Chapter 14
Radiocarbon in Natural Waters

Carbon has always played an important role in geochemical processes which take place in the upper layers of the Earth and, in the first instance, in the formation of the sedimentary terrestrial layer and the evolution of the biosphere. Radioactive carbon ^{14}C is often used as a tracer of various natural processes such as the circulation of natural waters, their redistribution between the natural reservoirs, water dynamics of the hydrosphere and its elements, and is applicable for estimating the age of such waters. The age of geological formations and groundwater within the time scale up to 60,000 years is of a great interest for modern geology and hydrogeology. The data of radiocarbon distribution in different carbon-bearing natural objects are used for reconstruction of their paleoclimatic changes and for solving astrophysical problems related to variation with respect to time of the cosmic rays. In this chapter the main attention is drawn to the distribution and application of radiocarbon with respect to dynamics of natural waters.

14.1 Origin and Distribution of Radiocarbon in the Nature

As it was shown in Chap. 1, the radiocarbon is formed in the atmosphere in the course of the interaction of secondary neutrons generated by cosmic rays, mainly with nitrogen-14, according to the reaction as shown in Eq. 14.1:

$$^{14}\mathrm{N} + n = {}^{14}\mathrm{C} + p + 0.626\ \mathrm{MeB}. \qquad (14.1)$$

The cross-section of the reaction is 1.81 ± 0.5 barn. Table 14.1 shows the main reactions responsible for radiocarbon production in the atmosphere, but their contribution to the total ^{14}C balance compared to the reaction (Eq. 14.1) is insignificant.

The radiocarbon produced is usually oxidized to $^{14}CO_2$ after several hours in the atmosphere, which is characterized by approximately the same carbon isotopic composition and takes part in general global circulation of the carbon dioxide. The total equilibrium amount of radiocarbon on the Earth (in the atmosphere, hydrosphere, and biosphere) can be theoretically estimated. According to Libby (1955), it is equal

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Table 14.1 Reactions of radiocarbon production in the atmosphere by the secondary neutrons' action. (© IAEA, reproduced with permission of IAEA)

Reaction	Reaction energy (MeV)+, exothermic; −, endothermic	Abundance relative ^{14}N	Relative rate production in atmosphere
$^{13}C(n, \gamma)^{14}C$	+8.17	0.23×10^{-5}	1.1×10^{-9}
$^{14}N(n, p)^{14}C$	+0.626	1.0	1.0
$^{15}N(n, d)^{14}C$	−7.98	0.37×10^{-2}	3.7×10^{-5}
$^{16}O(n, {}^{3}He)^{14}C$	−14.6	0.269	2.7×10^{-3}
$^{17}O(n, \gamma)^{14}C$	+1.02	0.99×10^{-4}	2.3×10^{-5}
^{20}Ne, ^{21}Ne (split)^{14}C	–	0.12×10^{-4}	1.2×10^{-7}

to 81 t and the estimations of Lal and other researchers (see Chap. 11) give 60–75 t which is equivalent to an activity of about 3×10^8 Ci.

Despite considerable variations in the secondary neutron flux from the equator to the poles, which differs by a factor of 3.5, the ^{14}C isotope is sufficiently homogeneously distributed on the Earth. This effect was well studied by the artificial bomb-radiocarbon which gives evidence of the high rate of mixing of the atmosphere. Experimental data show that variations with latitude and altitude do not exceed 3–5%.

Some amount of ^{14}C can be received on the Earth together with the meteoritic matter, where it is produced by interaction with cosmic rays. The lunar soil and rock studies showed that the carbon content in the sample No 14163 is 109 ± 12 g/t (109 ± 12 ppm together with correction on the Earth's contamination (Fireman and Stoenner 1982)). The radiocarbon activity in two fractions, extracted by heating in oxygen at $T = 1{,}000°C$, was 31.2 ± 2.0 disintegration min^{-1}/kg for the fraction of >53 μ and 11.2 ± 2.0 disintegration min^{-1}/kg for the fraction of <53 μ.

The above mentioned authors assume that the radiocarbon derived in that way was produced by action of the solar wind. The carbon activity is approximately the same for both fractions (19.2 ± 2 and 21.0 ± 15 disintegration min^{-1}/kg). This is explained by interaction of cosmic rays with the lunar rocks and direct partial production of the radiocarbon.

The studies of dynamics of the carbon exchange between the natural reservoirs, based on ^{14}C tracer and theoretical investigations of the radiocarbon redistribution between the natural reservoirs (boxes), their number is arbitrarily accepted from one (Gray and Damon 1970; Ralf 1972) to six (Craig 1957; Plesset and Latter 1960; Bacastrow and Keeling 1973; Ekdahl and Keeling 1973). However, the majority of studies were done using two or three box-models (Damon 1970; Lingenfelter and Ramaty 1970; Yang and Fairhall 1972; Keeling 1972).

Figure 14.1 shows schematic two-box model used by Sternberg and Damon (1979). In accordance with this model, the radiocarbon, being produced in the upper parts of the atmosphere with the rate $Q(t)$ atom cm^{-2} sec^{-1}, is immediately moved into the reservoir A composed of the atmosphere, biosphere, and mixing layer of the ocean. Between this reservoir and the reservoir B of the deep ocean waters, the radiocarbon exchange results with the rates K_{as} and K_{sa}. Due to the radioactive decay, the loss of radiocarbon from the reservoirs A and B occurs. The exchange rate K_{as}, as

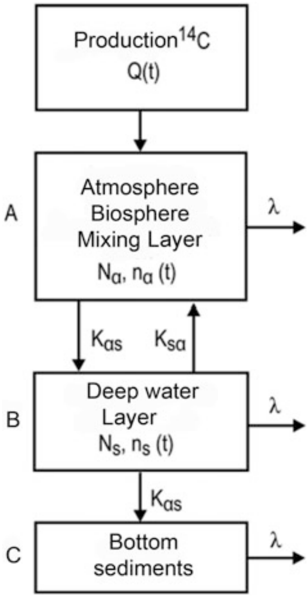


Fig. 14.1 Two-box radiocarbon exchange model. (After Sternberg and Damon 1979)

well as N_a and N_s, which are the total amount of carbon per cm^2 of the Earth surface as well as in the reservoirs *A* and *B*, are accepted constant in time. The amount of ^{14}C atoms/cm^2 in the reservoirs *A* and *B* ($n_a(t)$ and $n_s(t)$ accordingly), is the function of $Q(t)$.

The two-box model can be described by two differential equations

$$\frac{dn_a(t)}{dt} = Q(t) - K_{as}n_s(t) + K_{sa}n_s(t) - \lambda n_a(t), \tag{14.2}$$

$$\frac{dn_s(t)}{dt} = K_{as}n_a(t) - K_{sa}n_s(t) - K_{as}n_s(t) - \lambda n_s(t). \tag{14.3}$$

Note that the reverse value of the exchange rate is equal to the mean residence time *t* of radiocarbon in the reservoir. Taking into account that the specific activity of radiocarbon A_i in the i^{th} reservoir is $\lambda n_i/N_i$, the Eq. 14.2 can be written as:

$$\frac{d(\lambda n_a(t)/N_a)}{dt} = \frac{\lambda Q(t)}{N_a} - K_{as}\frac{\lambda n_a(t)}{N_a} + \frac{K_{sa}}{N_a}\lambda n_s(t) - \frac{\lambda^2 n_a(t)}{N_a}, \tag{14.4}$$

$$\begin{aligned}\frac{dA_a(t)}{dt} &= \frac{\lambda Q(t)}{N_a} - K_{as}A_a(t) + \frac{K_{sa}N_s}{N_a[\lambda n_s(t)/N_s]} - \lambda A_a(t)\\ &= \frac{\lambda Q(t)}{N_a} - K_{as}A_a(t) + \frac{K_{sa}A_s(t)N_s}{N_a} - \lambda A_s(t)\end{aligned} \tag{14.5}$$

Analogously for the reservoir *B*, one has

$$\frac{dA_s(t)}{dt} = \frac{K_{as}A_a(t)N_a}{N_s} - K_{sa}A_s(t) - K_{as}A_s(t) - \lambda A_s(t). \tag{14.6}$$

In equilibrium conditions, the process of the carbon exchange between the reservoirs *A* and *B* is satisfied to equality

$$K_{as}N_a = K_{sa}N_s \tag{14.7}$$

or

$$K_{as}/K_{sa} = N_s/N_a = \nu, \tag{14.8}$$

where ν is the ratio of the carbon content in the reservoirs *A* and *B*.

It follows from Eq. 14.8 that the carbon exchange rate is in reverse proportion to the total carbon reserve, and vice versa, the residence time *t* is proportional to the carbon amount in the exchange reservoirs. The effect of carbon isotope fractionation at its redistribution between reservoirs should be taken into account while studying the parameters K_{as} and K_{sa}. As shown by Craig (1957), the real value of the fractionation factor $\alpha_{\mathrm{s/a}}$ is equal to about 1.012.

On the basis of experimental data, by Eqs. 14.5–14.8, one may calculate values of ^{14}C distribution and assess the effect of dynamics of carbon exchange between the reservoirs. For these calculations, the values A_{q}, A_{s}, *Q* should be taken for the steady state condition. The *Q* parameter, as a rule, is determined by means of the decay rate *I* of radiocarbon, which relates to 1 cm^2 of the Earth's surface. In general case, *I* relates to *Q*(*t*) by equation $I = -\lambda \int\limits_0^\infty Q(t)e^{-\lambda t}dt$. It is obvious, if one considers that *Q*(*t*) does not depend on time (which is not entirely correct), then $I = Q$. Equating the left hand side of Eq. 14.5 to zero replacing $K_{\mathrm{sa}}N_{\mathrm{s}}/N_{\mathrm{a}}$ by K_{as}, for the stationary state condition one obtains

$$K_{as} = \frac{\lambda(Q/N_a - A_a)}{(A_a - A_s)}, \quad t_a = \frac{(A_a - A_s)}{\lambda(Q/N_a - A_a)}. \tag{14.9}$$

where t_{a} is the residence time of radiocarbon in the reservoir *A*.

On the basis of experimental data, Sternberg and Damon (1979) accept the following mean values: $\bar{A}_a = 14.5ppm/g(C)$, $\bar{A}_s = 12.6ppm/g$, $Q = I = 108$ ppm/cm^{-2} and $N_{\mathrm{a}} = 0.361$ g (C)/cm^2. In this case, the carbon residence time in the reservoir *A* is about 50 years. In a similar way, on the basis of more number of reservoirs (boxes), the residence time of carbon in the atmosphere exchanging with the fast mixing ocean layer can be estimated. For this case, Sternberg and Damon accept the following parameters: $\bar{A}_a(1.890) = 13.8ppm/g(C)$, $\bar{A}_{\Pi.\mathrm{c.}} = 0.965\bar{A}_{\mathrm{s}}$ and $N_{\mathrm{a}} = 0.125$ g(C)/cm^2. In this case, one has $t \approx 5$ years. The similar estimates of the carbon residence time in the biosphere, in the fast mixing layer of the ocean and its deep layers give mean values of 60, 10 and 1,500 years respectively. These are the approximate results because of low accuracy in the parameters calculated. The values of carbon in a number of exchange reservoirs used for theoretical calculations are given in Table 14.2.

The possibility of ^{14}C production in nitrogen-bearing objects (in the wood, for example) *in situ* by reaction with neutrons, generating by the cosmic rays or occurring spontaneously in rocks at nuclear reactions, were considered.

Table 14.2 The amount of carbon in some exchange reservoirs

Reservoir	Carbon amount (g/cm^2)	
	Libby (1955)	Rubey (1964)
Ocean carbonates	7.25	6.95
Ocean dissolved organic substance	0.59	–
Biosphere	0.33	–
Living organisms and non-decomposed organic substance	–	0.775
Atmosphere	0.12	0.125
Total	8.29	7.85

Radnell et al. (1979) considered a possibility of the radiocarbon accumulation with respect to time in woods by the thermal neutrons of cosmic origin irradiation. It was shown that in nuclear reaction with nitrogen-14 (fast neutrons) in bristlecone pine, the activity of about $(1.7 \pm 0{,}6) \times 10^{-3}$ ppm/g (C) during 8,000 years can be reached, i.e., this is only 0.03% of natural ^{14}C radioactivity in wood 8,000 years of age.

Zavelsky (1968) has shown that possibility of ^{14}C generation in situ is limiting the upper value of the measured radiocarbon age. According to calculation, such a limit for a number of objects can be age of 80,000–100,000 years.

The theoretical specific activity of ^{14}C in the modern carbon-bearing samples should be about 17 ppm/g (C) (Libby 1955). Numerous comparable studies in different regions have shown that the specific activity of ^{14}C in biosphere varies from 14 to 16 ppm/g for the inland specimens and from 13 to 17 ppm/g for the ocean specimens. The average activity is 15.3 per gram of carbon. For the ocean carbonates, this value averages around 16.0 ppm/g, i.e., approximately 5% higher than for the biogenic ^{14}C. Later on, these figures were refined.

The major proportion of carbon, which participates in the cycle in the form of dissolved carbon dioxide, carbonates, and bicarbonates ($H_2CO_3 - HCO_3 - CO_3^{2-}$), is in the oceans. If one accepts CO_2 contents in the atmosphere as $N_a = 0.62 \times 10^{12}$ t(C), then the ocean contains 65 N_a (C), and the biosphere 2.4 N_a (C), from which 90% is contained in the oceanic plankton (Oeschger and Siegenthaller 1979). The organic substances are subjected to decomposition after death. Carbon is cycling through the biosphere about every 300 years. This process can be observed, for example, in the biogenic ocean carbonates, the major portion of which is dissolved while precipitating on the ocean floor.

Besides this, the carbon present in the common exchangeable reservoir, which is contained in the sedimentary strata, representing its main terrestrial storage, takes part in the dissolution and admixing of the cosmogenic radiocarbon. Sedimentary carbonaceous rocks are, on the one hand, being continuously formed and, on the other hand, are being constantly disintegrated. In this form of solutions and suspended particles, the disintegrated rocks are carried out into the ocean. The amount of carbon contained in sedimentary rocks is estimated to be 2×10^{22} g. If the process of the formation of sedimentary carbonaceous rocks has taken place over the last 3 billion years with a variable rate of formation in various epochs, then, according to different estimations, less than 3% of the ^{14}C participates in this process at any one time.

An important question in radiocarbon dating concerns the efficiency of ^{14}C mixing in the main reservoirs over time. The homogeneity in ^{14}C distribution in a reservoir can only be attained if the mixing time is short compared with the lifetime of ^{14}C. The mixing time for the biosphere is not more than 300 years and in the atmosphere 10 years (Libby 1955). The mixing time of the Atlantic Ocean does not exceed 2,000 years, that of the Mediterranean Sea is about 100 years, and for the Black Sea it is about 2,500 years. Another fact in agreement with the assumption of complete mixing of the ocean is the magnitude of the heat flux from the oceanic floor, which is equal to that of the terrestrial crust at 30 cal/cm^2/year (Libby 1955). If this value is correct, the absence of a heat inversion near the bottom suggests good mixing of the ocean in the framework of a radiocarbon scale of time.

The constant rate of radiocarbon production and the constancy of the amount of stable carbon in the exchangeable reservoir is of importance in the problem of radiocarbon dating. The constancy depends upon (Stuiver 1965): (a) the variation of intensity of the cosmic radiation due to solar activity; (b) the variation of magnetic dipole and field of the Earth; (c) the climate change of the Earth. Libby (1955, 1967) has pointed out that considerable corrections in view of these factors should not be made since the ^{14}C lifetime is relatively small ($T_{1/2} = 5{,}730$ years). However, in the cold periods of glacial times, the stable carbon content in the ocean may drop and the specific activity of ^{14}C may increase by 5–10%. The amount of the living organic material has no effect on the specific activity of carbon (since its ratio in nature has always been small).

During the last 100 years, the content of CO_2 has markedly increased in atmosphere of the Earth as a result of the industrial burning of fossil fuels (coal, oil, and gas). This effect is known as ‘the industrial effect’ or ‘Suess effect’ consisting of a certain decrease (by about 3% for the northern hemisphere) of the ^{14}C (Houtermans et al. 1967; Oeschger and Siegenthaller 1979). However, as a whole, the natural equilibrium in the ^{14}C content has settled during the last two decades due to thermonuclear explosions conducted in the atmosphere. Due to these, the ^{14}C content in the northern hemispheric atmosphere has more than doubled and became higher in the biosphere, and in the surface oceanic layer increased by about 20% (Nydal et al. 1979). In the wooden rings of 1963–1965, the ^{14}C increased up to 180–190% compared with pre-bomb level (Cain 1979).

14.2 Natural Variations of Radiocarbon in the Atmosphere and Biosphere

The specific activity of radiocarbon in the atmosphere and, as a consequence, in the biosphere is mainly governed by variation of the cosmic rays’ intensity at the Earth’s surface. The natural ^{14}C variations can be divided between the short-periodic—governed by the Sun modulation of the galactic cosmic rays—and long-periodic—connected with the geomagnetic Earth’s field and climate variation (Dergachev and Kocharov 1977; Sternberg and Damon 1979). Long-periodic variation of ^{14}C level

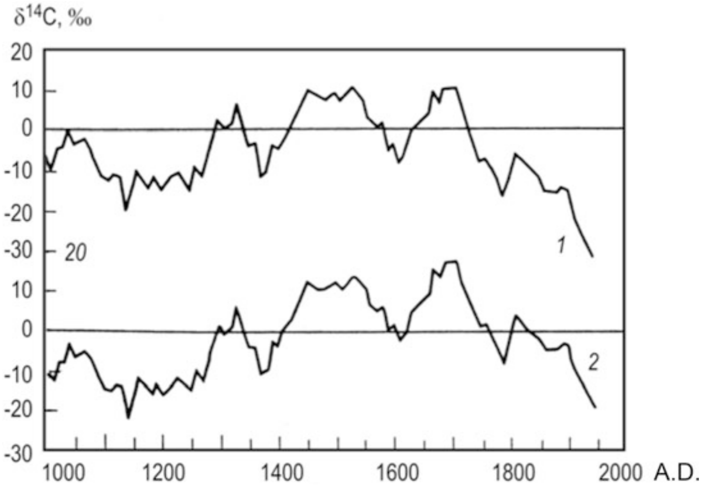


Fig. 14.2 ^{14}C variation in the atmosphere in the last 1,000 years: (*1*) non-corrected and (*2*) corrected on the basis of the long-periodic geomagnetic field change. (After Stuiver and Quay 1981)

can also be effected by the corpuscular radiation from the super-nova flashes and, by low probability, by occurrence of neutron flows during annihilation of the meteoric matter. The last problem has a more exotic than practical meaning (Sternberg and Damon 1979). As Dergachev and Kocharov pointed out, the degree of correctness of the solar activity (Wolf's numbers W) is high starting after 1749. The attempts were undertaken to extend the time scale up to 1610 and even to 648 before present (Dergachev and Kocharov 1977), but the correct measurements of 11 years solar cycle by W numbers were achieved to be only since 1749. The last time of the 80 years (century) cycle is tried to be checked, but the difficulty has arisen in connection with the short period of observations (230 years). In accordance with the calculations, the amplitude of specific ^{14}C activity for the 11 years' cycle of the solar activity is counted by 5%, and for the century cycle about 1%. Registration of the 11 years' variation in the yearly wooden rings' radiocarbon content is a difficult instrumental task. Stenhause (1979) used two high-stability proportional counters of quartz and metallic for its solution. This allowed obtaining relative error in the experiments equal to 6.4‰. In yearly oak rings over 1840–1890, he found ^{14}C peaks relating to 1851, 1869, and 1880 (at the level of about 1%). ^{14}C fluctuations on the level of 0.3–0.4% have not been reached, but it was sure that the 2–3% variations have not been found. The total ^{14}C activity from 1840 to 1890 has decreased on an average by 0.03% per year. After 1890, an increase of ^{14}C concentration in the atmosphere fixing in yearly wooden rings was observed. The radiocarbon variations in the past and changes in the solar activity during the last 300 years are considered in the study of Dergachev (1975). ^{14}C variation in the atmospheric carbon dioxide during the last 1,000 years are discussed by Stuiver and Quay (1981). Their results are presented in Fig. 14.2.

It was observed from the experimental data that natural reservoirs of the carbon do not stay in equilibrium relative to the atmospheric ^{14}C level. Before 1890, variation of the radiocarbon content resulted mainly due to the solar activity changes. Starting since 1890, the ^{14}C activity decrease was connected mainly with dilution of the atmospheric carbon dioxide by the "dead" CO_2 coming from burning the fossil fuel, but as it was shown by Stuiver and Quay, ^{14}C content in atmospheric CO_2 during twentieth century is not distinguished by something specific (see Fig. 14.2, (*1*)). These changes resulted due to long-periodic variation of the geomagnetic field. If one makes correction of ^{14}C long-periodic changes by means of sinusoidal curve of several thousand years period, then the ^{14}C level in atmospheric CO_2 (and biosphere) in twentieth century at least during the last thousand years will be minimal (see Fig. 14.2, (*2*)).

These data prove the anthropogenic influence on the increase of total carbon content in the atmospheric reservoir which has led to a decrease in the specific activity of radiocarbon in the atmosphere, biosphere, a mixing ocean layer. By the data of Stuiver (1980) with reference to Douglas, ^{14}C level in 1954 differed from the 'standard modern level' (0.95 activity of the NBS standard) by $24 \pm 2‰$.

The study of ^{14}C variation with respect to time by the yearly rings of the eighteenth and nineteenth century woods is convenient because at that time the anthropogenic impact on the atmosphere was weaker, the level of solar activity (W-number) change was well known, and the climate variations by the synoptic data can be restored. At present, a lot of data on ^{14}C concentration measurements in the yearly rings of woods from that time period are collected. By measurements of Stuiver (1965) over the time period from 1700 to 1870, a decrease in ^{14}C content by 2% from 1700 to 1790 is noticed. The maximum difference in ^{14}C activity within the studied period reaches 2.8%. It is noteworthy that due to small diameter of rings, Stuiver measured the ^{14}C activity in several rings simultaneously. In addition, the studies were performed on the ring slices of four trees from different locations of growth. This may lead to some errors depending on local conditions.

Analogous measurements on ^{14}C changes in yearly wooden rings of pines growing in Lithuania were done by Dergachev and Kocharov (1977). Figure 14.3 shows their results of a series of measurements on 5-year rings over 1707–1859 period of time.

It is seen that the ^{14}C change curve has a sinusoidal form with the amplitude of 1.5%. The period of ^{14}C variations for the time interval from 1780 to 1840 is equal to about 60 years. The curve itself shows an inverse proportionality in relationship between the solar W-numbers and radiocarbon content. The time shift, equal to about 10 years, is specified by the mean residence time of the carbon in the exchangeable reservoir (see Fig. 14.1 A) and depends on the period. The following expression of the changes in rate of ^{14}C generation depending on the W-number for the considered solar activity cycle, is proposed by Dergachev and Kocharov:

$$\Delta Q(W)/Q_0 = 0.4 - 0.01W,$$

where Q_o is the equilibrium rate of the ^{14}C generation.

Suess (1970) discovered in the yearly bristlecone pine rings a century ^{14}C variation with the period of 181 years within the time period of 7,000 years (from the middle of twentieth century up to 5000 years before present). The ^{14}C variation amplitude

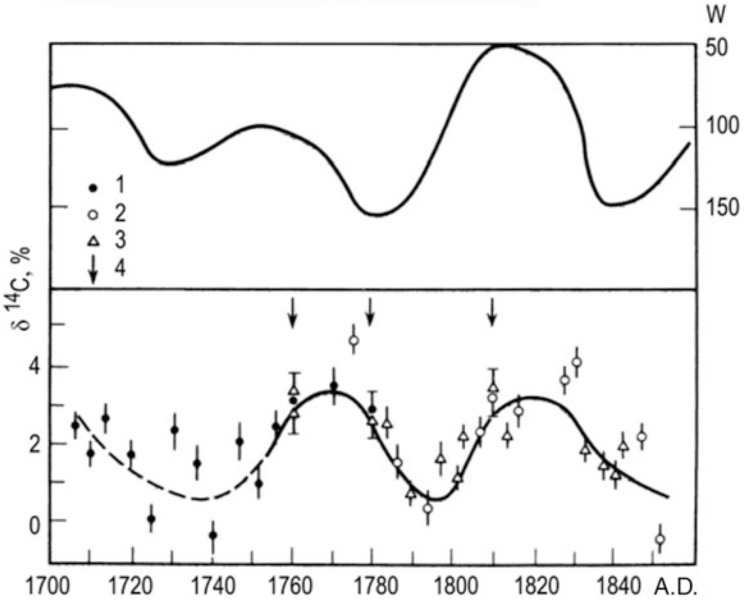


Fig. 14.3 Relationship between δ^{14}C variations in pine rings and solar W-number over 1707–1850: (*1* and *2*) measured by proportional counter; (*3*) measured by scintillation counter; (*4*) calibration points. (After Dergachev and Kocharov 1977)

is about 2–3% and the mean value of the ^{14}C activity is changed with respect to time by a sinusoidal law. In connection with solar activity changes and the corresponding climatic variation, it is noreworthy that Dansgaard et al. (1969) in ice core of 404 m length from the Greenland Camp Century covering the time interval from 1970 to 1200 years by the Fourier treatment derived the δ^{18}O values equal to 78 and 181 years (cited by Dergachev and Kocharov 1977). Obviously, the climatic changes are resulted by the solar activity and the 180-year period corresponds to the Suess data.

It seems the record in observation of the periodic climate changes based on the solar activity and registered by isotope data belongs to Libby and Pandolfi (1979). They studied distribution of deuterium and oxygen-18 in the yearly rings of Japanese cedar (*Cryptomeria Japonica*) within about last 1,800 years and derived there eight cycles with the periods of 58, 68, 90, 96, 154, 174, 204, and 272 years. The shorter cycles like 11 and 21 years were not discovered due to averaging of the measured wooden rings within 5 years, and also the 174th cycle of the authors corresponds to 183-year Suess period.

For the last relationship of δD and δ^{18}O in the Japanese cedar with radiocarbon in the bristlecone pine—measured by Suess for the same time intervals—Libby and Pandolfi discovered inverse correlation. To the lower values of δD and δ^{18}O there correspond the higher ^{14}C values. These relations have the form

$$\delta D = 0.677\delta^{14}\mathrm{C} - 75.5(\mathrm{SMOW}), \quad r = 0 - 0.62,$$

$$\delta^{18}\mathrm{O} = 0.0613\delta^{14}\mathrm{C} - 22.5(\mathrm{PDB}), \quad r = 0 - 0.77.$$

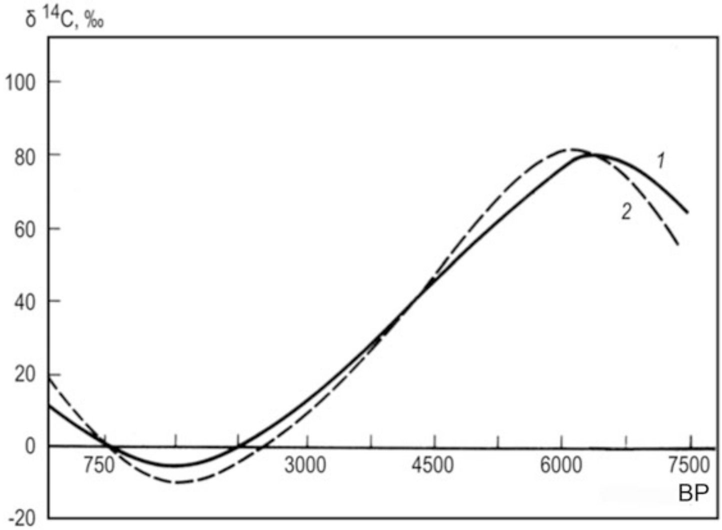


Fig. 14.4 Experimental and calculated data of ^{14}C variation in yearly wooden rings: (*1*) experimental data approximated by the polynomial of the fourth degree; (*2*) the curve obtained by calculation. (After Sternberg and Damon 1979)

The δD value was measured in relation to the SMOW standard and δ^{18}O in relation to the PDB standard. The above authors explain—by the climate change due to the solar activity—the relationship between the stable hydrogen and oxygen-18 isotopes and the radiocarbon in wooden rings with the ^{14}C amplitude of about 1%. The relationship between the rate of radiocarbon generation in the atmosphere and the solar activity variation seems to have physical basis, but the problem of the influence of the solar activity on the galactic cosmic rays' modulation and on the Earth's climate change has not been yet studied in detail. The search of cyclicity in the long- and short-periodic processes always attracted attention of the researchers, but as Gribbin (1980) pointed out, the cyclic attraction conceals in itself the risk to discover it there, where there is distribution of random values. To prove his words, Gibbin demonstrates the known graph, drawn by computer, generating random figures from 0 to 9, where deviation of the sliding average value from the mathematical expression appears to be equal to 4.5. On the graph of the random values distribution, a quasi-sinusoidal short-periodic fluctuations and long-periodic 'temporal' trend is traced.

The long-periodic variation of ^{14}C content in the atmosphere and correspondingly in the biosphere was reliably fixed by the radiocarbon concentration measurement in the long-living woods. Figure 14.4, taken from the Sternberg and Damon (1979) study and drawn on the basis of results obtained by many laboratories in the world, traces sinusoidal changes in the wood ring's ^{14}C concentration during about 7,500 years before present. The averaged data show that the minimal ^{14}C concentration (-5.5‰ from the level of 1890) comes approximately on 1,400 years and the maximum (+85‰) on about 6500 before present.

Sternberg and Damon assumed that the observed ^{14}C variation is related to the geomagnetic dipole moment changes. The relationship between the rate Q(t) of ^{14}C generation and the strength of the geomagnetic dipole moment has a reverse proportional dependence as

$$\frac{Q(t)}{Q_0} = \left(\frac{M(t)}{M_0}\right)^{-a}, \tag{14.10}$$

where Q_o is the equilibrium rate of generation of the magnetic moment M_0; α is the coefficient changing within 0.4–0.6.

It was also found by the data of paleomagnetic study that the magnetic dipole moment varies with respect to time within (4–12) × 10^{25} Gs.cm^3. It changes on quasi-sinusoidal law and during the last 10,000 years can be described by equation

$$M(t) = M_0 + M_1 \sin \omega(T - t + \theta),$$

where M_0 is the mean value of the dipole moment; M_1 is the amplitude variation; T is the period of oscillation; θ is the phase; $\omega = 2\pi/T$; t is the time.

Denoting $T - t + \theta$ by t', Eq. 14.10 can be rewritten in the form

$$Q(t) = Q_0[1 + (M_1/M_0) \sin \omega t']. \tag{14.11}$$

Applying the two-box model for the carbon exchanging reservoir (see Fig. 14.1), Sternberg and Damon reached good accordance between the experimental and calculating data on the long-periodic variation of the radiocarbon change in the atmosphere for the following conditions: $T = 8{,}500$ years; $M_{\max} = 12.5 \times 10^{25}$ Gs cm^3; $T_{M\max} = 2{,}500$ years; $\alpha = 0.45$; $\tau_a = 75$ years (see the residence time of carbon in a reservoir in Fig. 14.1); $K_{as} = 5 \times 10^{-4}$. The calculations were done by Eqs. 14.5, 14.6 and 14.11. The value of ^{14}C (‰) was calculated by the equation $\delta A_a(t) = [(A_a(t) - A_0)/A_0] \times 1000$, where A_0 is the activity of the modern carbon standard.

Figure 14.5 presents the compared experimental and calculated long-periodic changes of radiocarbon in the Earth's upper atmospheric layers (Sternberg and Damon 1979). The authors note that a delay of several hundred years in the phase between the geomagnetic field change and the radiocarbon variation in the exchange reservoirs is observed. This is due to the mean residence time of carbon in the reservoir A, the ratio of exchanging carbon funds in the A and B reservoirs, and the period T of the geomagnetic field variation.

In addition to the astronomical and climatic factors' effect on distribution of the natural ^{14}C concentration in the atmosphere and biosphere, the dilution of the atmospheric carbon dioxide by the endogenic CO_2 may have influence on local radiocarbon content changes which is typical to the volcanic and breaking Earth's crust regions. It was certain that in the modern volcanic regions, the ^{14}C content in the biosphere is lower than the present day level. This is because of throwing out of the endogenic carbon dioxide in the period of volcanic activity and CO_2 entering from the Earth's crust breaks (Sulerzhitsky and Forova 1966; Olsson 1979; Karasev

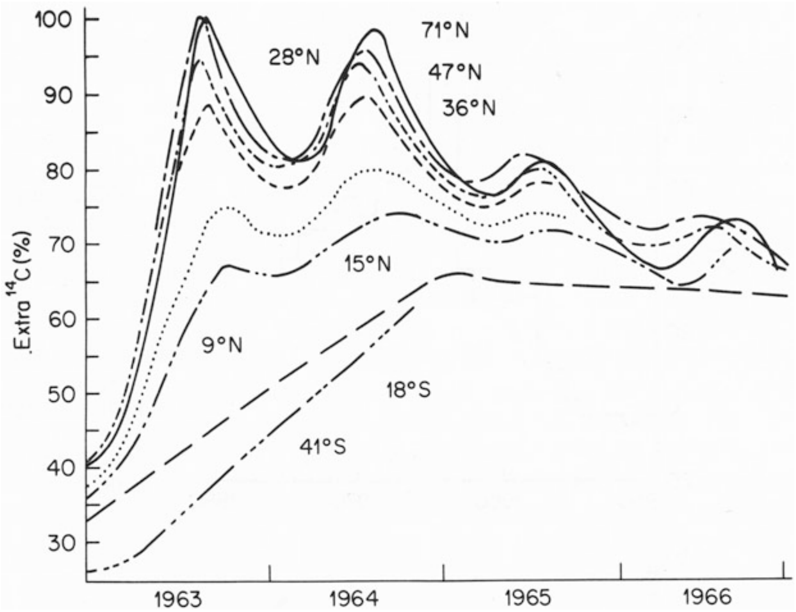


Fig. 14.5 Variation with respect to time of ^{14}C concentrations in tropospheric CO_2. (After Fairhall and Young 1970)

et al. 1981a). On this basis, Karasev et al. proposed a method to break the discovery in active tectonic zones by radiocarbon measuring in plant samples. As it was shown by the authors, in a break zone $\delta^{14}C = -50\%$ and at a distance of about 10 m $\delta^{14}C$ increases up to $+27\%$.

14.3 Natural Radiocarbon in the Oceans

A number of studies were devoted to the analysis of radiocarbon in the oceanic water's carbonate system and the water-bearing organic matter (Fonselius and Östlund 1959; Broecker et al. 1960; Broecker and Olson 1961; Bien et al. 1963; Fairhall and Young 1970; Fairhall 1971).

Starting in 1940–1950s of the last century, the studies on ^{14}C distribution in the ocean water were later on strained due to the bomb radiocarbon entering into the oceans. The artificial mark appeared by culminate tests in 1961–1962 allowed detailed further study of dynamics of the CO_2 between the atmosphere and oceans exchange, but became an irresistible obstacle for further study of the ^{14}C space distribution in the oceans and seas.

Radiocarbon enters into the oceans as a result of the carbon exchange between the dissolved marine carbonates and the atmospheric CO_2. The radiocarbon entered into the surface ocean layer is rather quickly and uniformly distributed in exchangeable layer ($h \approx 100\,m$, $r \approx 10$–15 years). From there, by the vortex diffusion and pelagic biogenic carbonate sedimentation, the radiocarbon enters the deep water layers, where its residence time (t), by different estimates, is equal to 1,500–2,000 years. As Craig (1957) notes, CO_2 exchange between the atmosphere and oceans is accompanied by the isotopic effects. The mean isotopic content of stable carbon of the dissolver—hydrocarbonates of sea water—has a value of $\delta^{13}C = -7‰$ (here and further relative to the PDB standard). Thus, as a result of exchange processes, the carbon of the hydrocarbonates becomes heavier by 7‰. Enrichment of the oceanic ^{13}C can be described by means of the fractionation coefficients $\alpha_{13_C} = R_0/R_a$, where R_o and R_a are the ratio of $^{13}C/^{12}C$ in the ocean and atmosphere.

The value R can be presented as $(1 + \delta^{13}C/1{,}000)$. Then the expression for α is rewritten as

$$\alpha_{13_C} = \frac{1 + \delta^{13}C_0/1000}{1 + \delta^{13}C_a/1000}.$$

Analogously, for ^{14}C one has

$$\alpha_{14_C} = \frac{1 + \delta^{14}C_0/1000}{1 + \delta^{14}C_a/1000} = \frac{(^{14}C/^{13}C)_0}{(^{14}C/^{13}C)_a}.$$

It is known (for example, Galimov 1968), that the fractionation constant increases by the square dependency on each additional neutron to the isotopic nucleus. Then, $\alpha_{14_C} = \alpha^2_{13_C}$, and applying the approximate equality $(1 + x)^2 = 1 + 2x$ at $x \ll 1$, one obtains

$$\alpha_{14_C} = \frac{1 + \delta^{14}C_0/1000}{1 + \delta^{14}C_a/1000} = \frac{1 + 2\delta^{13}C_0/1000}{1 + 2\delta^{13}C_a/1000}. \tag{14.12}$$

Using the last expression, it is possible to show that if ^{13}C of the ocean bicarbonate is enriched by 7‰, then at such enrichment, the ^{14}C should be equal to about 14‰. In other words, $\varepsilon_{14_C} = 2\varepsilon_{13_C}$, where $\varepsilon_{13_C} = \delta^{13}C_0 - \delta^{13}C_a$. This task is discussed in more details later on.

Thus, the theoretical consideration of the problem of CO_2 exchange between the atmosphere and the ocean shows that the surface oceanic water should be enriched in ^{14}C isotope by about 14‰ compared with the atmospheric carbon. Analogously, it is possible to show that the biosphere should have ^{14}C in deficit by about 3% ($\delta^{13}C_a = -25‰$) compared with the atmosphere. As it was shown earlier, the normalization of ^{14}C content is provided for unification of the radiocarbon measurements (−25‰ is the normalizing value for the studied samples). The formula for normalization from Eq. 14.12 was obtained. It was pointed out by Libby (1955) that the oceanic carbonates have ^{14}C activity 5% higher than the biogenic carbon. His statement coincided with theoretical consideration of the natural exchange processes, but later the studies have not proved the conclusion. In particular, it was shown that the hydrocarbons of the mixing layer in the Atlantic, Indian, and Pacific oceans to the north from 40°S have a practically constant ^{14}C content close to that in the biosphere (without the isotope correction) (Fonselius and Östlund 1959; Broecker et al. 1960; Broecker and Olson 1961; Bien et al. 1963; Bien and Suess 1967). This fact is explained by increase of ^{14}C content due to isotope fractionation in the exchanging processes eliminated at mixing with the deep layers.

Stuiver (1980), on the basis of studies of Broecker, Östlund, Craig, and other researchers compiled a short report on ^{14}C distribution in ocean waters during the pre-bomb period. It is evident from this summary that in nine surface water samples taken in the North Atlantic in 1955, the $\Delta^{14}C = -49 \pm 2‰$. The data from 13 stations of the South Atlantic (to the north from 40°S.), sampled during 1956–1957, have little lower values, namely, $\Delta^{14}C = -57 \pm 2‰$. Up to that time of measurements, the decrease of the pre-industrial ^{14}C level in the surface oceanic waters was about 12‰. From this, we can accept that $\Delta^{14}C$ for the surface Atlantic waters before the intensive thermonuclear tests is be equal to $-40‰$ from radiocarbon in the biosphere. It means that this value can be accepted as characteristic for the mixing layer over the thermocline. In the depth from 100 to 600 m, the content of radiocarbon decreases by exponent from -40 to -100, and at more depth it remains constant. The value $-110‰$ was characteristic for the Atlantic deep layers in the pre-thermonuclear epoch. The studies of Stuiver (1980) show that after thermonuclear tests, the 'natural' distribution of radiocarbon in the Atlantic ocean in 1970s was preserved only below 3,500 m.

Giant amounts of experimental data were collected by dating of mollusk shells living in the normal salinity marine water. Investigations of samples collected in the period between the mid-nineteenth century to 1950 near the shore areas of different oceans provides the basis for conclusion that the radiocarbon content (without isotopic correction) in the mixing ocean layer during pre-thermonuclear epoch was also lower of biogenic level determined as 0.95 activity of the NBS oxalic acid. By the data of Gillespie and Polach (1979) who studied the radiocarbon distribution in mollusk shells from near shore of the oceans in 1840–1950, the conclusion follows that ^{14}C content in the mixing layer varies in the natural conditions from $+8$ to -11% relative to the modern standard, and without taking into account the effects of the fresh river water recharge and the Suess effect, the variation range is narrowing. In average, the carbon is depleted by ^{14}C (without correction) by about 15‰. By the age and being corrected by 25‰, the value of $\overline{\nabla}^{14}C = -64.5‰$ (0.95 NBS). Then the "apparent age" of the shells related to the reservoir effect in the mixing layer appears to be 535 years. For the Australian shore area, the mean value of $\overline{\nabla}^{14}C = -55 + 4‰$ (non-corrected value is $\sim 5‰$), which corresponds to the "apparent age" as 450 ± 35 years.

For the shells from the North and South American shore, taken in 1878–1940, the non-corrected value of $\delta^{14}C$ varies from $+1$ to -8%, and the averaged value is about -3% ($-30‰$). The true ^{14}C value for the mixing layer in the pre-thermonuclear epoch is of great practical interest for radiocarbon dating using mollusk's shells. The ^{14}C differences in mollusk shells are hardly defined by the metabolic processes. They more likely reflect radiocarbon variations in off-shore ocean layers, which affect the river runoff and discharge of the continental groundwaters. Sternberg and

Table 14.3 Distribution of natural and thermonuclear ^{14}C at the end of 1962. (Fairhall and Young 1970)

Reservoir	Total amount of carbon (g)	^{14}C before 1950 (atom/g $\times 10^{10}$ C)	Natural ^{14}C, (atom $\times 10^{27}$)	Thermonuclear ^{14}C, (atom $\times 10^{27}$)
Atmospheric CO_2	6.8×10^{17}	6.07	41	54
Continental biosphere	3.1×10^{17}	5.85	18	< 1
Humus	1.1×10^{18}	< 5.8	< 64	< 1
Oceanic living biosphere	3×10^{15}	6	0.2	< 0.1
Oceanic non-decomposed rests	2×10^{16}	6	1	< 0.1
Dissolved organic matter in the oceans	8×10^{17}	5.3	42	< 1
Non-organic matter in the oceans				
Upper 100 m	1×10^{18}	5.8	58	~3
Below 100 m	3.8×10^{18}	5.1	1,940	~1
Total	42×10^{18}		2,160	~60

Damon (1979), after analyses of the large amount of collected experimental data, for theoretical calculation accepted that the mean radiocarbon activity in the mixing layer for the pre-thermonuclear epoch is equal to 0.965 from that in the biosphere in 1890 equal to 13.8 disintegrations $\text{min}^{-1} \times \text{g}^{-1}$ C.

The ^{14}C activity in different exchangeable reservoirs before 1950 can be estimated using the data from the study of Fairhall and Young (1970) shown in Table 14.3.

On the basis of the abovementioned Fairhall and Young data, it is possible to conclude that the ^{14}C activity of the mixing ocean layer in the pre-thermonuclear epoch should be 1% lower compared to the biosphere and by about 3% than in the atmospheric CO_2. A number of researchers (for example, Oeschger and Siegenthaller 1979), in their theoretical calculations, accept ^{14}C in the surface ocean layer before thermonuclear tests to be 95% from the atmospheric level in the mid-nineteenth century. The carbon distribution in the deep layers, as a result of the thermonuclear tests, inconsiderably changed due to the very long mean carbon residence time in this layer.

By the data of Fairfall (1971), who summarized his own results and the results obtained during 1958–1970 expeditions by Broecker, Bien, and Rafter before 1969 in the Atlantic, Indian, and Pacific oceans, the non-disturbed picture of radiocarbon distribution below 500 m was observed, and also its relative uniform distribution was fixed in the deep ocean layer. Radiocarbon comes to the deep layers from the mixing layer by the vortex diffusion (Oeschger and Siegenthaller 1979) and partly due to sedimentation of mollusk shells, which dissolved in deeper layers. By the Fairfall's calculations, the ^{14}C absolute concentration in the ocean water before 1950 was about 1.4×10^9 atoms per liter for the entire depth, for which the ^{14}C concentration depth gradient is equal to zero or correspondingly about 84% of specific radiocarbon activity in the atmosphere (see Table 14.3). Using the Fairfall's data, we may estimate the carbon mean residence time in the ocean deep layers. For this case, the following material balance can be used: $M\mathrm{d}A_2/\mathrm{d}t = q_1A_1 - q_2A_2 - MA_2\lambda$, where M is the carbon mass in the exchangeable layer; q_1 and q_2 are the carbon mass income; A_1 and A_2 are the specific carbon activities in the exchangeable and deep layers; λ is the ^{14}C decay constant. In the stationary state, the left hand side of the equation is equal to zero, and $\mathrm{q}_1 = \mathrm{q}_2$. Taking into account that $M/q = \tau$, then one has $\tau = (A_1 - A_2)/A_2\ \lambda$.

Accept $A_1 = 0.965$, $A_2 = 0.835$ and $\lambda = 1.21 \times 10^{-4}$, then one obtains $\tau = 1{,}300$ years. If $A_1 = 0.99$, which corresponds to many experimental data for the Atlantic ocean (Fairfall 1971), then $\tau \approx 1{,}500$ years, which corresponds to Libby's (1955) estimation.

14.4 Technogenic Radiocarbon in the Atmosphere and Oceans

According to data obtained by different authors (Fairhall and Young 1970), 6×10^{28} atoms of ^{14}C have been released into the Earth's atmosphere during thermonuclear tests. Since before the tests the ^{14}C content in the atmosphere was estimated to be 4.1×10^{28} atoms, the total amount of the carbon atoms has increased by 2.5 times. Compared with the total equilibrium amount of the isotope on the Earth (2.2×10^{30} atoms), the bomb component amounts to 2.5% (see Table 14.3).

On an average, at a thermonuclear, test 3×10^{26} atoms of ^{14}C per Mt are produced, which is equivalent to 7 kg of the radiocarbon. By the radiocarbon thrown into the atmosphere, over 200 Mt of total explosion power was done up to 1962, which injected about 1.4 t of artificial radiocarbon into the atmosphere.

Numerous measurements (up to a thousand specimens) were carried out in order to determine ^{14}C content variations in the troposphere and stratosphere both with latitude and altitude (Fairhall and Young 1970; Münnich and Vogel 1963; Fairhall et al. 1969; Hagemann et al. 1959). The most representative results of these studies according to the data of different authors for the troposphere CO_2 generalized from 1963 to 1966 are shown in Fig. 14.5.

There are distinct seasonal variations of ^{14}C concentrations in the northern hemisphere and a considerable latitudinal gradient of concentrations in 1963 indicated in the Fig. 14.5 but the gradient quickly decreased to zero by 1967. Both of these effects are a consequence of seasonal variations in the release of bomb ^{14}C from the stratosphere into the troposphere and the longitudinal mixing which occurs in the troposphere. The most intensive release of ^{14}C into the troposphere, as in the case of tritium, is detected in spring and early summer. At the same time, the most effective mixing of this isotope occurs in the longitudinal direction.

In contrast to the thermonuclear dust, which is removed as a rule quickly from the troposphere with precipitation, CO_2 has a rather long residence time in the troposphere. Therefore, the levels of bomb ^{14}C in the troposphere air were highest in the middle latitudes of the northern hemisphere and reached maximum concentrations late in the summer.

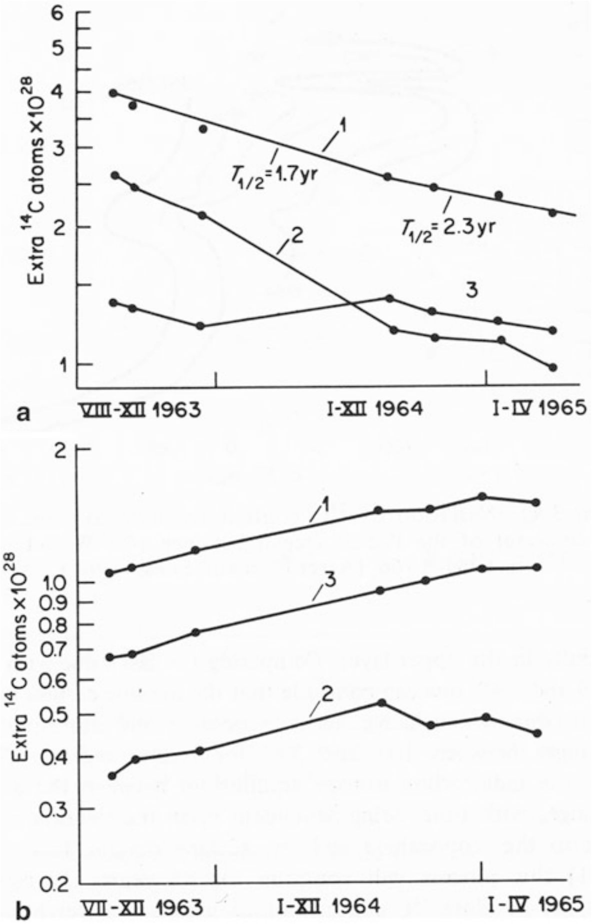


Fig. 14.6 Variation of total amount of bomb ^{14}C in northern (**a**) and southern (**b**) hemispheres for the atmosphere as a whole (*1*), the stratosphere (*2*), and the troposphere (*3*). (Fairhall and Young 1970)

The longitudinal mixing of ^{14}C extends southwards. Annually, from September to February, the level of ^{14}C in the northern latitudes decreased, and in the southern latitudes increased, up to the middle of 1966. Such a process took place until 1966 when the whole troposphere became homogeneous with respect to the ^{14}C.

It has been pointed out (Fairhall and Young 1970) that the relative amounts of tropospheric air participating in the circulation at various latitudes should be taken into account when comparing the latitudinal variations of the ^{14}C concentrations (Fig. 14.5). The convergence of the meridians and the descent of the tropopause at high latitudes result in a sharp decrease in the volume of tropospheric air with increasing latitudes, compared with the equatorial region. Thus for the same ^{14}C ejection from the stratosphere, its activity in high latitudes will be considerably higher than in the lower ones.

Figure 14.6 shows the variations with time of the absolute amounts of the bomb-radiocarbon in the troposphere, stratosphere, and atmosphere as a whole for the northern and southern hemispheres.

It is observed from the Fig. 14.6 that with the decrease in the ^{14}C concentrations in the northern hemisphere, the opposite process has taken place in the southern hemisphere during 1963–1965. The theoretical estimation of the total amount of the ^{14}C in the atmosphere based on experimental data shows that the time of half-removal of this isotope is equal to 3.3 years. In the subsequent years, the rate of the ^{14}C removal from the atmosphere decreased. Its amount in the troposphere up to 1970 compared with 1963 decreased by two times and by 1977 only one third of it was left (Berger 1979). Before 1984, the ^{14}C amount in the troposphere numbered about 125% with respect to pre-thermonuclear level. The residence time of CO_2 in the troposphere calculated by decrease of ^{14}C activity during period of 1963–1976 is about 10 years (7/0.693), and of 1970–1982 this time was about 15 years, which is close to the earlier estimates made by Arnold and Anderson (14–30 years) (Miyake 1969).

It is assumed that the rate of removal of bomb ^{14}C from the stratosphere is proportional to the difference (gradient) between its concentration in the stratosphere and the surface (mixing) ocean layer. While decreasing the gradient, the velocity of the radiocarbon removal from the troposphere is dropping. On this basis, the conclusion follows that during the 'peak' injections of radiocarbon (and tritium as well) into the atmosphere, the ^{14}C concentration changes between the atmosphere and hydrosphere take place in $^{14}CO_2$ but not in general CO_2. The sharp drop of ^{14}C half-removal from the atmosphere in the first years after nuclear tests stopped is shown in Fig. 14.6a. It is most probably, that the ^{14}C half-removal, measured by its activity before 1966, characterized in reality not only CO_2 exchange process between the atmosphere, ocean, and biosphere, but also ^{14}C activity decrease in the northern hemisphere as a result of its transfer with air masses into the southern hemisphere.

The altitudinal distribution of ^{14}C specific activity in the atmosphere is not uniform. In 1962, for example, ^{14}C activity in CO_2 of the lower troposphere was about 140% with respect to the natural level. In April 1962, before the USSR thermonuclear tests, at the height of 12.2 km at 36°N, the ^{14}C activity was measured to be three times higher than the natural one (Fergussen 1963). These measurements have shown that the considerable amounts of ^{14}C were accumulated in the stratosphere as a result of the nuclear tests. This fact is proved by the summer maximum of its coming into the troposphere (see Figs. 14.7 and 14.8).

Figure 14.8 shows the summarized Troncheim Laboratory data on radiocarbon concentration changes in the troposphere and the surface waters of the Pacific and Atlantic oceans (Nydal et al. 1979).

By the data of Fairhall and Young (1970), the radiocarbon concentrations in the troposphere and atmosphere are practically equal; however, the observations in 1968–1974 summer maximums gives evidence against this assumption (Berger 1979). In order to find the correct answer, the CO_2 stratospheric sampling at 18 and 21 km high was carried out during 1975–1977 in the framework of the NASA program. The results of this experiment are shown in Table 14.4.

As shown in Table 14.4, the spring peak of ^{14}C concentration has appeared in the lower stratosphere which looks like the summer maximum in the troposphere. In this connection, one may assume that during the summer the ^{14}C enriched air breaks the troposphere and comes there from the lower stratosphere. By Berger's opinion, the mean residence time of CO_2 in the stratosphere is about 15–20 years.

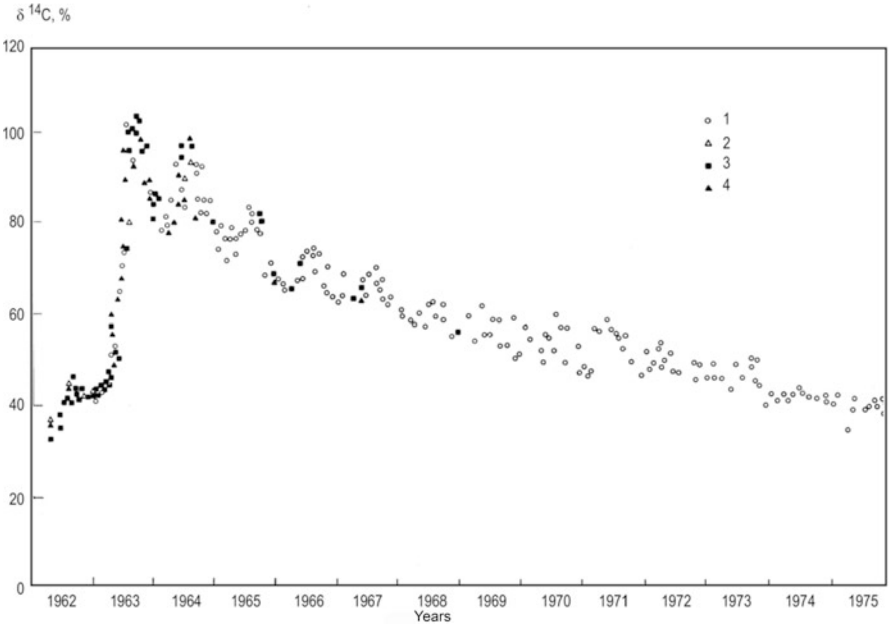


Fig. 14.7 Radiocarbon concentration changes in troposphere of high latitudes by data from the stations: (*1*) Nordcap, 71°N, 24°E; (*2*) Spitsbergen, 78°N, 19°E; (*3*) Troncheim, 63°N, 10°E; (*4*) Lindesnes, 58°N, 7°E. (After Nydal et al. 1979)

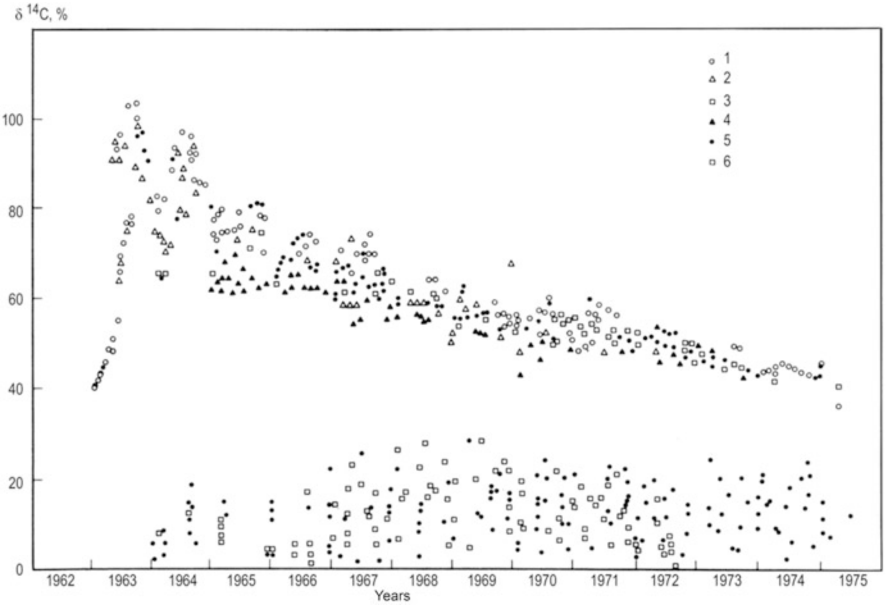


Fig. 14.8 Summarized radiocarbon content data on troposphere and ocean surface waters: (*1*) Nordcap; (*2*) Gran Canaria; (*3*) N'Djamena; (*4*) Madagascar; (*5*) surface waters of the Pacific Ocean; (*6*) surface waters of the Atlantic waters. (After Nydal et al. 1979)

Table 14.4 ^{14}C content in stratosphere. (From Berger 1979)

Sampling date	Sampling height	Sampling place	$\delta^{14}C$ (‰)
13.06.75	19.8	Northern Sierra	+127.4
25.09.75	19.8	California	+90.7
03.12.75	18–21	San Francisco—Phoenix	+79.1
02.06.76	18–21	San Francisco—Salt Lake City	+85.6
30.03.76	19.8	San Francisco—Oregon	+107.0
23.09.76	19.8	San Francisco—Denver	+99.2
22.03.76	19.8	Pacific Ocean—Los Angeles	+199.6

In 1963, the USSR, USA, and GB have signed the treaty on cessation of the nuclear weapon tests in the atmosphere, oceans, and on the Earth surface. Since that time, the exchange reservoirs were insignificantly replenished by the artificial ^{14}C during the French and Chinese explosions. The peak ejections of radiocarbon into the atmosphere, which created in the atmosphere and stratosphere some kind of marks, allowed a more detailed study of the mass exchange between the atmosphere, oceans, and biosphere, and also between different layers of the atmosphere and oceans. The wide program on the study of distribution of ^{14}C was caused by the bomb-tests, carried out in the Trondheim Laboratory starting 1962. In particular, the scientists who took part in the program, since 1963 published their results on the study of CO_2 exchange between the atmosphere and oceans. The study on ^{14}C redistribution between the northern and southern hemispheres on a profile Spitsbergen–Madagascar was also initiated. Before 1967, the ^{14}C concentrations in the lower atmosphere of the Earth were practically equal. This was allowed in calculations of carbon exchange cycles without taking account the time in different parts of the atmosphere. The obtained results are shown in Figs. 14.8 and 14.9.

The decrease of bomb ^{14}C in the atmosphere occurs due to its absorption by the terrestrial biosphere and CO_2 exchange between the atmosphere and the oceans. The latter reservoir is most important since more than 80% of the atmospheric CO_2 is exchanged with the ocean and 20% is replaced through the inland biosphere. In view of the role of the oceans in the absorption of bomb-^{14}C, considerable investigations have been carried out aimed at the measurement of its concentration in surface and deep oceanic waters (Bien and Suess 1967; Fairhall 1971; Nydal 1967; Fairhall et al. 1969). In contrast to the atmosphere, characterized by quick ^{14}C mixing (less than 10 years), the process of mixing in the ocean is more complicated and requires more time. The radiocarbon technique is advantageous in studying such oceanographic processes as mixing of the oceanic waters and their global circulation.

Figure 14.10 illustrates in isolines the picture of ^{14}C variation in the surface waters of the Pacific Ocean (from 140°W to 170°E), plotted by Bien and Suess (1967) on the basis of the data obtained by different authors. The main features of the character of the ^{14}C variations in the atmosphere of the northern and southern hemispheres are in principle present in the surface waters of the Pacific Ocean, but the effect of the motion of oceanic waters is also reflected, for example, regions of upwelling of deep waters to the surface are indicated, characterized by low ^{14}C content, near the equator and at 40°N.

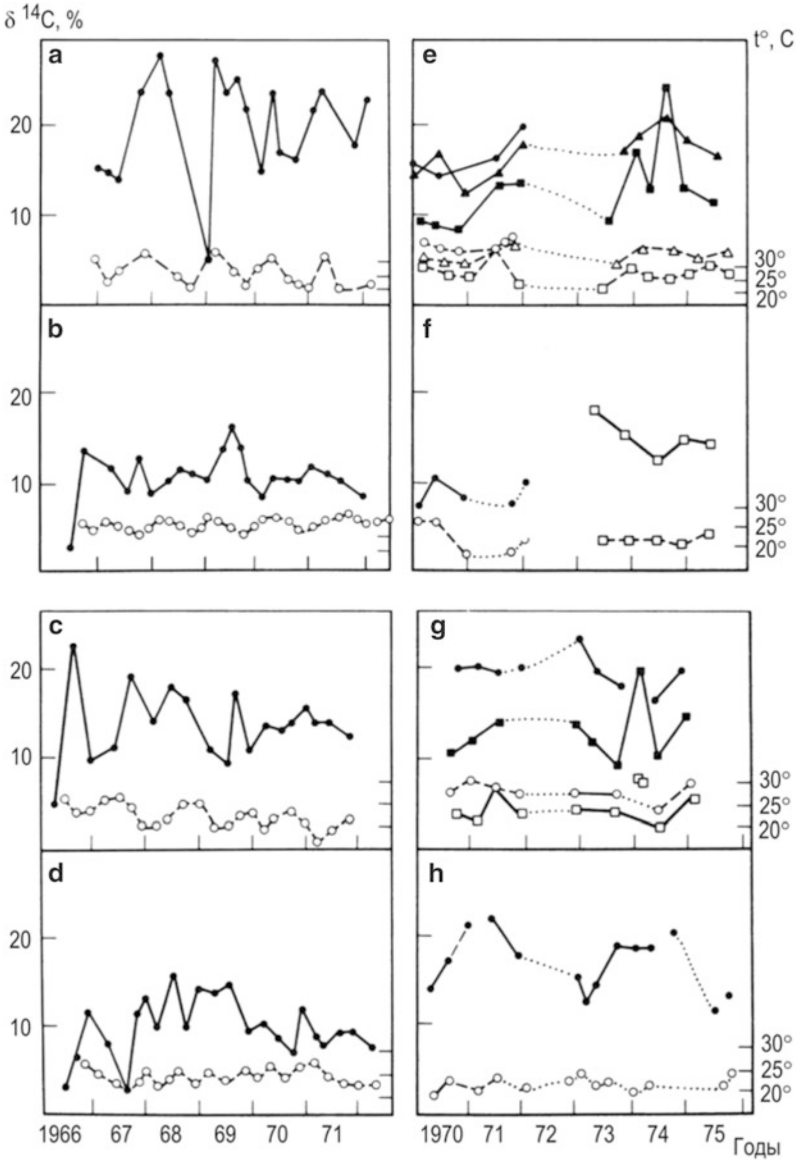
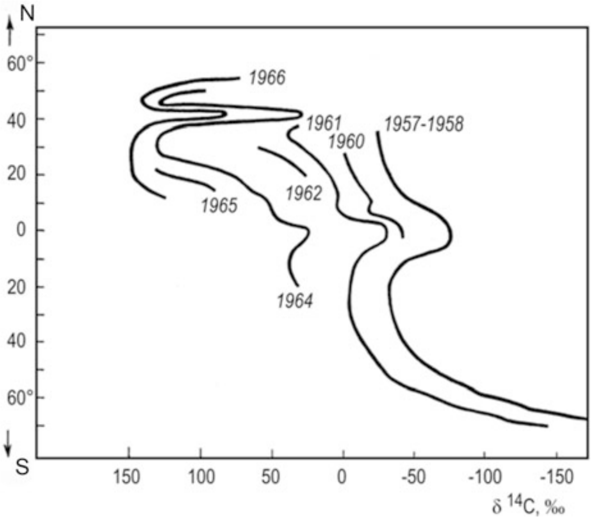


Fig. 14.9 ^{14}C concentration changes in surface of water oceans: (*a*–*d*) Atlantic ocean: (*a*) 31–33°S, 50–52°W; (*b*) 4–7°S, 31–33°W; (*c*) 20–30°N, 15–18°W; (*d*) 17–18°N, 20–22°W; (*e*–*h*) Pacific Ocean: (*e*) 25–36°S, 120–180°W; (*f*) 14–20°S, 110–120°W; (*g*) 28–34°N, 150–150°E, (*h*) 19–26°N, 119–126°W. (After Nydal et al. 1979)

Figure 14.11 shows the variation of the relative ^{14}C concentrations in a depth profile of the Pacific Ocean at high latitudes in the southern hemisphere. The experimental data, corresponding to the low latitudinal depth profile in the ocean, are shown in Fig. 14.12 (Fairhall 1971).

Fig. 14.10 Variation of ^{14}C content (relative to standard) in surface water of the Pacific Ocean between 140°W and 170°E in 1957–1966. (After Bien and Suess 1967. © IAEA, reproduced with permission of IAEA)



The spatial ^{14}C distribution in depth of the Atlantic Ocean was studied in framework of the GEOSECS Program (Stuiver 1980). Figure 14.13a shows location of the stations and also the stations of the research ship ‘Meteor’ (Germany). The ship’s route was adjusted to GEOSECS Program (Roether et al 1980). The δ^{14}C values’ distribution at the GEOSECS stations in 1972–1973 is presented in Fig. 14.13b, 14.13c. It is seen in Fig. 14.13c that the two main fields of the surface waters’ immersion into deep layers are observed. The first field is located between 36° and 40°S and the second between 20° and 30°S. The upward flow of the deep waters is traced around the equator. The two more localized upward flows are traced between 40°–50°S and 40°–50°N. It is observed from the Fig. 14.13b, 14.13c that significant amount of the bomb-radiocarbon was entered into the surface ocean layer and reached the deep layers in 1972. Analogous picture on the longitudinal profile, obtained during 23rd route of the ‘Meteor’ in 1971, is observed (Fig. 14.14; Roether et al 1980).

As it was pointed out above, the ^{14}C mark, occurred in the atmosphere after the thermonuclear tests during a short period of time, is used to study the atmosphere and oceans dynamical characteristics. The carbon concentration increase in the Earth’s atmosphere has a head form of δ-function at the well-known change of the carbon concentration in the atmosphere and oceans. This gives the possibility for estimation of the exchange parameters of the reservoir, the main of which are the atmosphere, oceans, and biosphere. Each reservoir can be presented by a number of ‘boxes’ (Dergachev 1977). For example, the oceans can be considered as two boxes reservoir that is the upper one over the thermocline (75 ± 25 m) in which intensive water mixing occurs, and lower, weakly mixing ‘box’ in which the carbon concentrates due to the diffusion process. The continuous carbon exchange between the deep ocean layer and the ocean sediments takes place. The natural border in the atmosphere is the tropopause which is at the height of 11–12 km. The tropopause divides the troposphere into the layer, well mixing in vertical direction, and the layer where the

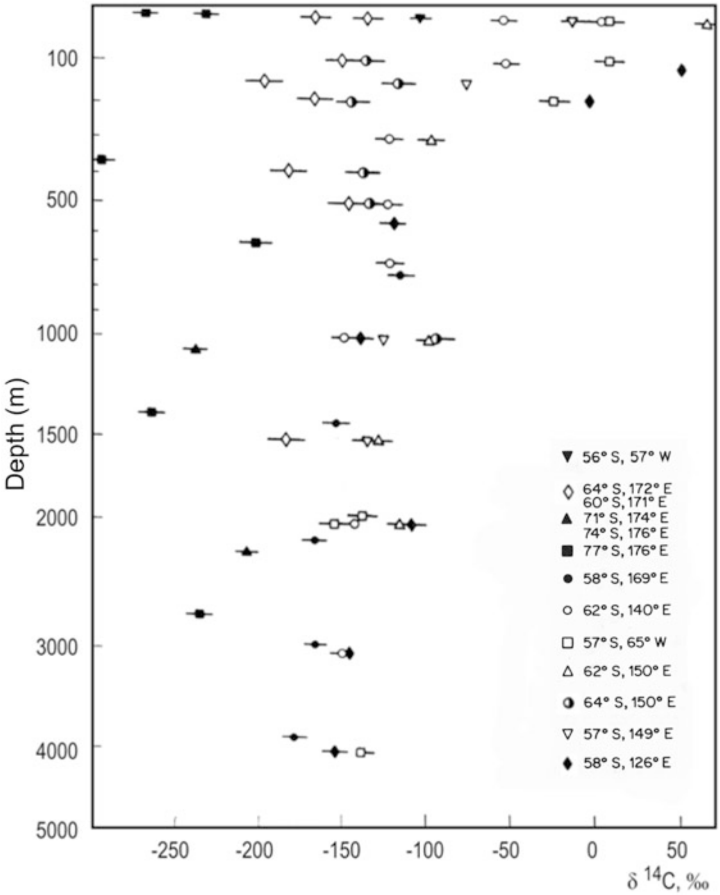


Fig. 14.11 ^{14}C distribution in a depth profile of the Pacific Ocean for high latitudes of the southern hemisphere in 1958–1969. (After Fairhall 1971)

meso-longitudinal exchange is prevailing. The use of the box models, the possibilities of which were discussed earlier, on the basis of experimental study of the ^{14}C distribution in reservoir in space and time, allows the rate of exchange processes and the carbon mean residence time in reservoirs to be estimated.

Dergachev (1977), after analysis of many studies on this problem, came to conclusion that the values of the exchange parameters, calculated on the basis of the artificial ^{14}C distribution, are too scattered. The scattering has two causes: first, due to incorrectness in determination of the reservoir borders of the exchange reservoir, and secondly, because of confusing the meaning of 'half-exchange time' and 'half-life time' of the ^{14}C in either part of reservoir. The following values of the above parameters have been obtained by Dergachev: the exchange time between the troposphere and stratosphere is equal to 1.5–2 years; the ^{14}C mean residence time in

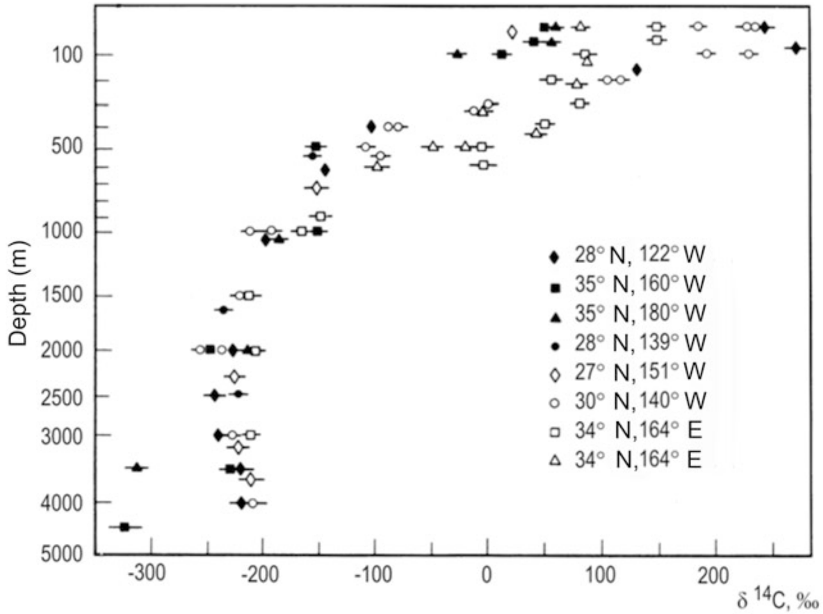


Fig. 14.12 ^{14}C distribution in a depth profile of the Pacific Ocean for low latitudes of the northern hemisphere in 1958–1969. (After Fairhall 1971)

the stratosphere is 3.5–4 years, and in the troposphere 1.5–2 years; the mixing time of the atmosphere between the hemispheres through the equator is about 1.5 years. The mean values for the both hemispheres are:

$$\tau_{ma} = 9.1;\ \tau_{ma} = 7.1;\ \tau_{ma} = 8.7;\ \tau_{md} = 4.3;\ \tau_{md} = 2.8;\ \tau_{md} = 3.8 \text{ years};$$

where *m* is the mixing layer; *a* is the atmosphere; *d* is the deep layer.

As Dergachev points out, the small values τ_{md} contradict to the results of calculations by box models, by which $\tau_{md} \approx 10$ years. This is possible because of dependence of exchange rate between the atmosphere and different ocean layers on the ^{14}C concentration gradient in exchangeable reservoirs. In this case, the decrease of the rate of the radiocarbon removal from the troposphere must lead to an increase in the mean residence time in the atmosphere and mixing ocean layer. In favor of such assumption, the experimental data on ^{14}C distribution in the atmosphere and oceans obtained in the recent years are evident. The authors of this book, applying the Trondheim Laboratory data (Nydal et al. 1979), on the basis of the one-box model, estimated the residence time of radiocarbon in the mixing and deep ocean layers. Table 14.5 shows the function (A) of the radiocarbon change in the atmosphere and the ^{14}C concentration increase in the mixing ocean layer H_m used in the calculations.

The data for the atmosphere before 1963 were taken on the basis of ^{14}C measurements in alcohols of the Georgian and Portuguese wines (Burchuladze et al. 1977; Lopes et al. 1977). For the mixing layer, the ^{14}C concentration before 1963 was

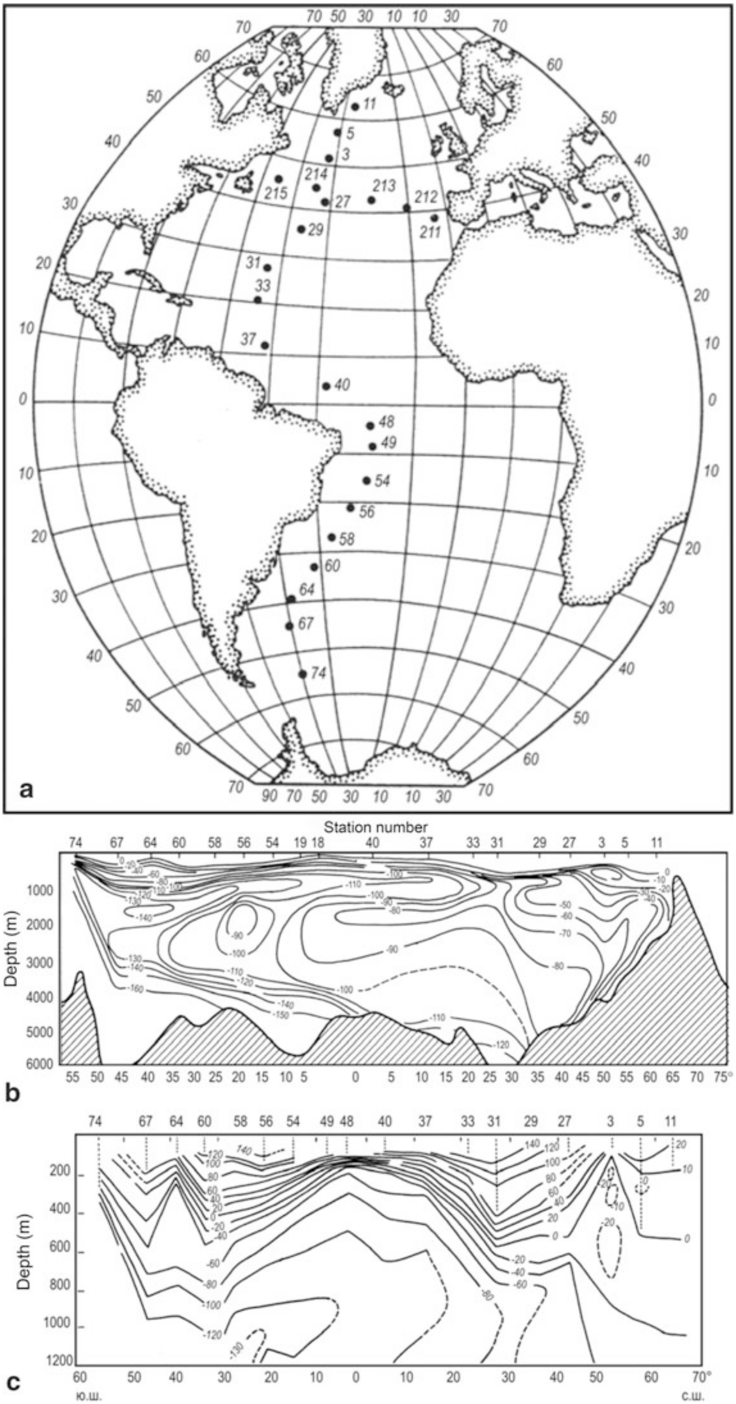


Fig. 14.13 Location of measurement and sampling stations for GEOSECS program (1972–1973, No No5-74) and 23rd 'Meteor' route (1971, NoNo 211-215) (*a*) (Stuiver 1980; Roether et al. 980); and $\Delta^{14}C$ vertical distribution in western part of Atlantic Ocean in 1972–1973 (*b*) (Stuiver 1980); the same for the depth up to 1,200 m (*c*))

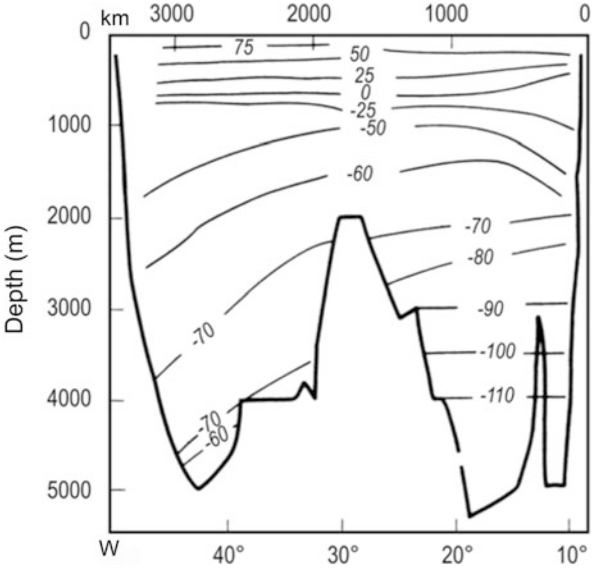


Fig. 14.14 $\Delta^{14}C$ vertical distribution obtained by ship 'Meteor' stations, 23rd route, 1971. (After Roether et al 1980)

Table 14.5 ^{14}C (%) content from the standard of modern carbon

Year	Reservoir	
	A	Hm
1957	104	98
1958	112	98
1959	123	99
1960	122	99
1961	116	100
1962	137	100
1963	193	102
1964	188	105
1965	170	108
1966	165	110
1967	160	112
1968	158	114
1969	155	118
1970	152	116
1971	150	116
1972	148	115
1973	145	115
1974	142	114
1975	140	113

obtained by extrapolation of the data published in the studies of (Bien et al. 1963; Broecker et al. 1960). The calculations were carried out by the formula analogous to that used for the tritium data interpretation (see Chap. 12):

$$A_t = \overline{A} + \sum_{1957}^{1975} \delta A_\theta \frac{1}{\tau} e^{-t/\tau -},$$

where A_t is the radiocarbon concentration in the mixing layer at t years after 1957; $\delta A_{\ominus}$ is the difference (%) between the biogenic radiocarbon level before 1950 (100%) in the calendar year $\ominus$; $\bar{A}$ is the ^{14}C concentration in the mixing layer (98%).

The best coincidence of the calculated and experimental data is achieved at value $\tau \approx 15$ years. The radiocarbon half-life was not taken into account because of the short time interval compared with the ^{14}C half-life. Certainly, the one-box model used for estimation of the dynamical parameters in the atmosphere-ocean system (Gray and Damon 1970; Ralf 1972) gives an approximate result, but the carbon constant of the reaction transfer rate from the deep to mixing layer by substitution of the value $\bar{A}$ was taken into account. The carbon exchange time of the mixing layer by Eq. 14.7 can be estimated. Taking into account that $N_{\Pi.c.} = 1.3N_a$, one obtains $\tau = 13$ years, if τ for the atmosphere is equal to 10 years. As in this case the carbon exchange in the system mixing-deep layers is not taken into account, the more realistic τ value for the mixing layer seems to be 10 years. This does not contradict to the three-box model of Dergachev (1977). The ^{14}C distribution in the surface layer of the central ocean parts is of interest. The observations on the Atlantic and Pacific Ocean stations show (Nydal et al. 1979) that ^{14}C concentrations in local areas do not stay constant with respect to time but vary within 10‰ (and even up to 20‰). A positive correlation between radiocarbon content in the surface layer and the surface ocean temperature is observed.

In the study of Rafter and O'Brien (1972), the ^{14}C distribution in the Pacific surface waters after 1968 is discussed. Figure 14.15 shows their results, where two belts of increased concentrations ($\delta^{14}\mathrm{C} \approx 20\%$) near 27°N and 27°S and minimal values around the equator ($\delta^{14}\mathrm{C} \approx +5\%$) are observed.

While considering the ^{14}C distribution in the surface Atlantic waters, Dergachev (1977) derived two maximum values: $\delta^{14}\mathrm{C} \approx +7\%$ (70°N) and $\delta^{14}\mathrm{C} \approx +19\%$ (27°N). It is interesting to note that the location of the above maximum values is unchanged up to the depth of 500 m (Fig. 14.16). The nature of this phenomenon is not explained. The only thing clear is that the maximum salinity of the oceans coincides with those from Fig. 14.15. The water zones are characterized by higher evaporation of the marine water and have a relationship with global circulation of the air and water masses. It is obvious that before the thermonuclear tests, the ^{14}C concentration in the surface ocean waters was not constant and changed under the same effects as after the tests.

The artificial radiocarbon from the mixing layer enters to the deep ocean layers. According to Ferhall (1971) calculations, the process of equilibrium state between the atmosphere and oceans will continue for 45 years (starting from 1970). Experimental study of this process will help in understanding the oceanic currents' nature and the mixing time of ocean waters.

14.5 Forecast of Carbon Dioxide Increase in the Atmosphere

The carbon dioxide increase in the atmosphere, in addition to the ^{14}C specific activity dilution in the exchangeable reservoirs, plays the own independent and important role. Increase of the carbon dioxide content may lead to a considerable change in

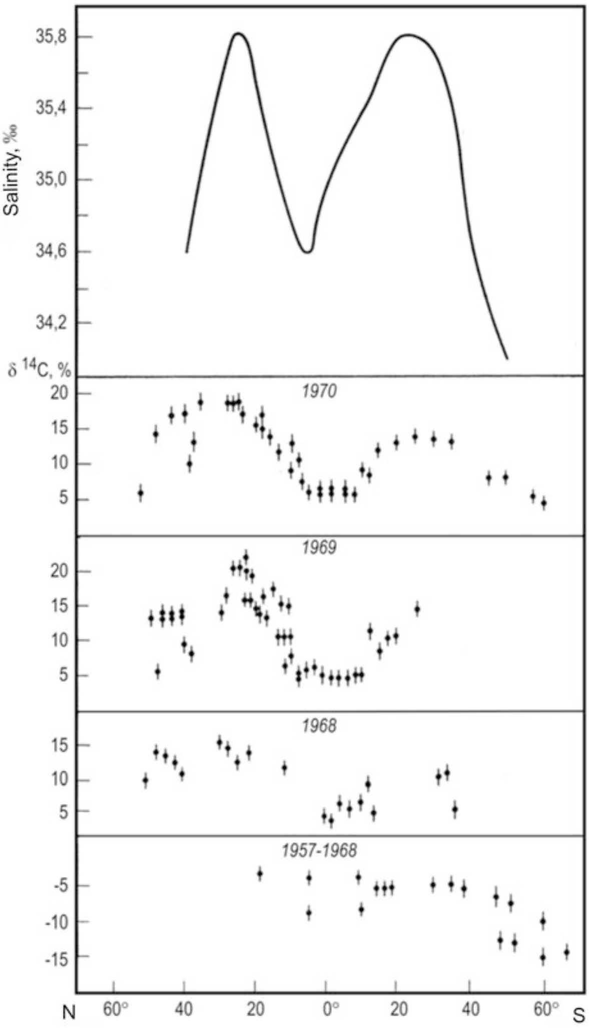


Fig. 14.15 ^{14}C concentration change in the Pacific Ocean surface layer over 1957–1970 (Rafter and O'Brien 1972) and salinity of the ocean surface layer. (After Miyake 1969. © IAEA, reproduced with permission of IAEA)

the mean yearly temperature on the Earth, which is a consequence of the 'green house' effect. The carbon dioxide is practically transparent for the solar radiation, but it absorbs the thermal radiation of the Earth in a number of lines of the infrared spectrum. If the water and carbon dioxide are absent in our planet, then the infrared radiation leaves it for the space and the lower layers of the atmosphere to lose the warmth. The carbon dioxide concentration growth leads to the stratosphere cooling and the near-earth air growth (Table 14.6).

Oeschger and Siegenthaller (1979) used CO_2 to change with respect to time parameters for the main reservoirs, obtained on the basis of the artificial radiocarbon distribution, and to predict the possible increase of CO_2 content in the atmosphere. They proposed models which based on the following assumptions.

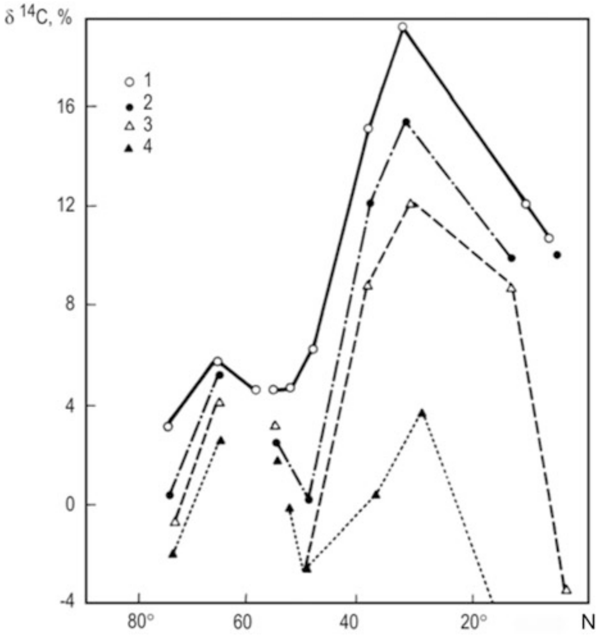


Fig. 14.16 Radiocarbon concentration change in upper layers in the North Atlantic Ocean: (*1*) surface layer; (*2*) at depth 100 m; (*3*) at 200 m; (*4*) at 500 m)

Table 14.6 Assuming CO_2 growth in the atmosphere. (From Kellogg 1980)

CO_2 content change in in atmosphere (%)	Assuming year of the change (year)	Growth of near-earth temperature (°C)
+25	2000	0.5–1.0
+100	2050	1.5–3.0

1. The study of ^{14}C content in deep Pacific and Atlantic oceanic waters over 1957–1959 has shown that distribution of radiocarbon in the deep waters practically was not disturbed by the thermonuclear tests.
2. As a result of the thermonuclear tests, the ^{14}C activity in the surface ocean waters is increased by 95% with respect to the present carbon content (its 'pre-industrial' value for the atmosphere is equal to 100%) in 1957 and by about 112% in 1970.
3. About 19% with respect to 'pre-industrial' amount of CO_2 has been injected into the atmosphere before 1970, but its concentration decreased only by 10%.
4. Because of dilution by carbon dioxide originated at combustion of the fossil fuel, the ^{14}C specific activity in the atmosphere before 1950 has decreased by about 2%.

Oeschger and Siegenthaller (1979) assumed for their model that the carbon transfer from the mixing layer to the deep waters results by the vortex (turbulent) diffusion (Fig. 14.17). Any increase in the partial pressure in CO_2 leads to its redistribution between the atmosphere and oceans. Such redistribution can be described by a parameter called the 'buffer-factor'. For example, if the CO_2 partial pressure in the

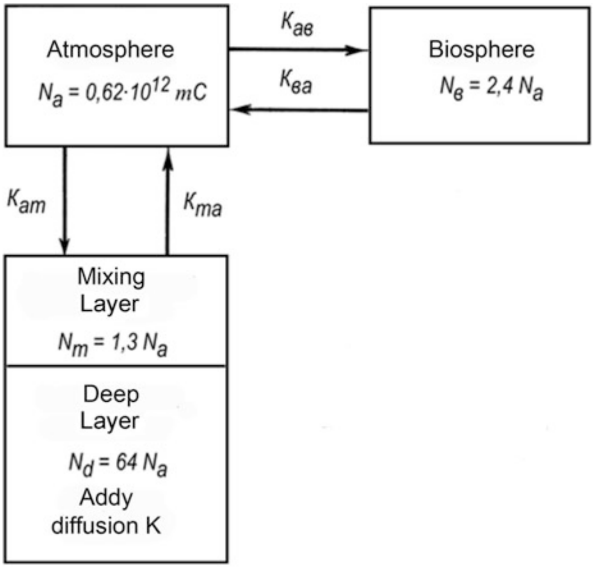


Fig. 14.17 Reservoirs of the carbon exchangeable system which takes into account diffusion transfer to the deep ocean layers. (After Oeschger and Siegenthaller 1979. © IAEA, reproduced with permission of IAEA)

atmosphere increases by α%, then the total CO_2 concentration in the ocean waters, to be in equilibrium with the atmosphere, increases in waters only by $\alpha/\xi\,\%$. The biosphere in the model is represented by the well mixed reservoir, the amount of carbon in which is 2.4 times more than in the atmosphere and its residence time is about 60 years. The partial pressure increase of CO_2 in the atmosphere leads to the photosynthetic activity of the plants described by the 'growth-factor' ε. If CO_2 pressure in the atmosphere increases by $\alpha\%$ then the carbon flow from the atmosphere to the biosphere increases by the value of $\varepsilon\alpha\%$. According to (Oeschger and Siegenthaller 1979), the ε value varies for different conditions from 0 to 0.4. For prediction of the CO_2 increase in the atmosphere, the following independent parameters were used (see Fig. 14.17):

N_a	CO_2 in atmosphere	Pre-industrial level	0.62×10^{18} g
N_b	CO_2 in biosphere		2.4 N_a
N_m	CO_2 in mixing layer		1.3 N_a
N_d	CO_2 in deep water layer		64.2 N_a
K_{am}	Exchange coefficient in system atmosphere—mixing layer		1/7.7 years
K_{ab}	Exchange coefficient in system atmosphere-biosphere		1/25 years
K	Coefficient of vortex diffusion		3,987 $m^2\ sec^{-1}$
ξ	Buffer-factor of CO_2 absorption by the ocean		10
ε	Growth-factor connecting with CO_2 absorption by biosphere		0.2

The authors give a prediction on the CO_2 content increase in the atmosphere at different input functions. For example, if single CO_2 concentration in the atmosphere increases by $\alpha\%$, then a new equilibrium is reached characterized by $\alpha_\infty\%$. The ratio α_o/α_∞ can be obtained by Equation,

$$\alpha_0 N_a = \alpha_\infty N_a + (\alpha_\infty/\xi)(N_m + N_d) + \alpha_\infty \varepsilon N_b,$$

or

$$\alpha_\infty/\alpha_0 = N_a/[N_a + (N_m + N_d)]/\xi + \varepsilon N_b.$$

At $\xi = 10$, $\varepsilon = 0.2$, $\alpha_o/\alpha_\infty = 0.125$, i.e., one eighth part of the total CO_2 input into the atmosphere. Here possible decrease of α_∞ value as a result of oceanic carbonates dissolution and weathering of the rocks has not been considered, but because of too slow CO_2 transfer into deep ocean layers these processes will continue for a long time. If the CO_2 inflow into the atmosphere stopped in 1970, then $\alpha \approx 10\%$, in 2000 α value to be 7%, and after several centuries it would reach equilibrium value, that is, $\alpha_\infty \approx 2.3\%$. The carbon content in the fossil fuel (oil, coal, and gas) recalculated by CO_2 is 11.64 times more than CO_2 in the atmosphere at pre-industrial epoch. According to the present-day knowledge, the CO_2 production rate can be described by the equation as

$$P(t) = \frac{d}{dt}\left[\frac{11.65 N_a}{1 + 61\ \exp(-t/22)}\right],$$

where t is the time in years ($t = 0$ in 1970).

The production rate $P(t)$ after 1970 comprises 4.5 N_a per year (the mean velocity over 1960–1970 is about 5% per year). The calculations show that at this rate of the fuel combustion more of 2,000% with respect to pre-industrial level of CO_2 will be accumulated in the atmosphere to 2,050. This amount of carbon dioxide may lead to an increase of near-ground temperatures from 3 to 4°C (Fig. 14.18), but this is unlikely. In twenty-first century, the fossil fuel use decreased because the other sources of energy are now involved. In addition, according to the recent scientific data on heat and mass exchange between the atmosphere and oceans, the green house effect is by orders of 3–4 overestimated (Sorokhtin 2002).

By the Kellogg's (1980) data, in this case, the near-ground temperature will increase only by 1–1.5°C.

14.6 Principles of Radiocarbon Dating

If any system exchange with the atmospheric carbon dioxide is finished, then the accumulated ^{14}C amount is decreased with respect to time by the radioactive decay law which is

$$A_t = A_0 e^{-\lambda t}, \tag{14.13}$$

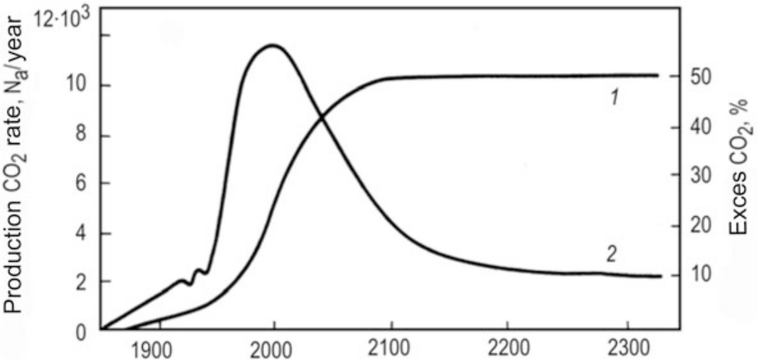


Fig. 14.18 Dependence of CO_2 variation in the atmosphere on present fossil fuel combustion (*1*) and on 30% reduction of its present combustion (*2*). (After Oeschger and Siegenthaller 1979. © IAEA, reproduced with permission of IAEA)

where A_t and A_0 are the radiocarbon activity (or concentration) at time t and $t = 0$; λ is the radiocarbon decay constant; $\lambda = \ln 2/T_{1/2} = 0.693/T_{1/2}$; T is the period of the ^{14}C half-life.

If the exchange processes stop, for example due to death, then the Eq. 14.13 can be used for calculation of the time passed after the process has broken off (the object age):

$$t = (1/\lambda)\ln(A_0/A_t) = 8033\ln(A_0/A_t). \qquad (14.14)$$

The half-life period equal to 5,568 years was used in the Eq. 14.14. In order to pass the 5,730-year period, all the age values calculated by Eq. 14.14 should be multiplied by the coefficient 1.03. The method of obtaining radiocarbon dates on organic specimens has been developed by Libby (1967).

Radiocarbon dating is based on a number of assumptions; the most important of which are (Olsson et al. 1970): (1) the intensity of cosmic radiation and, as a consequence, the ^{14}C concentration in the atmosphere, remained constant at least during the radiocarbon dating scale (0–80,000 years); (2) the time of exchange of atmospheric carbon with terrestrial carbon is considerably smaller than the half-life of carbon-14 and does not change with time; (3) secondary processes do not affect the isotopic composition of the studied specimens after sampling. This is equivalent to the assumption that the radiocarbon content in a specimen decreases only because of radiocarbon decay.

In natural cases, the above-mentioned assumptions do not hold strictly, although in most cases the age determined on the basis of radioactive dating are in good agreement with those obtained using other techniques (Libby 1967).

In the case of ^{14}C variations in atmospheric CO_2 and in biosphere (see Fig. 14.4) over long time periods starting from about 2,500 years, radiocarbon and dendrochronological timescale of the organic specimens becomes different (Fig. 14.19; Mook 1977).

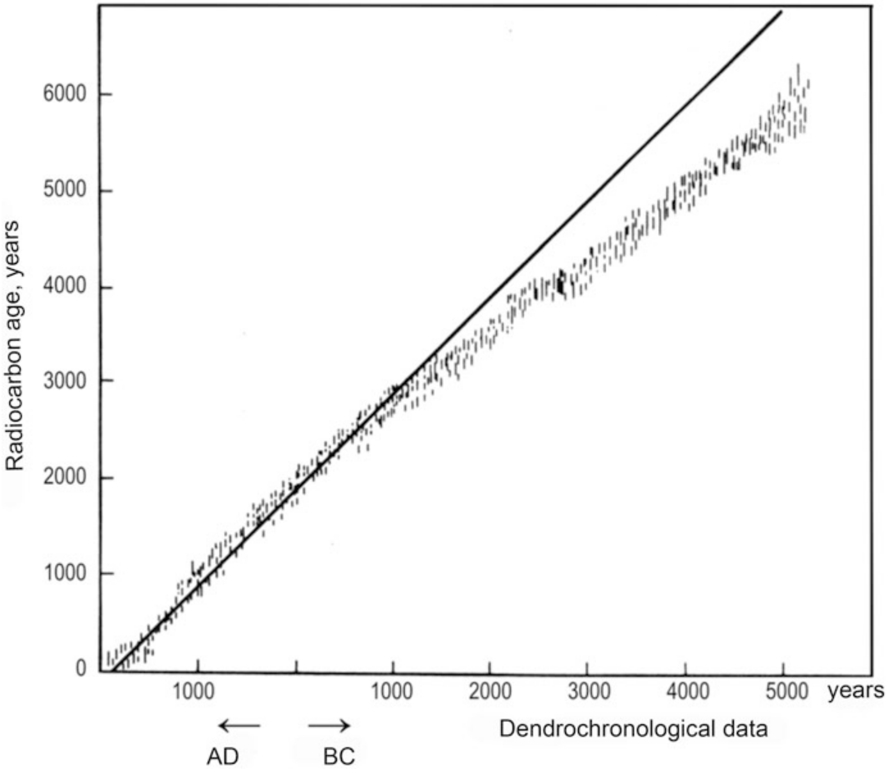


Fig. 14.19 Relationship between dendrochronological and radiocarbon ages of *Sequola gigantea* and *Pinus aristata*. (After Mook 1977. © IAEA, reproduced with permission of IAEA)

In order to reconcile the radiocarbon results with those obtained by the dendrochronological ones within 0–8,000 years, a number of correlations were proposed. According to Wendland and Donley (1971), the age correlation can be done by the third degree polynomial:

$$T_{corr} = 112 + (0.710T_{^{14}\mathrm{C}}) + \left(1.610 \times 10^{-4} T^2_{14\mathrm{C}}\right) - \left(1.50 \times 10^{-8} T^3_{14\mathrm{C}}\right).$$

For this purpose, there are also other correlation equations (Ralf and Klein 1979).

Radiocarbon dating on the basis of organic fragments has a wide application in the archeology, geology, geography, oceanography, and other Earth's sciences (Suess 1979).

Isotopic composition of the stable carbon in a carbonate system is used for correction of the radiocarbon age of groundwater. The processes of the carbon isotope fractionation were considered in Chap. 10.

As it is observed from the Eq. 14.14, the most stable carbon fractionation is between gaseous CO_2 and hydrocarbonate-ion (HCO_3^--ion is enriched in ^{13}C by about 10% at 0°C compared with the carbon dioxide). It is also obvious that the complete fractionation of the carbon isotopes in the gas-solution and gas-solid phase

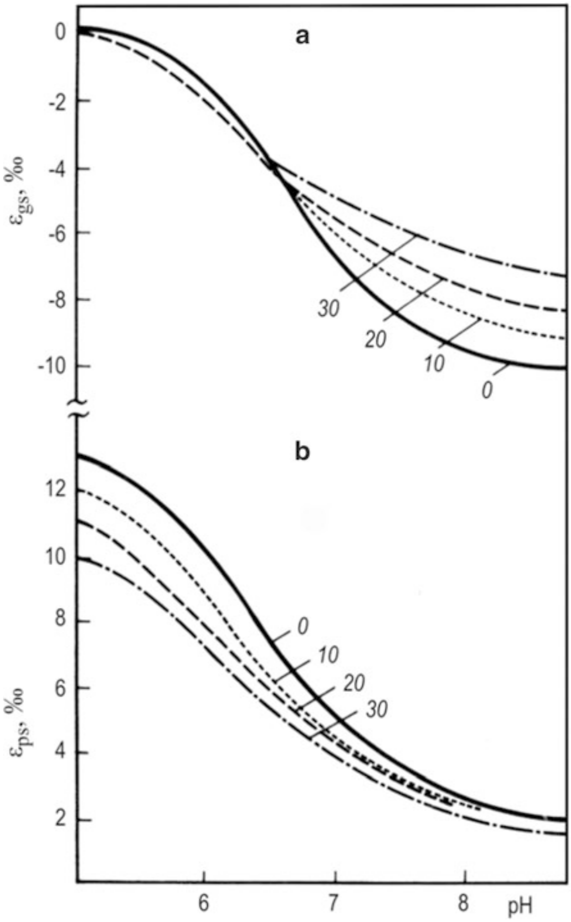


Fig. 14.20 Equilibrium fractionation of carbon isotopes versus pH and temperature for the systems: (*a*) gaseous CO_2—dissolved carbon components; (*b*) carbon sediments—dissolved carbonates. (After Wigley et al. 1978)

system should depend on the medium pH. A graphical relation of such dependence is shown in Fig. 14.20 (Wigley et al. 1978).

Fractionation of the carbon isotopes in the thermodynamically equilibrium processes, stipulated by the kinetic factors (for example, in biochemical reactions), leads to the nonsteady state in carbon isotopes of the carbon-bearing matter of different natural objects.

Figure 14.21 indicates the isotope variation limits in carbon contained in various objects (Stiel et al. 1979). It is observed from this figure that the carbonates precipitating from the oceanic water (mean values of $\delta^{13}C = 0$) are the most ^{13} Cenriched and relatively constant by isotopic composition. The PDB-1 isotope standard is composed of these carbonates. Compared with the standard, the atmospheric CO_2 is enriched in the light isotope of carbon by $-7‰$. Plants are even more enriched in the light isotope. The average value for ground plants is $\delta^{13}C = -25‰$; close to this value is the soil CO_2. A large value of the shift ($\delta^{13}C = -30‰$) is detected in oil and maximum enrichment in ^{12}C is observed in natural methane formed in sedimentary rocks (δ^{13}C up to $-90‰$).

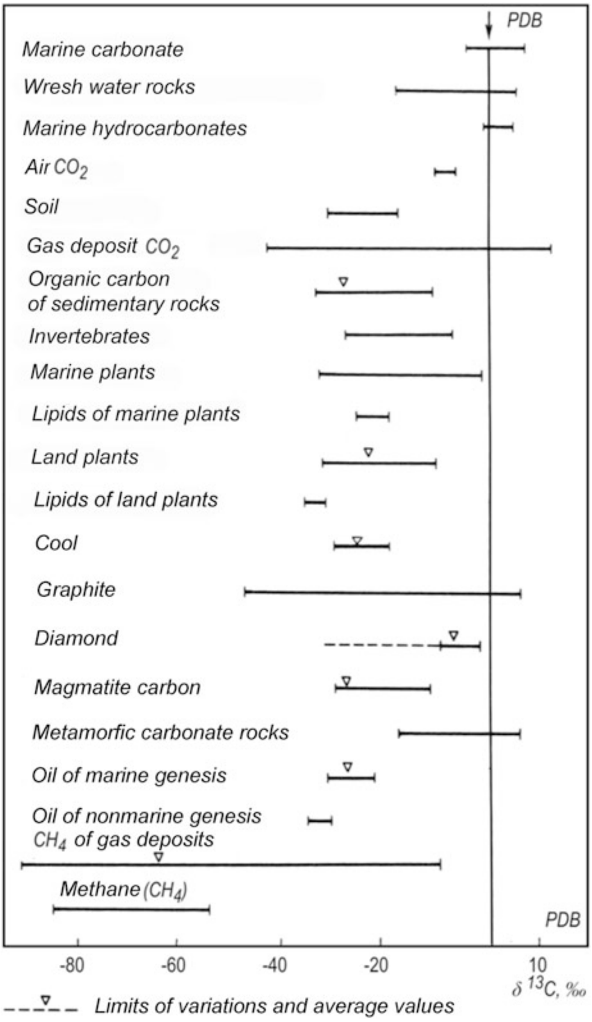


Fig. 14.21 Stable carbon isotope variations relative to the PDB-1 standard in various natural objects. (After Stiel et al. 1979)

Since the isotope fractionation factor increases by its square with the addition of each neutron, the corresponding isotope shift in ^{12}C–^{14}C isotope fractionation will be twice as great. Therefore vegetation should be depleted in ^{14}C compared with the atmosphere and have $\delta^{14}C = -50‰$.

14.7 Radiocarbon Dating of Groundwater

At present, for groundwater age determination, most of the researchers apply the piston model. It was earlier pointed out that the radioactive isotope concentration in a sampling point A, located at a distance x_0 from the recharge, is calculated by the expression:

$$A = A_0 \exp[-(x_0/v)\lambda] = A_0 \exp(-\lambda t), \tag{14.15}$$

where A_0 is the isotope concentration (activity) in the recharge area; v is the velocity of groundwater motion; λ is the ^{14}C decay constant; $\lambda = \ln 2/T_{1/2}$; t is the water age, determining as the transit time, during which the isotope reaches the distance from the recharge area to the sampling point.

The time t from Eq. 14.15 can be obtained by the formula:

$$t = (T_{1/2}/\ln 2)\ln(A_0/A) = (1/\lambda)\ln(A_0/A). \tag{14.16}$$

As it was noted earlier, the radiocarbon method of groundwater age determination was applied for the first time by Münnich (1957, 1968). The main assumptions of this method are as follows:

1. Radiocarbon concentration in the recharge zone is known and does not change at least over the range of the radiocarbon time-scale.
2. Radiocarbon does not enter the carbonate system of groundwater from outside the recharge zone.
3. If ^{14}C content in an aquifer decreases both due to radioactivity decay and other processes, then the effect of these processes can be taken into account.
4. The leakage of water from one aquifer into another (the mixing of water) is negligible.
5. The rate of movement of dissolved carbonates is equal to the rate of groundwater movement.

The reality of the above conditions is discussed in the later part.

It is worth to stress that the term 'age' of groundwater has a great indefiniteness compared with, to say, 'age' of a solid sample. In general case, the age of a groundwater can be defined by a certain period of time after some hydrogeological event has happened (Dubinchuk 1979). Such an event in radiocarbon dating is discontinuation of the water exchange with the soil air or the atmosphere. In framework of this definition, in the radiocarbon scale the natural waters appears to be modern if they are found in continuous exchange with the soil air or atmosphere, where radiocarbon concentration $A_0 = 100\%$.

In general case, the water 'age' is more easily described in the form of distribution function of residence time in the aquifer, applying corresponding models for a hydrogeological system, which satisfy to its real structure (Ferronsky et al. 1977; Dubinchuk 1979). At the present time, for the isotope data interpretation and for obtaining the groundwater's age characteristics, in addition to the piston model, there are the following models for the mass transfer in hydrological systems: (1) model of complete mixing (exponential or box-model); (2) dispersion model: (3) mixing model of different age waters.

According to the complete mixing (exponential) model (Nir 1964), water input at different times mixes quickly. The relative portion of water of t age in the system is expressed as an exponential function in the form

$$p(t) = (1/\tau)\exp(-t/\tau), \tag{14.17}$$

where τ is the average residence time of water in a system; $1/\tau = v/q$ is the water exchange rate, that is, the ratio of the total annual inflow of water to the output of the system. Concentration of the isotope in the system ($A_{\text{system}} - A_{\text{output}}$), in general case can be written as the following sum in the discrete form:

$$A_{\text{system}} = \bar{A}/(1+\lambda\tau) + \sum_{\theta=1952}^{1952+t} [A(\Theta - t) - \bar{A}]/p(t)e^{-\lambda t}, \tag{14.18}$$

where $\ominus$ is the current year of; ($\ominus - t$) the time of input into the water system with concentration of the isotope (^{14}C and others.) $A(\ominus - t)$, which was happened by t years from the sampling moment; $\bar{A}$ is a steady state concentration before the thermonuclear tests; other definitions are previous.

Applying the Eq. 14.18, by observed ^{14}C concentrations in the system (A_{system}), the mean residence time of water can be obtained if the function of the isotope distribution $A(\ominus - t)$ at the system entrance is known. The exponential model is used for interpretation of the tritium data, but it can also be used for estimation of dynamic characteristics of groundwater, applying the radiocarbon, because the function $A(\ominus - t)$ (radiocarbon input at the hydrogeological system entrance) is known (Ferronsky et al. 1977). The ^{14}C concentration change in groundwater in the time calculated by the exponential model is shown in Fig. 14.22 (Geyh 1974).

The Figure shows that the effect of ^{14}C concentration change induced in groundwater by the thermonuclear tests so much as the mean residence time in the system is less. If the function $A(\ominus - t)$ is constant the ^{14}C radiocarbon residence time of water $\tau = v/q$ can be determined by the formula:

$$\tau = (A_{\text{input}} - A_{\text{output}})/A_{\text{output}}\lambda = 8{,}033(A_{\text{input}}/A_{\text{output}} - 1), \tag{14.19}$$

where A_{input} and A_{output} are the radiocarbon concentrations (in % with reference to standard of the modern carbon) at the entrance and exit of the system.

It is not difficult to show that in framework of the exponential model if A_{input} is constant in time, then the water age t is related to the residence time τ by expression $t = (1/\lambda)(1 - \lambda\tau)$. Application of the integral or discrete expressions like Eq. 14.18 allows to estimate the residence time in hydrological system at different forms of the distribution function $P(t)$, but despite the wide application in tritium data treatment, interpretation of the radiocarbon data by such a way is not used.

As a special case, it is necessary to consider the model of different-age water (Ferronsky et al. 1977; Evans et al. 1979). If the hydrogeological system consists of n components of water with the ages T_i, then its age can be determined as a mean-weighted value

$$\bar{T} = \sum_{i=1}^{n} P_i T_i, \tag{14.20}$$

where P_i is the part of water of age T_i.

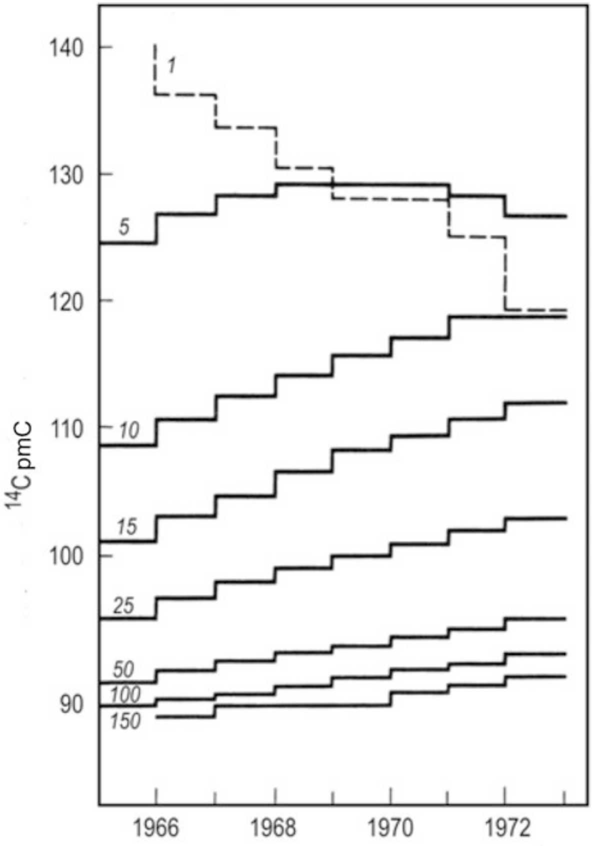


Fig. 14.22 Radiocarbon concentration change in groundwater as a function of residence time calculated by exponential model. Initial ^{14}C concentration was accepted equal to 85% relative to the standard of modern carbon. The figures on curves define residence time in years. (After Geyh 1974)

In such a system, the mean-weighted isotope concentration (for example, ^{14}C) is established:

$$\bar{A} = \sum P_i T_i. \tag{14.21}$$

If the source of the radioactive isotope input is the same, then the values A_i will be different due to partial radioactive isotope decay over the time T_i. Such a condition is satisfied for the radiocarbon concentration of which the recharge area can be accounted constant and equal to A_0. Then the Eq. 14.21 can be rewritten as:

$$\bar{A} = A_0 \sum P_i \exp(-\lambda T_i). \tag{14.22}$$

Determining the mixing age by concentration $\bar{A}$ and using the exponential formulae, we may obtain the value

$$T' = 8003 \ln(A_0/\bar{A}). \tag{14.23}$$

Comparing the Eq. 14.23 and 14.20, we find that $T' \neq \bar{T}$. It is observed from the above that: (1) the true age of mixture of the different waters is equal to the mean-weighted age of the water components; (2) in general case, the isotopic (radiocarbon) mixture of waters is not equal to the true age and its formal determination does not give unique time-information about a system (Ferronsky et al. 1977; Dubinchuk 1979). This problem can be solved correctly only in the case of independent measuring of the date and age for each component. For obtaining such information one may use, for example, the data on distribution of other isotopes (D, ^{18}O, T, and so on). Evans et al. (1979) have calculated the possible change in radiocarbon age for a two-component mixture depending on a portion of the modern component ($A_0 = 100\%$). It follows from their calculations that the groundwater of radiocarbon age equal to 57,000 years may represent a mixture of 99.9% of water with 100,000 years of age and 0.1% of modern water. This result is changes only a little if the present-day component has a 5,000 years of age, but despite this the radiocarbon age of water mixture does not give the true information which can be used to study a relationship between the aquifers, localization of recharge areas, and so on (Borevsky et al. 1981; Sobotovich et al. 1977; Seletsky et al. 1979; Fröhlich et al. 1977; Deak 1974).

14.8 Formation of Chemical and Isotonic Composition of Groundwater's Carbonate System

The consistent and complete analysis of chemical and isotopic composition of the carbonate system of groundwater can only be carried out if all the physicochemical processes involved in the formation of the saline composition of groundwater are accounted for. At present, it is difficult to realize such an analysis since many problems remain unsolved. Even in such simple systems, as the ocean and sea waters where the chemical composition, temperature, and pressure are well known and, as a rule, extra chemical reactions do not occur, the estimation of the carbonates equilibrium state often results in inconsistent conclusions. More complicated physicochemical processes of interaction between solutions and rocks in dispersion systems take place in groundwater. Besides, many of these chemical reactions are conditioned by the participation of micro-organisms. Therefore, the estimations of these system states can be carried out with a less accuracy than those of sea and ocean water systems. Consider only some of the physicochemical reactions resulting in changes of chemical and isotope composition of the carbonaceous system of groundwater.

The hydrocarbonate contained in the soil solutions is formed mainly due to the dissolution of limestone under the influence of carbon dioxide according to the equation (Fontes and Garnier 1979; Mook 1976; Wendt et al. 1967; Münnich 1968)

$$\mathrm{CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^-}. \tag{14.24}$$

The following additional reactions are also common: leaching by carbon dioxide of the siliceous rocks

$$\mathrm{CaAl_2(SiO_4)_2 + 2CO_2 + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^- + Al_2O_3 + 2SiO_2}; \tag{14.25}$$

the decomposition of carbonates in the presence of humites

$$\begin{aligned}&CaCO_3 + 2H^+(hum) \Leftrightarrow Ca(hum)_2 + CO_2 + H_2O;\\&2CaCO_3 + 2H^+(hum) \Leftrightarrow Ca(hum)_2 + Ca^{2+} + 2HCO_3^-;\end{aligned} \tag{14.26}$$

the reduction of sulfates

$$SO_4^{2-} + 2H_2O + 2C \Leftrightarrow H_2S + 2HCO_3^-; \tag{14.27}$$

the injection of atmospheric carbon

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-; \tag{14.28}$$

the oxidation of organic substances

$$6nO_2 + (C_6H_{10}O_5)_n + nH_2O \rightarrow 6nHCO_3^- + 6nH^+; \tag{14.29}$$

the subsequent interaction of the acid water with calcium carbonates

$$nH^+ + nCaCO_3 \Leftrightarrow nCa^{2+} + nHCO_3^-. \tag{14.30}$$

The list of reactions affecting the formation of chemical and isotope composition of groundwater can be extremely large. The contribution of each reaction to this process has not been completely studied. The contributions change depending upon the common hydrological and hydrochemical conditions of the formation of the groundwater; however, at present it is commonly accepted (Ferronsky et al. 1975; Bondarenko 1983; Giggenbach et al. 1983; Fontes 1976; Fontes and Garnier 1979; Mook 1976; Reardon et al. 1980; Wigley et al. 1978; Geyh 1972; Münnich 1975; Wendt et al. 1967; Tamers 1965) that the major portion of radiocarbon in groundwater is formed by the dissolution of the 'dead' soil carbonates in the unsaturated zone interacting with modern soil carbon dioxide. The modern CO_2 is provided by root respiration and bacterial decomposition of organic substances according to reaction (14.24). In the presence of isotope species of carbon-bearing molecules, this reaction can be written as

$$CaCO_3 + {}^{14}CO_2 + H_2O \Leftrightarrow (H^{14}CO_3^- + HCO_3^-) + Ca^{2+}. \tag{14.31}$$

This equation indicates that the hydrocarbon-bearing ion obtains one half of its carbon from biogenic carbon dioxide and the other half from sedimentary carbonates having no radiocarbon atoms.

The model is based on the assumption that the specific activity of radiocarbon in young groundwaters is equal to 50% of the activity of biogenic carbon dioxide. It follows from the experiments that the radiocarbon concentration of water in the recharge regions normally exceeds those mentioned above and ranges from 50 to 100% of the modern biogenic level. This may result due to two reasons which are the existence of isotope exchange between the biogenic carbon dioxide and the bicarbonate-ion, and the presence of radiocarbon in soil carbonates.

The first assumption is confirmed by the fact that approximately 98% of the biogenic carbon dioxide leaves the soil because this system is open relative to CO_2. In the open system, with isotope exchange occurring under conditions of counter-flow extraction (mass of $CO_2 >> $ mass of HCO_3^-), the ^{14}C content in the dissolved hydrocarbonates, formed by the reaction described by Eq. (14.24), can theoretically reach 102% of the radiocarbon content in the biogenic carbon dioxide, since in this case $\alpha_{HCO_3^- - CO_2}(r) \approx 1.02$, or $\varepsilon \approx 2\%$ (Galimov 1968; Wigley et al. 1978; Pearson and Swarzenki 1974).

It is important that the dead carbonates of the soil layer can contain a considerable amount of ^{14}C. As Geyh (1970) has shown, a higher radiocarbon content in the carbonate system of groundwaters than that theoretically predicted may result from the presence of radiocarbon of 2–15% (and sometimes up to 70%) of the modern level in the soil carbonates . By Geyh's assumption, the radiocarbon is accumulated in the upper part of the soil layer in the summer season when the amount of infiltrated atmospheric water is not high and precipitation of carbonates occurs due to the evaporation processes of salt concentration in the soil layer.

It is obvious that such an explanation does not truly reflect the whole complexity of the formation of pedogenic carbonates. Polynov (1953) has pointed to the process of calcium carbonate formation occurring in the soil itself during the growth of plants. This process produces lime shells of cells, calcium crystals in wood tissue, and scales of calcium carbonate on leaves and stems. Partly during their life and episodically when the plants die, these carbonates enter the upper soil layer, migrate with surface and soil waters, and accumulate in the soils. The formation of thick carbonaceous layers has also been reported during soil-formation processes by other researches (Afanasyeva 1947; Ponomarev and Antipov-Karataev 1947).

While studying the behavior of the stable carbon isotopes in these processes, it is assumed that calcium carbonate, involved in the reaction (14.24), originates from the sedimentary carbonates of sea genesis with $\delta^{13}C_{HCO_3^-} = 0‰$. The soil carbon dioxide in the humid zone of the plants' growth has, according to the Calvin photosynthetic cycle (C_3), $\delta^{13}C_{CO_2} = -25‰$ (Pearson et al. 1978; Galimov 1968; Pearson and Hanshaw 1970). If equilibrium isotopic fractionation in the system CO_2–HCO_3^- does not occur, then, by Eq. (14.24), hydrocarbonate in the solution will have $\delta^{13}C_{HCO_3^-} = -12.5‰$.

In the arid zones, where plants metabolize through a Hatch-Slack photosynthetic cycle (C_4), the soil carbon dioxide has $\delta^{13}C_{CO_2}$ from -12 to $-14‰$ and, therefore, neglecting isotope fractionation in the gas-liquid system, the hydrocarbonates' $\delta^{13}C_{HCO_3^-}$ average value in solution will range between -5 and $-7‰$. The data on the carbon isotope composition of the CO_2 produced by plants metabolizing through a Hatch-Slack cycle are taken from the study of Lerman (1972), who has also reported somewhat different values of $\delta^{13}C_{CO_2} = -27‰$ for the Calvin cycle.

In open systems, in a similar manner to radiocarbon, the isotope composition of stable carbon of dissolved carbonate ions can, in principle, reach the equilibrium value determined by the fractionation coefficient $\alpha_{HCO_3^- - CO_2} = 1.0077$ (25°C) (Vinogradov et al. 1967). In this case, for the Calvin plants $\delta^{13}C_{CO_2}$ equal from -17 to $-19‰$ and for the Hatch-Slack plants $\delta^{13}C_{CO_2}$ is from -4 to $-6‰$.

Typical Hatch-Slack plants are maize, papyrus, camel brushes, and other types of plants typical of arid zones. Further examples are those plants which produce CO_2 characterized by $\delta^{13}C_{CO_2}$ varying from -19 to $-34‰$, through the Crassulacean acid metabolism (CAM) cycle (Wong and Sackett 1978).

For the zone of semi-arid climate in Arizona, US, the $\delta^{13}C$ value of the soil carbonates is about $-3.73 \pm 1.31‰$, and the ^{14}C content amounts to $-23.8 \pm 15.3\%$ of the modern standard (Wallick 1976). For the soil carbon dioxide, the $\delta^{13}C$ value ranges from -11.7 to $-18.4‰$ with an average of $15.12 \pm 2.81‰$. As the author reported, this is close to the average isotope composition of CO_2, produced by plants through the Hatch-Slack photosynthetic cycle (from -13.9 to $-19.8‰$).

Experimental study of $\delta^{13}C_{HCO_3^-}$ values and of the specific activity of the hydrocarbonate ion in the north-eastern region of the Germany has shown that the ratio of $\delta^{13}C_{HCO_3^-}/\delta^{13}C_{CO_2} > 0.5$, and is close to 0.6, and the ratio of specific activity of the hydrocarbonate ion to that of the soil carbon dioxide is ~ 0.8 (Wendt et al. 1967). The specific activity of radiocarbon in the upper aquifers of groundwater varies greatly. Derivation from the average value may reach $\pm 25\%$ and more. In a number of cases, corresponding to Central Europe, the radiocarbon variations are less pronounced and are equal to $\pm 5\%$. Elevated radiocarbon contents (up to 95% of the modern level) and greater contents of the light carbon isotope $\left(\delta^{13}C_{HCO_3^-} = -15‰\right)$ have been found in water sampled from lysimeter without any plant cover (76% of the modern standard activity and $\delta^{13}C_{HCO_3^-} = -10‰$) (Münnich et al. 1967).

In the Kalahari region (South Africa), the carbon isotope composition of water in the upper aquifer is somewhat different from the European average $\left(\delta^{13}C_{HCO_3^-} = -11‰\right)$, but the radiocarbon content is close to that measured in other regions of the globe (85% of the modern standard) (Vogel 1970). All these facts indicate that a number of problems concerning the formations of the isotopic composition of the groundwater carbonate system should be considered more carefully and new models should be developed.

Wendt et al. (1967) have proposed the idea that equilibrium might occur between the soil solutions and the soil CO_2. The theoretical and experimental data show that the isotope exchanges occurring between the solution and the soil gases do result in changes in $\delta^{13}C$ and the specific activity of the bicarbonates. The experimental and theoretical values agree rather well, butin majority of cases the groundwaters' ^{14}C radioactivity is only 80–85% of the modern standard. This fact also indicates the involved nature of the formation of the isotopic composition of groundwaters, which are obviously related to the kinetics of the process.

It is observed from the consideration of even a simple scheme of radiocarbon contribution to groundwaters that it is impossible to determine the initial radiocarbon activity in groundwaters; one can only approximately estimate the ranges of ^{14}C variations in modern waters. This problem becomes even more complicated due to the fact that in the real conditions occurring in the unsaturated zone, as has been shown earlier, another process different from reaction (Eq. 14.24) may take place, resulting in the enrichment of water with the bicarbonate ion. The effect of these reactions upon the formation of the chemical and isotopic composition of the carbonate system of groundwaters is insufficiently understood. The temperature, type of plant cover, and other factors, depending on the climatic conditions and the geological structure of the unsaturated zone, all affect the procedure of chemical and biological reactions (Bondarenko 1983). The initial amount of ^{14}C also depends upon these factors. The fact that the climate of many regions of the globe has changed sharply during the last 10^4 years leads to uncertainty in choosing the initial ^{14}C concentration of the studied groundwaters. The problem is also complicated by the fact that during recent thermonuclear tests, the ^{14}C content in the atmospheric carbon dioxide has increased by a factor of 2 (see Fig. 14.5) and already, since 1965, thermonuclear radiocarbon has started to recharge into groundwaters (Münnich et al. 1967; Geyh 1974).

It has been found experimentally that the radiocarbon content in fresh groundwater is often equal to about 85 ± 5% relative to the modern standard. This value is taken by some authors as the initial concentration (Klitzsch et al. 1976; Vogel 1970).

14.9 Corrections in Groundwater Dating by Radiocarbon

The processes resulting in a decrease of the specific activity of dissolved carbonate components during groundwater circulation make the radiocarbon dating of groundwaters difficult. The decrease in the specific activity of carbon in the groundwater carbonate system may be accounted for by the following two main processes: the dissolution of the dead carbonates and the removal of radiocarbon from solution.

The dissolution of the vast amounts of carbonates from the water-bearing rocks is caused by:

1. the presence in the soil moisture which recharges the groundwaters of active carbon dioxide and organic acid;
2. the production of the carbon dioxide in groundwaters due to biological decomposition of the organic substances contained in water and rocks;
3. the change of the alkaline-earth metal cations for the alkali metal cations, for example calcium for sodium;
4. the injection into some aquifers of endogenic carbon dioxide;
5. changes in the thermodynamic conditions (those of temperature and pressure) in the immersed parts of the water-bearing complexes.

A likely cause of the removal of radiocarbon becoming incorporated in the groundwaters' solute is the exchange processes in the solid phase-solution system. The exchange processes do not result in considerable changes of radiocarbon content in the liquid phase at equilibrium conditions, when the dissolved carbonates are in thermodynamic equilibrium with carbonates of the water-bearing rocks. This has been shown by laboratory and natural studies (Münnich et al. 1967; Thilo and Münnich 1970; Vogel 1970). The fact that radiocarbon is present in groundwaters—and that a number of individual studies have produced coincidental ages by radiocarbon dating and from independent hydrodynamical considerations—leads to the conclusion that in many water aquifers the effects of the carbon exchange and decay are small, even during the movement of waters through the carbonate collectors. Thus, Vogel and Ehhalt (1963) have concluded that ^{14}C removal from water should be negligible. This conclusion is confirmed by the general knowledge that the surface of the rocks, which are in direct contact with water, undoubtedly favors isotope exchange on the one hand but on the other hand restricts the removal of radiocarbon from the water. Münnich and co-authors (Münnich and Roether 1963; Thilo and Münnich 1970) have proposed a model of the two reservoirs with the help of which an attempt has been made to show how small the effect of exchange processes in the carbonate collections is upon the change of the carbon isotope composition.

The removal of radiocarbon from the solution due to isotope exchange with carbonate rocks should be limited by the value of the diffusion coefficient of the carbonate ion in $CaCO_3$. According to laboratory data for crashed calcite (Thilo and Münnich 1970), the diffusion coefficient, extrapolated to 10°C, is about 10^{-28} cm^2/sec. According to estimations made by Thilo and Münnich this corresponds to the transition from water into the solid phase of about 50% ^{14}C during 10^4 years at temperature of 10°C. Thilo and Münnich assumed that the observed effect of isotope exchange upon radiocarbon removal is conditioned by the organization of the experiment, particularly by the use of finely-crushed calcite, each particle of which provides a fresh unstable surface. It should be pointed out that under such conditions recrystallization in the finely-crashed particles of calcium carbonate has occurred, resulting in an apparent increase in the diffusion coefficient which is equal to about 10^{-43} cm^2/sec at room temperature (Wendt et al. 1967).

In a discussion on a report by Thilo and Münnich (1970), Hanshaw has pointed out the estimations carried out by Anderson, according to which carbon isotope exchange does not exceed 2–3% during 10^7 years at a temperature below 50°C. In another work, Rye and O'Neil (1968) reported values of ^{13}C corresponding to liquid inclusions of carbonates in calcites, the age of which was estimated to be $n \times 10^7$ years. It has been shown that the value of $\delta^{13}C$ is greater than that of carbon isotope exchange at temperatures $> 50°C$ is small.

Processes of carbon isotope exchange most likely play a decisive role in hydrothermal systems and during the precipitation of the fine-grained calcium carbonate from the solution resulting from the change of the groundwaters' chemical composition, for example, during the alcalinization of gypsum. Thus, while studying thermal waters in the Neocomian deposits of the Rioni Depression (Caucasus), it was found (Polyakov et al. 1979), that the application of ^{14}C dating for local conditions cannot elucidate the ages because isotope exchange processes happen very quickly at high temperatures in the water-rock system. Here, the water circulation time at a number of sites in a hydrothermal system does not exceed 500 years. This water exchange time was obtained by hydrodynamic calculations and also by tritium and uranium isotope studies. But the ^{14}C content in these waters does not exceed 4–5% and the value of $\delta^{13}C \approx -2‰$. The total content of the carbonaceous components at different sites in the aquifer remains practically unchanged ($\sim$150 mg/l).

Isotope studies of groundwater dynamics in the Assel-Kljazmian aquifer (Upper Carbon) near Vladimir (Polyakov and Seletsky 1978) have shown that carbonate precipitation process occurring during the mixing of calcium-hydrocarbonate and calcium-sulphate waters result in considerable radiocarbon removal from solution. This is accounted for by the carbon isotope exchange processes in the fine-grained calcium carbonate precipitating from the liquid phase which is saturated with Ca^{2+} ions. According to the hydrodynamic and tritium data, the residence time of water in the studied aquifer does not exceed several hundred years. But the ^{14}C content decreases sharply from about 60% in the recharge region to 10% in the immersed part of the aquifer. The $\delta^{13}C$ value increases from -10 to $-2.5‰$, while the total content of carbonates decreases respectively from 300 to 80 mg/l.

Therefore, an account of the possible effect of carbon isotope exchange in the water-rock system upon the ^{14}C decrease in groundwater under specific hydrological conditions should be carried out on the basis of detailed analyses of hydrogeochemical and isotope data. But at present no reliable method has been proposed which takes into account the correlation between ^{14}C content and isotope exchange in the water-rock system.

The decrease in the specific activity of the carbonates in water due to the admixing of 'connate' carbonates to the sedimentary rocks can be estimated both by the increases of the total carbon concentration in the studied groundwaters compared with the waters in the recharge zone and on the basis of the stable carbon isotope studied in the soil carbon dioxide in the carbonate system of groundwaters and water-bearing rocks. In general, if the concentration of the carbonaceous complexes is equal to C_{initial} in the recharge zone, then the correction factor K accounting for changes in the radiocarbon concentration caused by dilution can be estimated by the ratio $C_{\text{sample}}/C_{\text{initial}}$. Since under real conditions the initial radiocarbon concentration can be always estimated, with some error, it was assumed (Tamers 1967, 1969; Tamers and Scharpenseel 1970) that in any carbonate system of groundwaters in agreement with Eq. (14.24) the amount of radoicarbon is equal to only half of the hydrocarbonate ion. According to Tammers the process of radiocarbon concentration change can be described by the equation

$$pA_{\text{initial}} + (1-p)A_{\text{CaCO}_3} = A_{\text{sample}}e^{-\lambda t}, \tag{14.32}$$

where P is the fraction of the dissolved carbonate arriving from the soil air; A_{initial} is the relative radiocarbon amount in the carbonaceous system, formed due to dissolution of the biogenic carbon dioxide (the latter is taken for 100%); A_{CaCO_3} is the relative radiocarbon amount, released in water due to the dissolution of the calcite (is accepted as 0%); A_{sample} is the relative radiocarbon amount in an altered sample.

From Eq. (14.32), it follows that half of the hydrocarbonate originates from $CaCO_3$. Then

$$p = \frac{[C_{\text{total}}] - \frac{1}{2}[C_{\text{HCO}_3^-}]}{[C_{\text{total}}]}, \tag{14.33}$$

where $|C_{\text{total}}|$ is the total carbon concentration in the water specimen; $|C_{\text{HCO}_3^-}|$ is the hydrocarbonate ion concentration.

From Eq. (14.32), and on account of relationship (14.33), one can estimate the age:

$$t = 8033 \left\{ \ln\left(\frac{A_{\text{initial}}}{A_{\text{sample}}}\right) + \ln\frac{[\mathrm{C}_{\text{total}}] - \frac{1}{2}\left[\mathrm{C}_{\mathrm{HCO}_3^-}\right]}{[\mathrm{C}_{\text{total}}]} \right\}. \tag{14.34}$$

It follows from Eq. 14.34 that the correction factor by which one should multiply the value of the experimentally determined radiocarbon content in a sample A_{sample} or divide by the value A_{initial} (accepted as 100%), is

$$K = \frac{[C_{\text{total}}]}{[C_{\text{total}}] - 1/2[\mathrm{HCO}_3^-]}. \tag{14.35}$$

It should be pointed out that Tamers' approach is not well grounded from the viewpoint of the carbonate components' geochemistry. It is known (Garrels and Christ 1965; Sokolov 1974) that the carbonate system consists mainly of three components: undissociated molecules of carbonic acid H_2CO_3, hydrocarbonate ions HCO_3^{2-}, and anions of carbonic acid CO_3^{2-}. The forms of weak carbonic acid ate the pH-determining components for a great many types of groundwaters. In turn, the concentration of each of the forms depends on the pH and the ionic strength of a solution. At pH = 6.0 the fraction H_2CO_3 is equal to 69% and that of HCO_3 is 31%. At pH = 7.0, they are equal to 18 and 82%; at pH = 8.0, they are equal to 2 and 98%. Therefore, the chemical correction factor, calculated from Eq. 14.35, depends on the pH and the ionic strength of a solution and for a great many natural waters (at $\mathrm{pH} \geq 7$) is close to 2.

A somewhat different approach for the estimation of corrections, based on the use of stable isotopes, has been suggested by Pearson, Ingerson, and Hanshaw (Ingerson and Pearson 1964; Pearson 1965; Pearson and Hanshaw 1970; Pearson and White 1967). The specimen radioactivity is introduced by the formula

$$A_{\text{sample}} = \frac{\sum\limits_{i=1}^{n} m_i A_{0i}}{\sum\limits_{i=1}^{n} m_i} e^{-\lambda t}, \tag{14.36}$$

where A_{0i} is the initial radioactivity of the ith component; m_i is the mass of the component.

Usually, radioactivity is introduced by one source with mass m_{initial} and radioactivity A_{initial}. Then

$$\frac{A_{\text{sample}}}{A_{\text{initial}}} = \frac{m_{\text{initial}}}{\sum\limits_{i=1}^{n} m_i} e^{-\lambda t}. \tag{14.37}$$

The concentrations of $CaCO_3$ in water after the dissolution of carbonate-bearing minerals, in simple schemes of carbonate generation, are related to the value of $\delta^{13}C$ by the expression

$$\frac{m_{\text{initial}}}{\sum_{i=1}^{n} m_i} = \frac{\left(\delta^{13}C_i - \delta^{13}C_{\text{CaCO}_3}\right)}{\left(\delta^{13}C_{\text{initial}} - \delta^{13}C_{\text{CaCO}_3}\right)}, \tag{14.38}$$

where ${}^{13}C_{\text{initial}}$ is the isotopic composition of the soil CO_2; $\delta^{13}C_{\text{CaCO}_3}$ is the isotope composition of the calcium carbonate.

From Eq. 14.37, it is observed that the radiocarbon activity of a water sample is inversely proportional to the content of the dissolved carbon in water. The possibility of the introduction of the correction for measured radiocarbon content in a specimen with the use of data on the isotope composition of stable carbon is observed from Eq. 14.38:

$$t = 8033\left[\ln\left(\frac{A_{\text{initial}}}{A_{\text{sample}}}\right) + \ln\left(\frac{\delta^{13}C_{\text{sample}} - \delta^{13}C_{\text{CaCO}_3}}{\delta^{13}C_{\text{CO}_3} - \delta^{13}C_{\text{CaCO}_3}}\right)\right], \tag{14.39}$$

where A_{initial} is the relative ${}^{14}C$ content of the soil carbon dioxide; A_{sample} is the measured ${}^{14}C$ content in a specimen; $\delta^{13}C_{\text{sample}}$, $\delta^{13}C_{\text{CaCO}_3}$ are relative content of ${}^{13}C$ isotopes in a sample and carbonate rocks.

Assuming that $A_{\text{initial}} = 100\%$, $\delta^{13}C_{\text{CaCO}_3} \approx 0‰$, and $\delta^{13}CO_2 = -25‰$ for zones covered with plants having a Calvin photosynthetic cycle, Eq. 14.39 can be simplified:

$$t = 8033\left[\ln\left(\frac{100}{A_{\text{sample}}}\right) + \ln\left(\frac{\delta^{13}C_{\text{sample}}}{-25}\right)\right]. \tag{14.40}$$

It is observed from Eq. 14.40 that the correction factor by which the measured value of ${}^{14}C$ in a sample should be multiplied as in this case $K = (-25/\delta^{13}C_{\text{sample}})$ or in a more general case:

$$K = \frac{\delta^{13}CO_2 - \delta^{13}C_{\text{CaCO}_3}}{\delta^{13}C_{\text{Sample}} - \delta^{13}C_{\text{CaCO}_3}}. \tag{14.41}$$

As shown earlier, in the case of open systems (unsaturated zone), where the formation of the initial radiocarbon concentration occurs, the $\delta^{13}C = -15‰$ and the ${}^{14}C$ content ranges over 85 ± 5% according to numerous experimental data for dissolved carbonates. Using these data, the correction of the measured ${}^{14}C$ content (85%) in a sample, estimated by Eq. 14.41, gives values which are considerably greater than 100%. This fact indicates that more complicated models of the formation of the isotopic composition of the carbonate system should be used, accounting for chemical and exchange reactions occurring in the open and closed hydrogeological systems.

More general models, accounting for the effect of both dissolution of the solid carbonates and exchange in the carbon dioxide dissolved carbonates system, developed for the interpretation of radiocarbon data, are considered by a number of researchers (Fontes and Garnier 1977; Mook 1976; Wigley 1976; Wigley et al. 1978; Wendt et al. 1967; Pearson and White 1967).

Mook has studied three stages of the formation of carbon in the carbonate complex of groundwater. The first stage is the dissolution of soil carbonates while interacting with soil CO_2. The second stage represents isotopic exchange between the hydrocarbonate ion and the gaseous carbon dioxide in the unsaturated zone. The last stage corresponds to the attainment of isotope equilibrium between the dissolved carbon dioxide and hydrocarbonate ion under conditions of chemical equilibrium between the carbonate system components in the groundwaters. The initial ^{14}C concentration (as a percentage of the modern carbon activity), at the suggested formation of the groundwaters' isotope composition, is described by the Eq. 14.42, which uses Mook's notation:

$$A_\Sigma = \frac{1}{\Sigma}\left\{(\Sigma - b)A_{a_0} + 0.5b\left(A_{a_0} + A_1\right) + \left[A_{g_0}\left(1 - 2\frac{\varepsilon_g}{10^3}\right) - 0.5a\left(A_{a_0} + A_1\right)\right]\right.$$
$$\left. \times \left[\frac{\Sigma\delta_\Sigma - a\delta_{a_0} - 0.5b\left(\delta_{a_0} - \delta_1\right)}{\delta_{g_0} - \varepsilon_g\left(1 - \delta_{g_a}/10^3\right) - 0.5a\left(\delta_{a_0} - \delta_1\right)}\right]\right\}, \tag{14.42}$$

where A_Σ, δ_Σ are the general ^{14}C activity (in percent of the modern carbon) and $\delta^{13}C$ (in permil) in the dissolved carbonate dioxide and hydrocarbonate in the aquifer; a, b are the molal concentrations of the total dissolved carbon dioxide and hydrocarbonate; Σ is the molal concentrations of the total dissolved carbon $\left[H_2CO_3 + CO_3^{2-} + HCO_3^-\right]$; A_{a_0}, δ_{a_0} are the ^{14}C (in percent of the modern carbon) and $\delta^{13}C$ (in permil) of the dissolved soil carbon dioxide; A_{g_0}, δ_{g_0} are the ^{14}C activity (in percent of the modern carbon) and $\delta^{13}C$ (in permil) of the soil carbon dioxide; A_1, δ_1 are ^{14}C activity (in percent of the modern carbon) and $\delta^{13}C$ (in permil) of the soil carbonates; ε_g is the difference between $\delta^{13}C$ (in permil) in the gaseous CO_2 and $\delta^{13}C_{HCO_3^-}$ in the dissolved HCO_3^-: $\delta^{13}C_{CO_3^-} - \delta^{13}C_{HCO_3^-}$.

The dependence of the factor ε_g on temperature can be obtained from the below data calculated by Mook (1976):

t(°C)	0	5	10	15	20	25	30
ε_g(‰)	−10.83	−10.20	−9.60	−9.02	−8.46	−7.92	−7.39

The value of A_1 can be set by calculation:

$$A_1 \approx \left(A_{a_0} + 0.2\varepsilon_k\right)\frac{\delta_1 - \delta_{10}}{\delta_{a_0} + \varepsilon_k - \delta_{10}}, \tag{14.43}$$

where δ_{10} is $\delta^{13}C$ (‰) of carbonates of sea genesis is equal to about 0‰; ε_k accounts for the effect of isotope fractionation between solid calcium carbonate and dissolved CO_2, equal to $\delta^{13}C_{CaCO_3} - \delta^{13}C_{CO_2(solution)}$.

It should be pointed out that in Eqs. 14.42 and 14.43, $A_{a_0} \approx A_{g_0} \approx 100\%$ and ε_k is practically independent of temperature and is equal to about +10‰. The values of a/Σ and b/Σ can be obtained by the precise measurement of pH = −ln a_H (a_H is the activity of H^+ in solution):

Table 14.7 Comparison of groundwater ages determined by different methods. (From Mook 1976)

Sampling location	Groundwater age (years)						
	pH	δ_Σ	A_m	Vogel 1970	Pearson 1965	Tamers 1967	Mook 1976
Ezulwini	8.6	−13.6	47.6	4,800	1,100	460	2,370
Lomamba 2	7.9	−14.5	43.6	5,540	2,370	1,390	4,180

Table 14.8 Experimental and calculated values of groundwater parameters. (From Mook 1976)

Sample number	δ_{a_0}	pH	δ_Σ	A_m (%)	$A_\sum$ (%)
16	−15.0	7.3	−8.4	53.3	50.4
	−15.1				53.3
17	−15.0	7.4	−7.4	54.7	95.2
	−13.6				54.2
40	−15.0	8.2	−6.2	54.0	126.9
	−12.5				54.1

$$\begin{aligned} a/\Sigma &= a_H^2/\left(a_H^2 + a_H k_1' + k_1' k_2'\right) \\ b/\Sigma &= a_H k_1'/\left(a_H^2 + a_H k_1' + k_1' k_2'\right), \end{aligned} \tag{14.44}$$

where k_1' and k_2' are the first and second dissociation constants of the carbonic acid.

On the basis of Mazor's experimental data (Mazor et al. 1974b), Mook (1976) has compared groundwater age estimated by Pearson's formula (Eq. 14.39), Tammers's (Eq. 14.34), Fogel's ($A_\Sigma = 85\%$), and his own expression (Eq. 14.42). These data are presented in Table 14.7.

Here the water age by Mook is estimated with the use of a typical exponential formula (piston flow model)

$$t = \frac{T_{1/2}}{0.93} \ln \frac{A_\Sigma}{A_m},$$

where A_m is the measured ^{14}C content in a sample as a percentage of the modern carbon; A_Σ is the value obtained from Eq. (14.42), assuming that: $A_{a_0} = 100\%$, $\delta_{a_0} = -25‰$, $\delta_{10} = \delta_1 = 0‰$.

It follows from the data shown in the table that all four methods give different water ages. Mook considers his technique to be the best, since it accounts for the highest number of factors affecting the formation of the carbon isotope composition of groundwaters.

It should be pointed out that Eq. 14.42 is such that A_Σ depends greatly upon the values of δ_{a_0} and δ_Σ which follows from the data presented in Table 14.8, reported by Mook, who cited the experimental data of Gonfiantini et al. (1974).

As a rule the value of δ_{a_0} cannot be accurately determined on a regional scale, being dependent on the geochemistry of the landscape and the physicochemical conditions of the soil layer. δ_{a_0} also undergoes seasonal and long-term variations (for example, during the climatic changes in Holocene). All these circumstances result

Table 14.9 The groundwater ages from Lincolnshire limestones, United Kingdom. (Evans et al. 1979)

Sampling location	A_{sample} (%)	$\delta^{13}C_{\text{sample}}$ (‰)	Percent of modern carbon or the age
Tallington	45.9	−11.7	90.2%
Kates Bridge	60.0	−12.6	109%
Baston Fen, 1	1.9	−2.8	15,200 years
Baston Fen, 2	2.6	−2.8	12,600 years
Six Score Farm	0.4	−2.2	26,000 years
Tongue End Farm	1.1	−2.0	16,800 years
Cuckoo Bridge, 1	2.4	−1.8	9,500 years
Cuckoo Bridge, 2	2.2	−1.8	10,000 years

in considerable uncertainty regarding the determination of parameter A_Σ, estimated from Eq. 14.42.

Wigley (1976) has made an attempt to account for the effect of $CaCO_3$ precipitation from the solution upon the carbon isotope composition of the carbonate system of groundwaters. Wigley's model has been used by Evans et al. (1979) for the interpretation of data on the radiocarbon dating of groundwaters of some aquifers in England. In agreement with this model, the age can be found by the Eq. 14.45 as

$$t = \frac{T_{1/2}}{\ln 2} \ln \frac{50}{A_{\text{sample}}} \left[\frac{k - \delta^{13}C_{\text{sample}}}{k - \delta^{13}C_{\text{initial}}} \right]^{(1+\varepsilon_{13}/1000)}, \tag{14.45}$$

where the value of $T_{1/2}/\ln 2 = 8{,}267$ (accepted by Evans); A_{sample} is the measured ^{14}C activity in a sample (as a percentage of the modern carbon content); $\delta^{13}C_{\text{initial}}$ is the relative ^{13}C content in the carbonate system at the initial stage of dissolution of the soil carbonates; $\varepsilon_{13} = \delta^{13}C_{\text{rock}} - \delta^{13}C_{\text{solution}}$; $k = \delta^{13}C_{\text{rock}} - \varepsilon_{13}$.

An example of groundwater age calculation by Eq. 14.45 is presented in Table 14.9, taken from the study of Evans et al. (1979).

While calculating the data in Table 14.9, it has been accepted that $\varepsilon_{13} = +24‰$; $\delta^{13}C_{\text{rock}} = +2.35‰$; $\delta^{13}C_{\text{initial}} = -11.5‰$.

It should be pointed out that Wigley's model, as used by Evans, is not quite correct, since it only accounts for the equilibrium carbon isotope distribution between the liquid and soil phases in the one-stage process. In real conditions, the processes of $CaCO_3$ precipitation are permanent (of the fractional crystallization type). In this case, the isotope fractionation factor should be multiplied by the coefficient n (n is the number of theoretical plates), which cannot be determined precisely in the case of real aquifers. In particular, according to the data obtained by Evans (Evans et al. 1979), the isotopic composition of modern and ancient water is identical. For the modern waters in England, $\delta D = -52‰$, $\delta^{18}O = -8.3‰$. For waters 29,000 years old, these values are practically the same ($\delta D = -52‰$, $\delta^{18}O = -8.5‰$), although the formation of groundwaters in the last case should have occurred during the Pleistocene under much cooler climatic conditions than those typical for Europe today.

Fontes and Garnier (1979) have suggested carrying out an interpretation of radiocarbon data based on the chemical and isotope balance of the components of the carbonate system of groundwaters. According to their model, the initial concentration A_{initial}, being used for the age estimation, can be calculated by the equation:

$$A_{\text{i}} = \left(1 - \frac{\text{C}_{\text{rc}}}{\text{C}_{\Sigma}}\right) A_{\text{s}} + \frac{\text{C}_{\text{rc}}}{\text{C}_{\Sigma}} A_{\text{rc}} + (A_{\text{s}} + 0.2\varepsilon - A_{\text{rc}}) \\ \times \frac{\delta_{\Sigma} - (\text{C}_{\text{rc}}/\text{C}_{\Sigma})\,\delta_{\text{rc}} - [1 - (\text{C}_{\text{rc}}/\text{C}_{\Sigma})]\,\delta_{\text{s}}}{\delta_{\text{s}} + \varepsilon - \delta_{\text{rc}}}, \tag{14.46}$$

where A_{s} and A_{rc} are ^{14}C concentrations in soil carbon dioxide and in carbonate rocks C_{rc} and C_{Σ} are carbon concentrations from the dissolution of the carbonate rocks and the total concentration of carbonate; δ_{s}, δ_{rc}, δ_{Σ} are $\delta\,^{13}$C values (in ‰) of the biogenic carbon dioxide, carbonate rocks, and samples; $\varepsilon = (\delta^{13}\text{C}_{\text{CaCO}_3} - \delta^{13}\text{C}_{\text{soil}})$‰.

It is easy to show that this model supplements the results of Tammers on changes in the initial ^{14}C activity due to dissolution of the 'dead' carbonate components of rocks but accounting for the carbon isotopic fractionation in the gaseous phase-solution system. The term K can be written as

$$K = (A_{\text{s}} + 0.2\varepsilon - A_{\text{rc}}) \times \frac{\delta_{\Sigma} - (\text{C}_{\text{rc}}/\text{C}_{\Sigma})\delta_{\text{rc}} - [1 - (\text{C}_{\text{rc}}/\text{C}_{\Sigma})]\delta_{\text{s}}}{\delta_{\text{s}} + \varepsilon - \delta_{\text{rc}}}.$$

According to Fontes and Garnier, the concentration of C_{rc} can be calculated, using the experimental data, by equation

$$\text{mC}_{\text{rc}} = \text{mCa}^{2+} + \text{mMg}^{2+} + 1/2(\text{mNa}^{+} + \text{mK}^{+} - \text{mCl}^{+} - \text{mNO}_3^{-}) - \text{mSO}_4^{2-}. \tag{14.47}$$

Wigley et al. (Wigley 1976; Wigley et al. 1978) have proposed the model which accounts for the highest number of factors affecting the carbon isotope composition of the carbonate system. The authors distinguish the following three stages in the formation of the carbonate system: the processes of interaction in the unsaturated zone; congruent dissolution in the unsaturated zone; incongruent reactions occurring in the saturated zone. The carbon isotope composition at each stage of formation of the system can be calculated by the corresponding equations. This system of equations permits the determination of carbon radioactive decay. It is assumed that in the first stage of formation of the system, the carbon isotope composition changes by the equilibrium isotopic exchange process between soil gas and soil solutions under open conditions relative to the CO_2 system. At this stage, the ^{14}C activity and δ^{13}C can be estimated on the basis of the equilibrium isotope fractionation theory. The degree of carbon isotope fractionation between the solution and carbon dioxide gas at this stage is determined by the relative amount of the dissolved carbon-bearing components. The isotope composition of the dissolved carbon (A_1 for ^{14}C and δ^{13}C for ^{13}C) at the end of the first stage is determined completely by the isotope composition of the CO_2 and the pH of the soil solution.

At the second stage, congruent (without change of the isotopic composition) dissolution of soil carbonates occurs under closed conditions relative to the CO_2 system. The change of the isotopic composition in this case can be estimated by Eq. 14.39 proposed by Ingerson and Pearson (1964).

At the third stage, the processes occur under conditions of a closed system by an incongruent mechanism, that is, with the involvement of carbonate isotope fractionation effects. At the end of the third stage, the ^{14}C radioactivity (as a percentage of the modern carbon), neglecting radioactive decay (A_{nd}), can be described by the equation

$$A_{nd} = A_1 x_2 x_3, \tag{14.48}$$

where A_1 is the ^{14}C radioactivity (as a percentage of the modern carbon) at the end of the first stage; $\mathrm{x}_2 = \mathrm{mC}_1/\mathrm{mC}_2$ is the fraction of the molal concentrations of the inorganic carbon in the system at the end of the first and second stage;

$$\mathrm{x}_3 = (\mathrm{mC}/\mathrm{mC}_2)^{\beta\Gamma/(1-\Gamma)},$$

where mC is the molal general inorganic carbon concentration at the end of the third stage; β and Γ are constants related to the change of carbon content in a system and the carbon isotope fractionation between precipitation and solution; $\beta = 1+\varepsilon_{\mathrm{ps}}/1{,}000\Gamma$.

The carbon isotope composition after the second stage will be determined as follows:

$$\delta^{13}\mathrm{C}_2 = \delta^{13}\mathrm{C}_\mathrm{S} + x_2(\delta^{13}\mathrm{C}_1 - \delta^{13}\mathrm{C}_\mathrm{s}), \tag{14.49}$$

where $\delta^{13}\mathrm{C}_\mathrm{s}$ and $\delta^{13}\mathrm{C}_1$ are the carbon isotope composition of the solid $\mathrm{CaCO_3}$ and soluted carbon at the end of the first stage.

At the end of the third stage, we have

$$\beta\delta^{13}\mathrm{C}_{\mathrm{sample}} = \delta^{13}\mathrm{C}_\mathrm{s} - \frac{\varepsilon_{\mathrm{ps}}}{\Gamma} + \chi_3\left(\beta\delta^{13}\mathrm{C}_2 - \delta^{13}\mathrm{C}_\mathrm{s} + \frac{\varepsilon_{\mathrm{ps}}}{\Gamma}\right), \tag{14.50}$$

where $\varepsilon_{\mathrm{ps}} = \delta^{13}\mathrm{C}_{\mathrm{precipitation}} - \delta^{13}\mathrm{C}_{\mathrm{solution}}$.

Taking into account Eqs. 14.48–14.50, one obtains

$$A_{\mathrm{nd}} = A_1\left(\frac{\delta^{13}C_2 - \delta^{13}C_s}{\delta^{13}C_1 - \delta^{13}C_s}\right)\left(\frac{\beta\delta^{13}C - \delta^{13}C_\mathrm{s} + \varepsilon_{\mathrm{ps}}/\Gamma}{\beta\delta^{13}C_2 - \delta^{13}C_\mathrm{s} + \varepsilon_{\mathrm{ps}}/\Gamma}\right). \tag{14.51}$$

Putting A_{nd} into exponential form $t = (1/\lambda)\ln(A_{\mathrm{nd}}/A)$ and assuming that $A_1 = 100\%$, one obtains the following expression for age estimations:

$$t = 19035\left\{\lg\left(\frac{100}{A_s}\right) + \lg\left(\frac{\delta^{13}\mathrm{C}_2 - \delta^{13}\mathrm{C}_s}{\delta^{13}\mathrm{C}_1 - \delta^{13}\mathrm{C}_s}\right)\left(\frac{\beta\delta^{13}\mathrm{C}_s - \delta^{13}\mathrm{C}_s + \varepsilon_{\mathrm{ps}}/\Gamma}{\beta\delta^{13}\mathrm{C}_2 - \delta^{13}\mathrm{C}_s + \varepsilon_{\mathrm{ps}}/\Gamma}\right)\right\}. \tag{14.52}$$

where A_s and $\delta^{13}\mathrm{C}_\mathrm{s}$ are ^{14}C activities (in percentage of the modern carbon) and $\delta^{13}\mathrm{C}_\mathrm{s}$ values (in ‰) in a sample.

Equation 14.52, being too complicated in practice, can be simplified, assuming that $\delta^{13}\mathrm{C}_\mathrm{s} = 0$ and $\delta^{13}\mathrm{C}_1 = \delta^{13}\mathrm{C}_{\mathrm{CO_2}} + 4.5$ (the isotope fractionation effect of carbon

Table 14.10 Age correction accounting for incongruent dissolution (t_3) and error in the t_3 value when the error of δ^{13}C determination is equal to 0.2% (δt_3)

δ^{13}C, ‰	−10	−7	−5	−4	−3
t, πeT	−600	−1,900	−4,000	−6,300	−13,000
Δt_3, πeT	60	130	330	690	2,800

in the soil carbon dioxide components system at pH = 6.5). For the plant system fixing carbon dioxide according to Calvin cycle (C_3), we have $\delta^{13}C_{CO_2} = -25‰$, and for the Hatch-Slack cycle (C-4) we have $\delta^{13}C_{CO_2} = -13‰$. The account of the carbon isotopic exchange in the first stage (the open system) results in the difference between the age estimated by Eq. (14.52) and by the Ingerson-Pearson equation (Eq. 14.39), where carbon isotopic fractionation during dissolution of carbon dioxide has been neglected. These differences are 1,600 years and ~3,500 years for ecosystems with C_3 and C_4 plant cycles respectively. Assuming that $\delta^{13}C_s = 0$, $\delta^{13}C_{CO_2} \approx -13‰$, which is characteristic for groundwaters at the second stage in ecosystems with C_3 plant cycle, $\Gamma = 1$, $\beta \to 1$, one can obtain some difference between the age obtained by Eq. 14.39, which takes into account dissolution of the carbonates in the closed system only, and that obtained by Eq. 14.52, accounting isotopic fractionation at noncongruent dissolution. This difference is shown in Table 14.10.

A convenient practical method of introducing corrections on the basis of data on stable and radioactive carbon isotope distribution has been suggested (Karasev 1979; Polyakov and Karasev 1979; Polyakov and Seletsky 1978) as follows.

If the increase in the content of carbonates in water occurs at conditions of underground circulation due to the congruent dissolution of the carbonate rocks of a collector, then by normalizing the total content of carbonate components in water, a simple equation can be written (Ingerson and Pearson 1964; Pearson and Hanshaw 1970):

$$\mathrm{p}\delta^{13}\mathrm{C}_{\mathrm{sc}} + (1-\mathrm{p})\delta^{13}\mathrm{C}_{\mathrm{rc}} = \delta^{13}\mathrm{C}_{\mathrm{wc}}, \tag{14.53}$$

where $\delta^{13}C_{sc}$, $\delta^{13}C_{rc}$, $\delta^{13}C_{wc}$ are the relative ^{13}C contents in the soil carbon dioxide, carbonates of the water-bearing rocks, and in the water carbonate system.

From Eq. 14.53, it is observed that the fraction of the initial soil carbon dioxide, with which practically all the radiocarbon is bound, is equal to

$$p = \frac{\delta^{13}\mathrm{C}_{\mathrm{wc}} - \delta^{13}\mathrm{C}_{\mathrm{rc}}}{\delta^{13}\mathrm{C}_{\mathrm{sc}} - \delta^{13}\mathrm{C}_{\mathrm{rc}}} \tag{14.54}$$

Assuming that the case of limestones of sea origin $\delta^{13}C_{rc} = 0$, the Eq. 14.54 becomes:

$$p = \frac{\delta^{13}\mathrm{C}_{\mathrm{wc}}}{\delta^{13}\mathrm{C}_{\mathrm{sc}}}. \tag{14.55}$$

Similarly, the Eq. 14.53 can be written for radiocarbon, assuming that the effect of radioactive decay is negligible:

$$\mathrm{P}A_{\mathrm{sc}} + (1-\mathrm{p})A_{\mathrm{rc}} = A_{\mathrm{wc}}, \tag{14.56}$$

where A_{sc}, A_{rc}, A_{wc} are the activities of the radiocarbon isotope in the soil carbon dioxide, soil carbonates and carbonate system of the studied waters.

From Eq. 14.56, it is observed that

$$p = \frac{A_{\mathrm{wc}} - A_{\mathrm{rc}}}{A_{\mathrm{sc}} - A_{\mathrm{rc}}}. \tag{14.57}$$

At $A_{\mathrm{rc}} \to 0$, which is the case for carbonaceous water-bearing

$$p = \frac{A_{\mathrm{wc}}}{A_{\mathrm{sc}}}. \tag{14.58}$$

Equating the Eqs. 14.55 and 14.58, one obtains

$$\frac{\delta^{13}\mathrm{C}_{\mathrm{wc}}}{\delta^{13}\mathrm{C}_{\mathrm{sc}}} = \frac{A_{\mathrm{wc}}}{A_{\mathrm{sc}}}. \tag{14.59}$$

Hence it follows that

$$A_{\mathrm{wc}} = A_{\mathrm{sc}} \frac{\delta^{13}\mathrm{C}_{\mathrm{wc}}}{\delta^{13}\mathrm{C}_{\mathrm{sc}}}. \tag{14.60}$$

Assuming that $A_{\mathrm{sc}} = 100\%$, $\delta^{13}\mathrm{C}_{\mathrm{sc}} \approx -25‰$, Eq. 14.60 can be simplified to

$$A_{\mathrm{wc}} = -4\delta^{13}\mathrm{C}_{\mathrm{wc}}. \tag{14.61}$$

For the above assumptions, the Eq. 14.61 represents a straight line passing through the origin and the point with coordinates $\delta^{13}\mathrm{C}_{\mathrm{sc}} = -25‰$ and $A_{\mathrm{sc}} = 100\%$.

In a similar manner, assuming that the initial radiocarbon activity $A_{\mathrm{initial}} = 85\%$ and the isotope composition of the carbonate system in the recharge region $\delta^{13}\mathrm{C}_{\mathrm{initial}} = 15\%$, one can derive a second equation relating radiocarbon content in a studied sample A_{wc} to the $\delta^{13}\mathrm{C}_{\mathrm{wc}}$ isotope composition of carbon:

$$A_{\mathrm{wc}} = -5.7\delta^{13}\mathrm{C}_{\mathrm{wc}}. \tag{14.62}$$

The straight line described by the equation is plotted in Fig. 14.23 (curve II).

If the values of $\delta^{13}\mathrm{C}$ and A_{c} in Eqs. 14.54 and 14.57 are not equal to zero, we obtain a more general form for dependency of A_{wc} from $\delta^{13}\mathrm{C}_{\mathrm{wc}}$:

$$A_{\mathrm{wc}} = \mathrm{a} + \mathrm{b}\delta^{13}\mathrm{C}_{\mathrm{wc}}, \tag{14.63}$$

where

$$\mathrm{a} = A_{\mathrm{rc}} - \frac{(A_{\mathrm{sc}} - A_{\mathrm{rc}})\delta^{13}C_{\mathrm{rc}}}{(\delta^{13}\mathrm{C}_{\mathrm{sc}} - \delta^{13}\mathrm{C}_{\mathrm{rc}})},$$

and

$$\mathrm{b} = \frac{A_{\mathrm{sc}} - A_{\mathrm{rc}}}{\delta^{13}\mathrm{C}_{\mathrm{sc}} - \delta^{13}\mathrm{C}_{\mathrm{rc}}}.$$

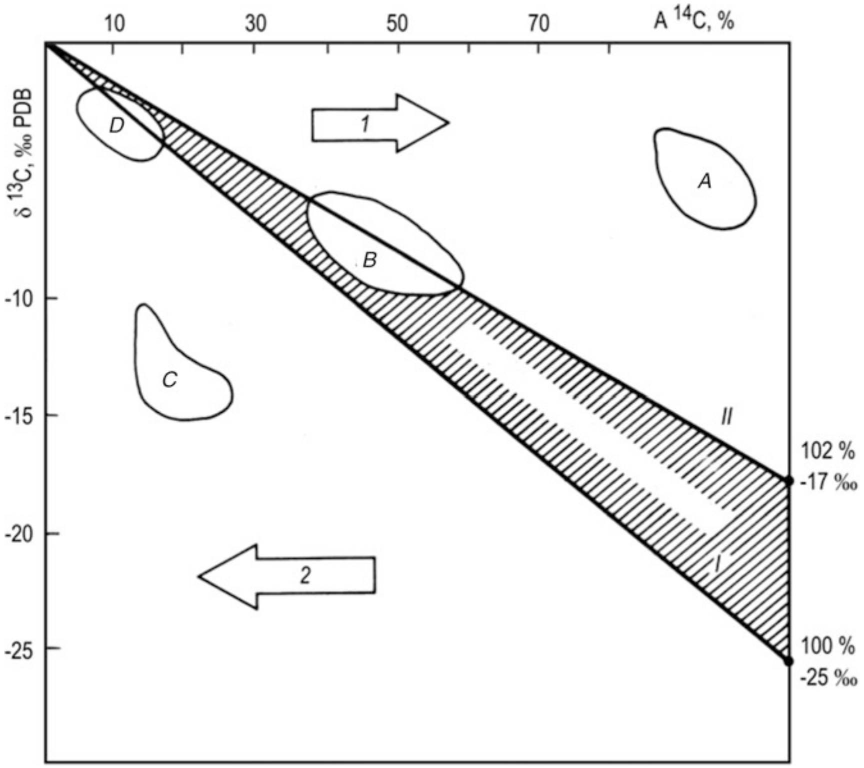


Fig. 14.23 Relationship between parameters ^{14}C (% of the modern carbon content) and δ^{13}C of carbonate system of water: (*I, II*) modern waters ^{14}C of which has decreased due to 'dead' carbon entering ($\delta^{13}C = 0$); (*A*) water from the North Kasakhstan lakes; (*B*) groundwaters from Riony depression; (*C*) thermal waters of Neocomian aquifer of Riony depression; (*D*) groundwaters from Paleozoic aquifer, North Kasakhstan; (*1*) region of post-thermonuclear epoch, or region of 'heavy' carbon entering; (*2*) region of water age determined by Eq. 14.64)

It is difficult to apply Eq. 14.63 to real conditions since the value $A_{\mathrm{rc}}, A_{\mathrm{sc}}$, and $\delta^{13}C_{\mathrm{sc}}$ cannot be determined experimentally. This follows both from the spatial variability of geological structures of the recharge regions and transition zones, and from the fact that the climatic conditions at the time when water passed from the recharge zone to the aquifer could have been considerably different from those of today.

The Eqs. 14.61–14.63 describe the changes in the radiocarbon activity of the carbonate system of 'young' waters due to the process of normal dissolution of the carbonate water-bearing rocks. At such an approach, the age estimation is determined by formula;

$$T = 8033\ln(A_{\mathrm{wc}}/A_{\mathrm{sc}} = 8033)\ln\left(-5.7\delta^{13}C_{\mathrm{wc}}/A_{\mathrm{sc}}\right), \qquad (14.64)$$

where A_{wc} and $\delta^{13}C_{sc}$ are the measured ^{14}C activity in a sample and isotopic composition of carbon in a carbonate system. The term 5.7 accounts conformity between the % and ‰ dimensions.

Curve II in Fig. 14.23 passes through the point with coordinates A = 102% and $\delta^{13}C = -17$‰, being close to the equilibrium state of carbon isotope exchange in the gas-fluid system at fractionation factors ^{13}C and ^{14}C equal to 1.0070 and 1.016, and the isotopic composition of modern soil carbon dioxide characterized by the $\delta^{13}C_{sc} = -25$‰, $A^{14}C_{sc} = 100\%$ (relative to the modern standard). Such an assumption is fully justified for climatic zones where plants with a Calvin photosynthetic cycle exist. It is obvious that the plants lying near the correlation line will correspond to the 'young' waters, in which the decrease in the carbon specific activity is due to dilution with the old dissolved carbonates but not due to radioactive decay. The deviation of the experimental points to the left of the curve may indicate the arrival of ultramodern radiocarbon. The deviation of the points to the right of the curve may be indicative of ^{14}C radioactive decay and also the arrival of the carbon with light isotope content. A similar analysis of radiocarbon data has been used by Deak while studying groundwaters in Hungary (Deak 1979).

Figure 14.23 indicates points corresponding to ground and surface waters sampled in some regions of the former USSR. In those regions where Hatch-Slack plants are typical, the correlation line should pass through the point with the coordinates 102% and from −4 to −6‰, which reflects the isotope equilibrium between coil carbon dioxide ($A_{^{14}C} = 100\%$, $\delta^{13}C$ from −12 to −14‰) and the dissolved components.

The admixing of carbonates during groundwater circulation can be determined for a studied aquifer by the analysis of the dependence of the radiocarbon content upon the inverse value of the total content of dissolved carbonates. In fact, if the initial concentration of carbonates in water of the recharge zone is C_o and the total concentration becomes equal to C_{wc}. Then the initial fraction of the carbonates in groundwaters is:

$$p = \frac{C_0}{C_{wc}}, \tag{14.65}$$

Equating the Eqs. 14.65 and 14.57, one obtains

$$\frac{C_0}{C_{wc}} = \frac{A_{wc} - A_{rc}}{A_{sc} - A_{rc}}, \tag{14.66}$$

hence it follows that

$$A_{wc} = A_{rc} + \frac{C_0(A_0 - A_{rc})}{C_{wc}}. \tag{14.67}$$

As pointed out earlier, if the water receives carbonates from ancient sedimentary limestones, then the term A_{rc} in Eq. 14.67 can be ignored. In the last case, Eq. 14.67 becomes similar and describes the linear dependency of A_{rc} on $1/C_{wc}$ since it is accepted that, for waters of the same age, A_o and C_o are constants. Pearson and Swarzenki (1974) have shown that, under real conditions occurring in some aquifers,

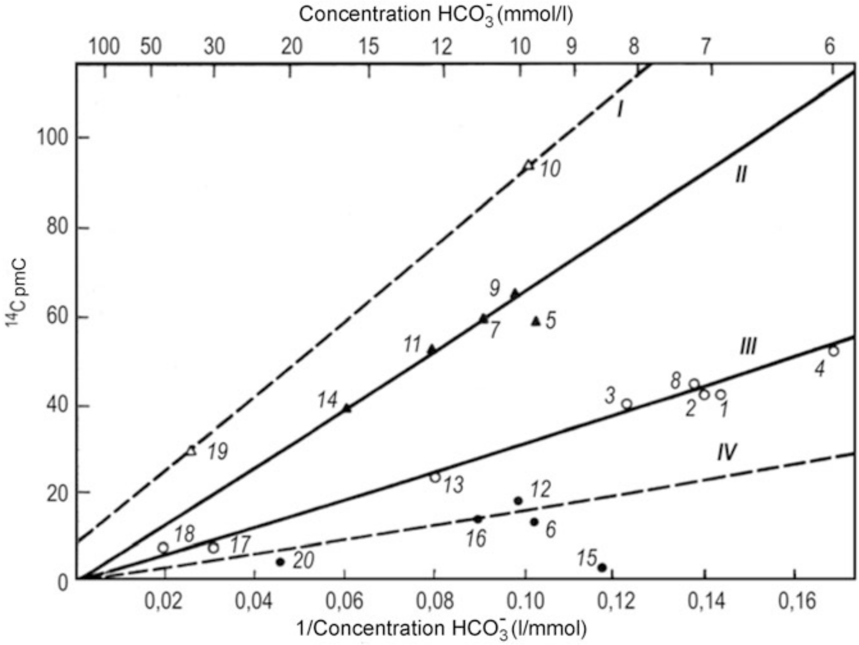


Fig. 14.24 Relationship between the determined ^{14}C content and the reverse value of carbonate component concentration in groundwaters for the Upper Quaternary rocks in the north-eastern province of Kenya. The figures show number of boreholes. (*I*) Modern waters; (*II*) age of water about 2,500 years; (*III*) ~8,000 years; (*IV*) ~14,100 years. (After Pearson and Swarzenki 1974. © IAEA, reproduced with permission of IAEA)

Eq. 14.67 can help to derive waters of the same age even with different radiocarbon specific activities (Fig. 14.24). A similar equation can be derived the dependency of $\delta^{13}C_{wc}$ on $1/C_{wc}$

$$\delta^{13}C_{wc} = \delta^{13}C_{rc} + \frac{C_0\left(\delta^{13}C_0 - \delta^{13}C_{rc}\right)}{\delta^{13}C_{wc}}. \tag{14.68}$$

It should be pointed out that Eqs. 14.67 and 14.68 describes the decrease of ^{14}C activity due to the congruent dilution of the initial carbonate components of groundwater by the dead carbonates of the water-bearing rocks.

Besides such processes as the dissolution of the dead carbonates (resulting in the decrease of the radiocarbon specific activity of the groundwater carbonate system)—and $CaCO_3$ precipitation and isotope exchange in the soil CO_2-hydrocarbonate and hydrocarbonate-rock systems—other processes affecting the reliability of radiocarbon (and tritium) groundwater dating were considered. These processes are:

a. the diffusive transfer of ^{14}C and T isotopes through impermeable thicknesses from one aquifer into another (Matthess et al. 1976; Klitzsch et al. 1976);
b. stratification of the ^{14}C and T concentrations through the aquifer's section and the effect of borehole construction—which facilitates taking the samples of water—upon the obtained radioisotope age (Vogel 1967; Matthess et al. 1976; Dubinchuk 1979; Banis and Yodkasis 1981);
c. differences in the motion rates of water (solvent) and soluted carbonate components containing radiocarbon along the aquifer (Tamers and Scharpenseel 1970; Thilo and Münnich 1970).

Klitzsch et al. (1976) have shown, on the basis of Matthess' estimations (Matthess et al. 1976), that with diffusion coefficient of carbonates through the clay impermeable layer thickness of 1.2×10^{-5} cm^2/sec, the transfer of radiocarbon from an aquifer with a ^{14}C concentration of about 85% (relative to the modern level) can result in decreases in the water age in the underlying aquifer from 40,000 to 18,000, 27,000, and 36,500 years at depth within the impermeable clay layer, lying between modern and ancient waters, of 30, 50 and 70 m, respectively. In the course of estimations, it has been assumed that the porosity of the aquifer containing ancient waters is equal to 0.3 and its thickness is 100 m.

Stratification of radiocarbon through a section of an aquifer in which recharge is distributed down its thickness results in errors in groundwater dating in the framework of the piston model since the samples taken from imperfect boreholes cannot be considered reliable (Dubinchuk 1978).

In Vogel's opinion (Vogel 1967), the water age down the section of an aquifer should vary with $\ln(H/h)$ (where H is the thickness of the aquifer and h is the distance from the base of its bed). Vogel's model is derived from simple geometrical constructions and, therefore, can be far from the conditions occurring in real hydrogeological systems. For example, at $h \to 0$ the water age, according to the above-mentioned model, tends to infinity independent of the aquifer's thickness, which is in disagreement with hydrodynamical calculations.

The ^{14}C radioisotope becomes incorporated in the dissolved component of the carbonate system of groundwaters. From common knowledge regarding sorption chromatography dynamics (Helfferich 1959; Rachinsky 1964), it is observed that the motion of water and solute at conditions of underground circulation occurs at different rates to those observed in the chromatography section. A similar phenomenon should take place during ^{14}C motion, especially in the course of groundwater migration through the carbonate collectors. The rate of a trace motion (v) is related to the rate of the solvent motion (u) by the equation $u = v\mathrm{R}$, where R is the retardation factor. If $\mathrm{R} > 1$, then the rate of the trace transfer (in our case it is ^{14}C) is in by R times less than the rate of water filtration. In general case $\mathrm{R} = 1 + \mathrm{k_d}$ (Dubinchuk et al. 1988), where $\mathrm{k_d}$ is ratio between volumetric trace concentration (^{14}C) in solid ($\mathrm{C_s}$) and liqid ($\mathrm{C_l}$) phases; $\mathrm{k_d} = [n(1-n)]\mathrm{k} = \mathrm{C_s}/\mathrm{C_l}$. Here n is the porosity and k is the coefficient of sorption distribution of the trace in solid ($\mathrm{m_s}$) and liquid ($\mathrm{m_l}$) phases; $\mathrm{k} = \mathrm{m_s}/\mathrm{m_l}$. In the volumetric concentration units, one has $\mathrm{m_s} = \mathrm{nC_l}$, $\mathrm{m_s} = (1-\mathrm{n})\mathrm{C_s}$.

Thus, the radiocarbon age of water estimated in the framework of a piston model should differ from the true age by the value of hk_d. The value of this quantity, according to experimental data (Thilo and Münnich 1970), varies for different carbonate rocks from 1 to 0.3. This circumstance in turn results in the fact that the peaks of T and ^{14}C, which occurred, for example, during the thermonuclear tests, will arrive at a sampling point in the recharge region, which both isotopes have reached simultaneously, at different times (radiocarbon will arrive later than tritium). This phenomenon can be responsible for the higher tritium content than of ^{14}C observed in some groundwaters (Tamers and Scharpenseel 1970).

In conclusion of this chapter, we summarize some results of the theoretical and experimental studies of formation the isotope composition in a carbonate system of groundwaters in order to increase reliability of the groundwater age determined by the radiocarbon.

Firstly, the most proposed equations include a number of parameters which practically are not determinable in the field. Moreover, in many cases the stages of the formation and observation of isotopic composition of groundwaters are divided by significant time intervals during which climatic changes affecting the hydrological conditions in unsaturated zone have happened. Secondly, the use of more complicate equations does not mean that they improve the reliability of the determined age. In the end, the experimental values of the parameters, which are substituted into the equations, being determined for a specific water point, do not take into account their space variability. In this connection the age determined by the radiocarbon is called in literature as "radiocarbon age" which has meaning of indeterminancy, characteristic for the method. As a rule, ^{14}C is defined the upper border of the age (i.e., the maximal age).