Schleiden's equations contain all reaction compounds in double numbers. He gives $C_{12}H_{24}O_{12}$ as the formula for glucose. It was soon realized that the reaction equation above is a simplification and that photosynthesis consists of a number of partial processes.

F. F. Blackmann and *G. L. C. Mathgel* (1905, University of Cambridge, Great Britain) were among the first to study this topic systematically. They cultivated plants under different but controlled carbon dioxide concentrations, different light intensities and different temperatures and they noted the effects of these parameters on the rate of photosynthesis. Two decisive aspects were revealed. Under strong light and limited amounts of carbon dioxide is the rate of photosynthesis dependent on the temperature. This shows that the carbon dioxide fixation is based on normal, temperature-dependent biochemical reactions. Under carbon dioxide excess and too little light was no temperature-dependence found. This hints at the fact

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[38] Julius von Sachs (1832-1897) Born in Breslau. German botanist; 1856 Privatdozent for plant physiology in Prague, assistant to the Agricultural Academy at Tharandt in Saxony, 1861 Professor of Botany in the University of Freiburg in Breisgau. 1868 he took over the chair in Botany at the University of Wursburg.

[39] Julius Robert von Mayer (1814-1878) Born in Heilbronn. He studied medicine but physics became his new passion. In June of 1841, he completed his first scientific paper entitled, "On the Quantitative and Qualitative Determination of Forces." It was largely ignored by other professionals in the area. He also was the first person to describe the vital chemical process now referred to as oxidation as the primary source of energy for any living creature. 1867, he published "Die Mechanik der Wärme" (The Mechanis of Heat). In the same year he was awarded personal nobility (von Mayer). Mayer was the first person to develop the law of the conservation of energy (first law of thermodynamics).

[40] Matthias Jakob Schleiden (1804-1881) At first solicitor, later botanist. Founder of the cell theory. Author of "Grundzüge der wissenschaftlichen Botanik" (*Basic Scientific Botany*), the definitive textbook on botany at the middle of the 18th century. He pointed out that water and not carbon dioxide is split during photosynthesis. It was he, who prompted *Carl Zeiss* (Jena) to produce microscopes on a commercial basis.

that the light-induced reactions are independent of the temperature. This statement applies to all photochemical reactions.

In 1925 put *O. Warburg* (Kaiser-Wilhelm-Institut [later Max-Planck-Institut] für Zellphysiologie at Berlin-Dahlem) the results of *Blackmann* down to the existence of two classes of photosynthetic reactions: the light and the dark reaction. During the 1930s analyzed *C. B. van Niel*[41] the photosynthesis of a number of purple bacteria. In addition to CO_2 do these bacteria need hydrogen sulphide (H_2S) for photosynthesis. *Niel* was able to determine

$$6\ CO_2 + 12\ H_2S > \textit{(light)} > C_6H_{12}O_6 + 12\ S + 6\ H_2O$$
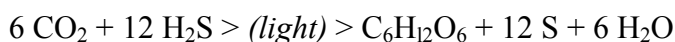
as the reaction's equation. Based on it did he extrapolate a general equation of photosynthesis:

$$CO_2 + 2\ H_2X > \textit{(light)} > (CH_2O) + H_2O + 2\ X$$
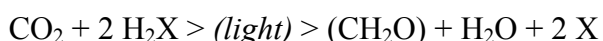
According to this equation is photosynthesis a redox reaction with H_2X as the electron donator (the oxydizable substance). In the case of green plants is it H_2O and this means that not the carbon dioxide but the water is broken down.

A first experimental prove that the oxygen developed during the photosynthesis of green plants stems indeed from water was delivered by the British physiologist *Hill*[42]. He detected that isolated chloroplasts give off oxygen in the presence of unnatural reducing agents like iron oxalate, ferricyanide or benzoquinone after exposure to light. The reaction went down in literature as the *Hill*-reaction:

$$2\ H_2O + 2\ A > \textit{(light, chloroplasts)} > 2\ AH_2 + O_2$$

where A is the electron acceptor. If $A = Fe^{3+}$, then is

$$2\ H_2O + 4\ Fe^{3+} > \textit{(light, chloroplasts)} > 4\ Fe^{2+} + O_2 + 4\ H^+$$

The process is linked to a photolytic breakdown of water that precede the reduction of Fe^{3+}.

$$4\ H_2O > \textit{(light, chloroplasts)} > 4\ H^+ + 4\ OH^-$$

This shows that (a) oxygen can also be set free in the absence of carbon dioxide, (b) the oxygen produced stems from the breakdown of water, and (c) isolated chloroplasts are able to perform at least partial processes of photosynthesis.

The statement that the oxygen produced during photosynthesis stems only from the breakdown of water was confirmed by *Ruben* and his coworkers[43] in 1941 after the isotope

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[41] (Michael) Cornelius B. van Niel (1897-1985), Dutch microbiologist (Van Niel was the third important figures of the Delft School of microbiology: *Martinus W. Beijerinck* ,1851-1931; *Albert J. Kluyver*,1888-1956). In 1923, he received Chemistry Engineering degree. His Ph.D. dissertation was entitled *"The Propionic Acid Bacteria"* and published in 1928. He came to the U.S.A. in in the same year upon the invitation of *L.G.M Baas-Becking* (1895-1963), professor of physiology of Stanford University. He developed a revolutionary concept of the chemistry of photosynthesis that was to influence research on the topic for many years. He also was the first in the United States to teach "General Microbiology." His teaching resulted in the great blossoming of microbiology in 20. century. Many distinguished microbiologists including Nobel Laureates, were influenced by him directly or indirectly.

[42] Robert (Robin) Hill (1899-1991) British biochemist. He was educated at Cambridge and remained researching there until 1938. From 1943 to 1966 he was a member of the scientific staff of the Agricultural Research Council. Hill's experiments in 1937 confirmed that the light reactions of photosynthesis occur within the chloroplasts of leaves, as well as elucidating in part the mechanism of the light reactions.

[43] Ruben, S. M., M. Randall, M. D. Kamen and J. L. Hyde (1941) Heavy oxygen (^{18}O) as a tracer in the study of photosynthesis. *J. Am. Chem. Soc.* **63**, 877-879.

technique had found its way to biochemistry. They could shown that a suspension of *Chlorella* grown in $H_2{}^{18}O$, gives off 18 O_2, after light exposure. Shortly afterwards confirmed *Ruben* and his collaborators the postulate of *Warburg* that the fixation of carbon dioxide is energy consuming but independent of light. In addition could *Racker*[44] prove that light can be replaced by the addition of energy-rich compounds.

Appendix 2: The GAIA Hypothesis

"Gaia" is the name for the goddess of Earth in Greek mythology. The English words geology, geochemistry, geography all contain the same root referring to Earth. "Gaia" and "Gaia Hypothesis" are concepts introduced by the British engineer and science writer *James Lovelock* (born 1919). They represent the thought that the dynamic life support systems of Earth (including the ocean, air, soil and the flux of elements) act much like an organism and appear to be internally controlled. An analogous concept from the early history of economics was *Adam Smith*'s "Invisible Hand" that controls market dynamics. "Gaia" is the "Invisible Hand" of biogeochemistry. *Lovelock* suggests that life processes regulate the radiation balance of Earth to keep it habitable. Since Earth is indeed habitable, and since the carbon cycle has helped to keep it that way throughout Earth history despite any changes in the Sun's brightness, there can be little argument that the "Gaia hypothesis" cannot be falsified. Some critics have made much of the fact that this personified "Life" cannot be expected to do things for future life. Yet, somehow life processes did help to keep the system "in check" - if this were not so, humans would not be here. Nevertheless, just as the "Invisible Hand" does not prevent market crashes, thus also "Gaia" cannot prevent major setbacks to life on Earth, from outside disturbance or even from internal runaway processes. While not strictly a "hypothesis" in the scientific sense since it cannot be falsified, the "Gaia hypothesis" has great merit as an educational tool, regarding the concepts of biogeochemical cycling. Do biogeochemical processes indeed combine forces to favor life on Earth? Critics suggest that the processes of living organisms in the past were not necessarily favorable for the long-term survival of the then existing life. For example, the growth of oxygen in the atmosphere, through expanding photosynthesis, greatly diminished opportunities for anaerobic organisms. However, new life forms evolved that took advantage of the new situation (for example, highly mobile multicellular organisms, including humans).

In 1987, *Robert (Bob) Charlson* and his colleagues (Charlson et al., 1987) suggested that phytoplankton don't just simply affect climate by producing the gas dimethyl sulphide (DMS) but actually play a role in regulating the climate of the Earth. The CLAW hypothesis (named after the authors of the paper) says that if a change in the temperature of the Earth occurs, for example due to global warming, phytoplankton respond to reduce this change. The authors idea was that if temperature increases, phytoplankton will grow more and produce more DMS. The increase in DMS concentrations would subsequently lead to an increase in the amounts of sulphate aerosol in the atmosphere and these aerosols would both directly and indirectly cool the planet, reducing the initial temperature rise, see Fig. 3.12.

The CLAW hypothesis is an example of a negative feedback loop where some mechanism acts to counteract the initial change in such a way to maintain the *status quo*. Positive feedback occurs when the initial change is amplified by subsequent processes. All scientific

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[44] Efraim Racker (1913-1991) Born in Poland but soon moved to Vienna. Studied medicine at the University of Vienna. In 1938 he fled via Denmark to Great Britain where the biochemist J. Hirsh Quastel offered him a job at Cardiff City Mental Hospital in Wales. 1941 he moved to USA. His career as a biochemist started in earnest only in 1944 with his appointment as staff member in the Microbiology Department of New York University Medical School. In 1954 he accepted the position of chief of the Nutrition and Physiology Department at the Public Health Research Institute of the City of New York. 1966 member of National Academy of Sciences. Same year a Cornell University, Ithaca, N. Y.

studies conducted so far show that sulphate aerosols are important in climate control and models suggest that they do cause cooling. Ice cores, which give a record of the Earth's past, show that sulphate aerosol levels in the atmosphere have changed in phase with climate cycles over glacial and interglacial time scales. Recent studies have also shown that there is a link between DMS emissions and the number of cloud condensation nuclei (CCN) present in the atmosphere and that increases in the temperature of surface seawater do lead to increases in DMS concentrations in the air.

So we now have evidence that some of the steps within the CLAW hypothesis are correct but we still don't know whether the system really operates as a negative feedback loop. This makes it very difficult to represent the process in climate models and so we are still unsure quite how important DMS is to the cooling of our planet.

Fig. 3.11

simplified representation of the CLAW Hypothesis, an example of a negative climate feedback loop. DMS stands for dimethyl sulphide and CCN for cloud condensation nuclei.
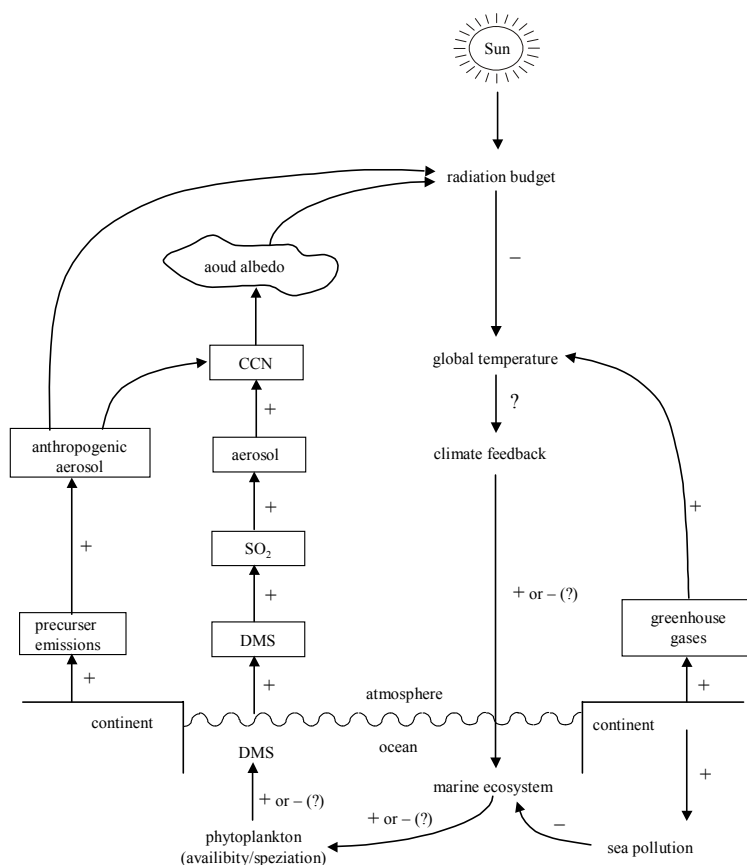
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