The Global Carbon Cycle Change: Le Chatelier Principle in the Response of Biota to Changing CO_2 Concentration in the Atmosphere.

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Summary. — The long-term existence of natural biota in the environment means that such a system is stable with respect to external disturbances. This system must follow the Le Chatelier principle which is based on the processes that compensate the disturbing effects. The use of the Le Chatelier principle makes it possible to choose between contradictory observational data. Available observational data on variations of the concentration of rare carbon isotopes in various media show that the oceanic biota follows the Le Chatelier principle and absorbs about half the carbon which the ocean gets from the atmosphere, compensating an increment of carbon in the atmosphere caused by an anthropogenic impact. The strongly anthropogenically disturbed land biota does not follow the Le Chatelier principle, starting from the middle of this century. The land biota not only cannot absorb excess carbon accumulated in the atmosphere: it ejects carbon to the atmosphere in quantities equal to halved emission of carbon through fossil fuel burning. All the quantitative results considered in the paper have been obtained without using models of the biota and of the ocean.

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1. – Introduction.

Equations have been obtained [1] which simulate the changes in the global cycles of basic and rare isotopes of carbon. These equations do not use the models of the biota and the ocean and are as follows (all notations coincide with the notations used in [1]:

$$\dot{x}_{\mathrm{a}} = \dot{x}_{\mathrm{f}} - \dot{x}_{\mathrm{b}} - k_{\mathrm{s}} - x_{\mathrm{a}} , \tag{1}$$

$$\Delta \delta^{v} \dot{C}_{\mathrm{a}} = {}^{v}\sigma_{f}\dot{x}_{f} + {}^{v}\sigma_{\mathrm{b}}\dot{x}_{\mathrm{b}} - K\Delta\delta^{v}C_{\mathrm{a}} + k_{\mathrm{s}}{}^{v}\sigma x_{\mathrm{a}} , \tag{2}$$

$$K = \overset{*}{k}_{\mathrm{s}} + \overset{*}{k}_{\mathrm{b}} . \tag{3}$$

Equation (1) determines variations in basic isotope concentration (without ν index), and eq. (2) in rare isotopes with $\nu = 13$ and 14. Lower indices denote a reservoir of carbon (a: atmosphere, f: fossil fuel, b: land biota, s: ocean); x_i is the ratio of changing carbon content in the reservoir to the initial (undisturbed) mass of carbon in the atmosphere. The quantity

$$\Delta \delta^\nu C_a = \delta^\nu C_a - \delta^\nu C_{a0} = {}^\nu x_a - x_a$$

is the variation of the shift of the relative content of a rare isotope $(\delta^\nu C_a)$ in the atmosphere with respect to an undisturbed value $(\delta^\nu C_{a0})$. The latter formula holds at $x_a \ll 1$, both at ${}^\nu x_a \sim x_a$ and at ${}^\nu x_a \sim 1$. The k_s and $\overset{*}{k}_s$ constants are expressed through the coefficients of the diffusion of CO_2 across the interface k_a (exchange coefficient) and the coefficients of absorption of carbon, both inorganic (k^-) and organic (k^+):

$$(4) \qquad k_s = (k_a^{-1} + k^{-1})^{-1}; \qquad k = k^+ + k^-/\zeta,$$

$$(5) \qquad \overset{*}{k}_s = (k_a^{-1} + (k^-)^{-1})^{-1},$$

where ζ is the known buffer factor [1]. The $\overset{*}{k}_b$ coefficient (in [1] it was denoted by the symbol k_b) determines the absorption of carbon by the short-living land biota. As was shown in [1], $\overset{*}{k}_b \ll \overset{*}{k}_s$. The ${}^\nu\sigma$ value takes into account the isotopic fractioning and is

$$(6) \qquad {}^\nu\sigma = (\overset{*}{k}_s/k_a^- k)({}^\nu\sigma^+ k^+ + {}^\nu\sigma^- k^-/\zeta),$$

where ${}^\nu\sigma^+$ and ${}^\nu\sigma^-$ are the differences between the shifts of the relative concentration of isotopes in dissolved $CO_2(\delta^\nu C)$, in the oceanic biota $(\delta^\nu C^+)$, and in totally dissolved inorganic carbon $\Sigma CO_2 (\delta^\nu C_\Sigma)$, respectively:

$$(7) \qquad {}^\nu\sigma^+ = \delta^\nu C - \delta^\nu C^+; \qquad {}^\nu\sigma^- = \delta^\nu C - \delta^\nu C_\Sigma.$$

Along with (1) and (2), a relationship can be obtained between variations in the shifts of the relative atmospheric concentration of a rare inorganic carbon isotope $(\Delta\delta^\nu C_a)$ and that in the ocean surface layer $(\Delta\delta^\nu C)$ by equalizing the right-hand parts of eqs. (33) and (34) in [1]:

$$(8) \qquad \Delta\delta^\nu C = (\overset{*}{k}_s/k^-) \Delta\delta^\nu C_a + (k_s/k_a) {}^\nu\sigma x_a.$$

Due to the time independence of ${}^\nu\sigma^-$ (7) the value of the variation of the shift in the ocean is the same for dissolved CO_2 and dissolved total inorganic carbon ΣCO_2 (the Bolin-Erickson ratio [1]):

$$(9) \qquad \Delta\delta^\nu C = \Delta\delta^\nu C_\Sigma.$$

In this paper eqs. (1), (2), (8) will be analysed from the viewpoint of fulfilment of the Le Chatelier principle which makes it possible to substantially reduce the uncertainty in final results and gives a criterion to identify the correct information from the controversial observational data.

2. – The Le Chatelier principle for absorption of carbon by the ocean.

The rate of penetration of all carbon isotopes from the atmosphere to the ocean is limited by the value of the exchange coefficient k_a[1], which characterizes the transmissivity of the interface. Therefore, k_a can be chosen as the basic reference unit when introducing the dimensionless ratios of all the remaining coefficients k_i to the k_a value:

$$(10) \qquad x \equiv \frac{k_s}{k_a}, \quad \overset{*}{x} \equiv \frac{\overset{*}{k_s}}{k_a}, \quad x^{\pm} \equiv \frac{k^{\pm}}{k_a}, \quad \overset{*}{x_b} \equiv \frac{\overset{*}{k_b}}{k_a}$$

$$\frac{k_s}{k_a} \qquad \frac{\overset{*}{k_s}}{k_a} \qquad \frac{k^{\pm}}{k_a} \qquad \frac{\overset{*}{k_b}}{k_a}.$$

Using (4), (5) the $x^{\pm}$ coefficients can be expressed through x and $\overset{*}{x}$:

$$(11) \qquad x^{-} = \overset{*}{x}/(1 - \overset{*}{x}); \quad x^{+} = x/(1 - x) - \overset{*}{x}/(1 - \overset{*}{x})\zeta.$$

The correction for isotopic fractionation (6) can also be expressed through the x and $\overset{*}{x}$ coefficients:

$$(12) \qquad x\,'\sigma = x(1 - \overset{*}{x})\,'\sigma^{+} - \overset{*}{x}(1 - x)('\sigma^{+} - '\sigma)/\zeta.$$

Relationship (8) between variations in the relative shifts in the ocean surface layer and in the atmosphere becomes

$$(13) \qquad \Delta\delta^{v}C = (1 - \overset{*}{x})\Delta\delta^{v}C_a + x\,'\sigma x_a.$$

The long lifetime of the atmosphere-ocean-biota system indicates that this system was stable. Hence, this system ought to have followed the Le Chatelier principle: having become disturbed, the system ought to have suffered feedback processes which would have compensated the effect of disturbance[2]. So, for instance, with atmospheric CO_2 concentration growing, compared to standard (undisturbed) values, the ocean absorbs an excess atmospheric CO_2 through the interface. It means that the exchange coefficient $k_a > 0$. If the condition $k_a < 0$ were satisfied, with CO_2 increasing in the atmosphere, the ocean would have started ejecting CO_2 to the atmosphere, and the system could not have been stable. The absorption coefficient $\overset{*}{k_b}$ for absorption of excess rare isotopes in the atmosphere by land biota should be positive, too. With k_a positive, the $\overset{*}{x_b}$ coefficient must be positive either.

Since anthropogenic disturbance of the World ocean structure is still negligible, the ocean may be considered to preserve its stability. It means that the k^{+} and k^{-} coefficients, which characterize the internal structure of the ocean, are positive: $k^{\pm} \geqslant 0$. For instance, the condition $k^{+} \geqslant 0$ means that with increased atmospheric CO_2 the biota of the ocean either starts absorbing CO_2 from the atmosphere ($k^{+} > 0$) or remains insensitive ($k^{+} = 0$) to this process. The case $k^{+} < 0$ would mean the system's instability and violation of the Le Chatelier principle. Letting $k^{\pm} \geqslant 0$ and $k_a > 0$, we obtain from (11) the following conditions for satisfying the Le Chatelier principle:

$$(14) \qquad x^{-} \geqslant 0 \quad \text{or} \quad 1 \geqslant \overset{*}{x} \geqslant 0,$$

$$(15) \qquad x^{+} \geqslant 0 \quad \text{or} \quad 1 \geqslant x \geqslant x_{\min},$$

where

(16)
$$x_{\min} \equiv \frac{\overset{*}{x}}{(1 - \overset{*}{x})\zeta + \overset{*}{x}} = \frac{1}{1 + \zeta/x^-} \approx \frac{x^-}{\zeta}.$$

Since $\overset{*}{x}_b$ is positive, we have the following constraints on the value of the exchange coefficient k_a:

(17)
$$0 < k_a = \frac{K}{\overset{*}{x} + \overset{*}{x}_b} \leqslant K/\overset{*}{x}.$$

Note that in the absence of the oceanic biota response to increased CO_2 in the atmosphere, i.e. $x^+ = 0$ (this has been assumed in all previous models), we have $x = x_{\min}$. Hence, in this case, the total coefficients of absorption x and k_s are determined by the $\overset{*}{x}$ (or x^-) coefficient, independent of the characteristics of the land biota. As shown in [1] and below, the $\overset{*}{x}$ coefficient can be estimated from the data of variations in the ^{14}C concentration in the atmosphere and in tree rings. The data on ^{13}C are not needed to assess $\overset{*}{x}$. The data on the ^{13}C isotope in tree rings, atmosphere and ocean enable one to estimate the x^+ coefficient, i.e. the quantity of biological absorption of carbon by the ocean and the contribution by the land biota.

3. – Estimation of $\overset{*}{x}$ and K constants from the radiocarbon data.

Nuclear tests in the atmosphere have almost doubled the ^{14}C concentration in the atmosphere by the year 1962 [3, 4]. Therefore, after 1962 the first, second and last terms in the right-hand part of (2) and the last term in the right-hand part of (13) at $\nu = 14$ can be rejected, because $\Delta\delta^{14}C_a \sim 1$, and $\delta^{14}C_i \sim 10^{-2}$ for all other media.

As a result, we obtain

(18)
$$\overset{*}{x} = 1 - \Delta\delta^{14}C/\Delta\delta^{14}C_a,$$

(19)
$$\Delta\delta^{14}\dot{C}_a = -K\Delta\delta^{14}C_a \quad \text{or} \quad K = -\frac{\Delta\delta^{14}\dot{C}_a}{\Delta\delta^{14}C}, \qquad t \geqslant 1963,$$

where $\Delta\delta^{14}C$ and $\Delta\delta^{14}C_a$ are variations of the shift of relative ^{14}C concentration in the surface layer of the ocean and in the atmosphere, respectively.

The ^{13}C concentration exceeds that of ^{14}C by ten orders of magnitude. Hence, $\delta^{13}C$ has not changed after nuclear tests [4]. Therefore, a change in $\delta^{14}C$ coincides with that of conventionally used value $\Delta^{14}C \approx \delta^{14}C - (2\delta^{13}C - \delta^{13}C_b)$ [5], corrected for isotopic fractionation. (In choosing the value of $\Delta^{14}C$ it is assumed that the correction for ^{14}C is twice as large as for ^{13}C, since the difference of the masses for ^{14}C and ^{12}C is twice as large as for ^{13}C and ^{12}C. The correction value is chosen so that it be zero for the land biota.) Undisturbed values of $\Delta^{14}C_0$ in all media are closer to zero and vary less compared to $\delta^{14}C_0$. Bearing in mind that the post-nuclear $\Delta^{14}C$ has grown hundreds-fold compared to the before-nuclear $\Delta^{14}C_0$ value, $\Delta\delta^{14}C = \Delta(\Delta^{14}C)$ can be changed for $\Delta^{14}C$ in (29) and (30) both for the atmosphere and the ocean, i.e. we take

$$\Delta\delta^{14}C_a = \Delta^{14}C_a, \qquad \Delta\delta^{14}C = \Delta^{14}C.$$

Formula (18) makes it possible to directly estimate the relative coefficient $\overset{*}{x}$ from the data of measurements of the ^{14}C concentration in the atmosphere ($\Delta^{14}C_a$) [4] and in

the surface waters of the ocean (Δ^{14}C)[6]. This formula contains neither time derivatives nor contribution by land biota.

To calculate $\overset{*}{x}$ and K, the data of measurements of atmospheric Δ^{14}C$_a$ were used[4] for 14 stations (2051 observations), while the data of Δ^{14}C measurements in the ocean surface layer[6] included 8 stations (480 observations). Calculations of $\overset{*}{x}$ were made in the following way. The published sources give weekly averaged values, starting from the first week of 1963. The data of all stations were averaged over each year for the atmosphere and for the ocean. The 1st of September was taken as the beginning of the year as corresponding to maximum seasonal values of Δ^{14}C$_a$ in the atmosphere. Averaging was made with the weight which takes into account the contribution by each quantity inversely proportional to the square of measurement errors, in accordance with the standard formula.

The data for the ocean are characterized by broad scattering. However, Δ^{14}C in the ocean does not exceed one third of Δ^{14}C$_a$ in the atmosphere. Therefore, the variability of Δ^{14}C in the ocean does not affect substantially the errors in $\overset{*}{x}$ (eq. (18)).

The data for the atmosphere, for most of the stations, are characterized by reduced seasonal oscillations taking place in counter-phase with the seasonal course of CO_2 concentration for the principal isotope[7]. These oscillations are clearly seen, starting from 1963 and, practically, fade by 1968. The reason of Δ^{14}C$_a$ oscillations in counter-phase with the seasonal course of CO_2 can be explained in the following way. After the 1963 nuclear tests, with supposed fast mixing of ^{14}C in the atmosphere, an exponential decrease of excess ^{14}C in the atmosphere ought to have been observed due to the absorption of ^{14}C by the ocean and by continental biota. The seasonal course of CO_2 due to the respiration of land biota[7] causes seasonal variations in the ^{14}C/^{12}C ratio in the atmosphere.

When CO_2 concentration in the atmosphere increases due to CO_2 emission from biota, with normal (not enriched by nuclear explosions) ^{14}C/^{12}C ratio, this ratio in the biosphere decreases. When the biota absorbs CO_2 from the atmosphere, the ^{14}C/^{12}C ratio in the atmosphere should not have changed, since the fractionation of isotopes by biota is negligible. Observations during this period showed that the ^{14}C/^{12}C ratio in the atmosphere increases drastically, which points to the input of ^{14}C to the atmosphere, despite the ceased nuclear explosions. This carbon flux can be explained only by time-dependent atmospheric mixing, i.e. by the input of ^{14}C to the observation point from other regions of the atmosphere due to latitudinal and vertical (including the stratosphere) mixing[8].

Since the latitudinal and vertical mixing takes about a year, which, by the order of magnitude, coincides with the characteristic time of the cycle of the short-lived land biota, all oscillations must completely fade during several years, which agrees with observations. In order not to introduce the errors connected with an inadequate knowledge of the parameters of atmospheric mixing, in calculations of averaged coefficients $\overset{*}{x}$ and K the authors took into account only the data, starting from 1968, when the seasonal oscillations in the ^{14}C/^{12}C ratio in the atmosphere do not show themselves and the values of $\overset{*}{x}$ and K stop decreasing with time.

However, after 1968 France and China continued nuclear tests in the atmosphere. These explosions have not affected the $\overset{*}{x}$ value, which depends only on an observed increase in the ^{14}C/^{12}C ratio both in the atmosphere and in the ocean. The post-1968 explosions must be taken into account in the balance equation (2) which determines the K value. This was done in the following way.

Explosions raise the ^{14}C concentration in the atmosphere, and therefore the annual

decrease of $\Delta^{14}C_a$ is less than in the absence of explosions. It can be assumed that a certain number of ^{14}C atoms forms in the atmosphere per unit power of nuclear explosions, and $\Delta^{14}C_a$ grows by a definite quantity. Explosions of 100 Mt TNT before 1960[9] have led to an increase of $\Delta^{14}C_a$ by about 230‰[3]. Explosions of 330 Mt TNT in 1961 and 1962[9] have led to a further increase of $\Delta^{14}C_a$ by about 760‰[3, 4], with a one-year delay, fig. 1. Therefore, explosions of 1 Mt TNT can be considered to enhance
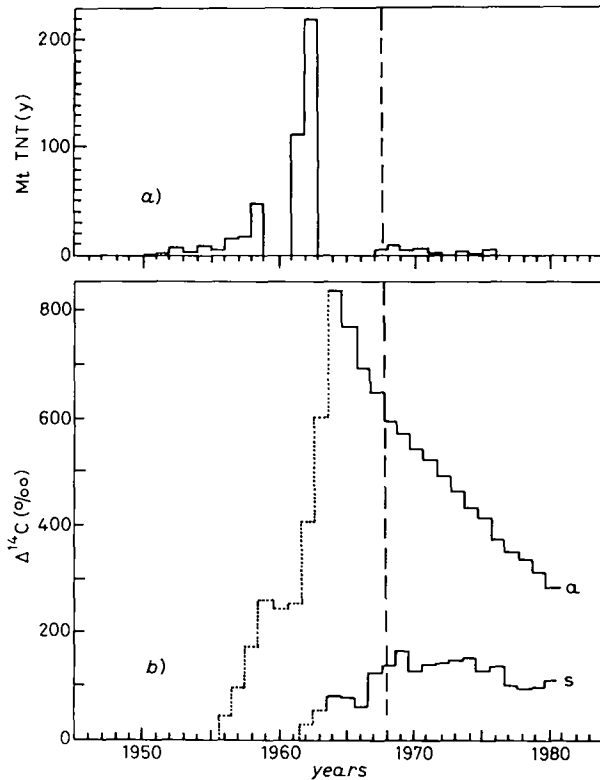

Fig. 1. – Post-nuclear concentration of ^{14}C in the atmosphere and in the ocean. a) Power of nuclear explosions in the atmosphere in different years[11]; b) variation of $\Delta^{14}C$ in the atmosphere (a) and in the ocean (s). The estimate for each year is averaged over the data of all the stations[29, 30]. The dotted line of the before-1962 histogram is drawn from the data of[8]. The dashed line is the year of cessation of seasonal oscillations depending on atmospheric mixing.

$\Delta^{14}C_a$ by 2.3‰, with a one-year delay. This corresponds to an input of $0.8 \cdot 10^{26}$ atoms of ^{14}C to the atmosphere per each Mt of the nuclear explosion, which constitutes about half total production of ^{14}C per nuclear explosion[9] (the second half may be absorbed on the Earth's surface). The values of the power of nuclear explosions in the atmosphere in the period 1945-1976 were taken from[9]. The results of calculations of $\overset{*}{x}$ and K are shown in fig. 2. An average value of $\overset{*}{x}$ from fig. 2 is

$$(20) \qquad\qquad \overset{*}{x} = 0.70 \pm 0.02.$$

Measurements of $\Delta^{14}C$ in the ocean and of $\Delta^{14}C_a$ in the atmosphere prior to nuclear
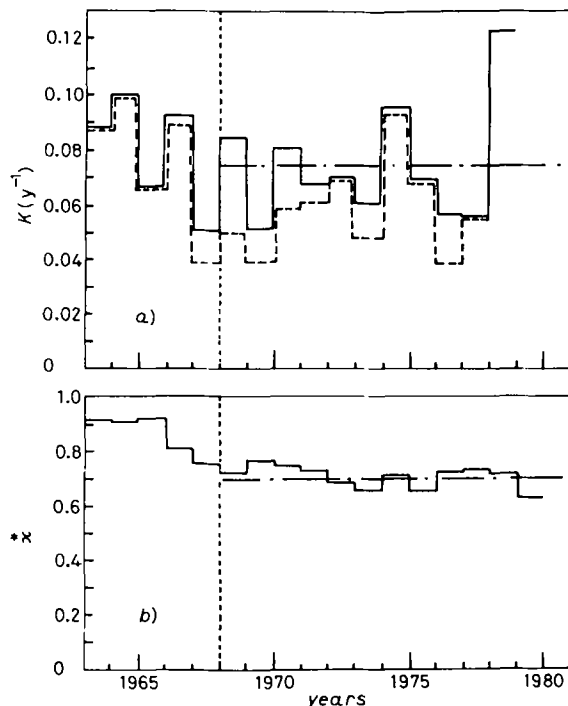
Fig. 2. – The constants of absorption of rare isotopes. a) The value of the constant K (19) in different years; the solid line is with account of correction for post-1962 nuclear tests, the dashed line is without account of this correction; b) values of the constant $\overset{*}{x}$ (18). The dotted line is the year of the cessation of seasonal oscillations in the atmosphere, starting from which K and $\overset{*}{x}$ averages were calculated (the dash-dotted line).

tests were made in the shells of marine organisms and in tree rings, respectively. According to these measurements, we have $+ 6\% \leqslant - \Delta\delta^{14}C \leqslant 12\%$ in the ocean[3] and $- \Delta\delta^{14}C_a = 25\%$ in the atmosphere[10]. These data determine $\overset{*}{x}$ (18) within the following limits: $0.5 \leqslant \overset{*}{x} \leqslant 0.76$, which agrees with (20). From (20) and (16) we obtain the minimum value of the dimensionless total coefficient of absorption of carbon by the ocean:

$$(21) \qquad\qquad x_{min} = 0.19 .$$

For the average K coefficient from fig. 2 we have

$$(22) \qquad\qquad K = (0.075 \pm 0.015)\, y^{-1} .$$

An account of the contribution of the post-1968 nuclear tests reduces the fluctuations of the K value and raises its average value. (In the absence of correction for continued nuclear tests an average K value—the dotted line in fig. 2—constitutes $K = 0.063\, y^{-1}$.) Within the measurement errors (22) coincides with the K value in[1], the difference in K averages being connected with the exclusion of the region of seasonal oscillations in $\Delta^{14}C_a$ and with account of measurement errors when calculating averaged values of $\Delta^{14}C_a$.

The obtained K value is 25% less than that determined from the data of the Suesse effect before 1953. This difference can be explained by fluctuation in the atmosphere, which, by estimates from [10], constituted about 15% of the observed decrease of the $^{14}C/^{12}C$ ratio. Note that fluctuations of natural background, comparable with the Suesse effect, are negligible compared to post-nuclear variations in the $^{14}C/^{12}C$ ratio. Therefore, the K value (22) obtained from the data of nuclear tests should be considered more reliable than the K value obtained from the data of the Suesse effect [1].

Values (20) and (22) give the following upper limit for the exchange coefficient k_a:

$$(23) \qquad\qquad k_a \lesssim 0.11 \, y^{-1}$$

which coincides with k_a used in [1].

The upper limit of the value of the exchange coefficient k_a thus obtained agrees with the k_a values used in the previous models [11-16]. Note that the global mean value of the exchange coefficient k_a has been earlier determined with the use of a certain World ocean circulation model. Here we determine the upper limit of the k_a value taking into account the positive sign of the $\overset{*}{k}_b$ coefficient which determines the contribution of the short-lived land biota to the carbon cycle. Thus, the obtained limit of the k_a value is not connected with the models of the ocean and continental biota.

4. – Biological absorption of carbon by the ocean from the data of ^{13}C concentration in tree rings and in the ocean.

With the oceanic biota considered not to respond to the increased CO_2 content in the atmosphere, taking the coefficient of biological absorption $\varkappa^+$ (eq. (11)) equal to zero, the coefficients of total absorption of carbon by the ocean become minimum (eq. (16)), which agrees with the Le Chatelier principle. Here k_s and $\varkappa$ are totally determined by the coefficient $\overset{*}{\varkappa}$ found from the data of measurements of ^{14}C concentration in the atmosphere and in the ocean.

With the exchange coefficient k_a of CO_2 transport across the interface assumed to be known from independent sources, no data are needed on the change in the concentration of another rare isotope ^{13}C. The obtained results on total absorption of carbon by the ocean and on the rate of reduction of the organic concentration in the land biota agree with the results of the previous models [14, 15, 17, 18].

Now, at $\varkappa^+ = 0$, $\varkappa = \varkappa_{min} = 0.19$ and $k_a = 0.12 \, y^{-1}$ used in [15, 19], we obtain for the total coefficient of the absorption of carbon by the ocean $k_s = 0.023 \, y^{-1}$. This gives for the rate of absorption of carbon by the ocean $\dot{m}_s = km_a = 3.2$ Gt C/y ($m_a = 140$ Gt C [20] is the increase of the carbon mass in the atmosphere). At the present rates of variation of the carbon mass in the atmosphere $\dot{m}_a = 3$ Gt C/y [20] and fossil fuel burning $\dot{m}_f = -5$ Gt C/y [21] from the balance equation (1) we obtain for the rate of reduction of carbon in the land biota $\dot{m}_b = -1.5$ Gt C/y, which agrees with the results of the previous models [14, 18, 22].

To assess the contribution of the biotic absorption of carbon by the ocean we may use the basic equations (2) and (13) for stable rare carbon isotope ^{13}C. From these equations we obtain, respectively, the following expressions for the coefficient of total

absorption $\varkappa$:

$$(24) \quad \begin{cases} \varkappa = \dfrac{a(\overset{*}{\varkappa} + \overset{*}{\varkappa}_b) - \overset{*}{\varkappa}\varepsilon}{1 - (1 - \overset{*}{\varkappa})\,C^+ - \overset{*}{\varkappa}\varepsilon}; \quad a \equiv \dfrac{-K\,\Delta\delta^{13}C_a - \Delta\delta^{13}\dot{C}_a - {}^{13}\sigma_b\,\dot{x}_a}{K\,{}^{13}\sigma_b\,x_a}, \\[2em] \varepsilon = (C^+ - C^-)/\zeta, \quad C^\pm \equiv {}^{13}\sigma^\pm/{}^{13}\sigma_b, \end{cases}$$

$$(25) \quad \varkappa = \dfrac{b + \overset{*}{\varkappa}\varepsilon}{(1 - \overset{*}{\varkappa})\,C^+ + \overset{*}{\varkappa}\varepsilon}; \quad b \equiv \dfrac{\Delta^{13}C - (1 - \overset{*}{\varkappa})\Delta\delta^{13}C_a}{{}^{13}\sigma_b\,x_a}.$$

Formula (24) coincides with the similar formula in [1] and differs from the latter only due to the use of dimensionless coefficients (10).

The principal contribution to (24) is made by the term containing $\Delta\delta^{13}C_a$. Corrections for isotopic fractionation contained in the terms proportional to C^+, only slightly change the $\varkappa$ coefficient. The errors of these corrections practically do not affect the reliability of the results. On the contrary, the principal contribution to the $\varkappa$ value (25) is made by corrections for isotopic fractionation. The reliability of the results strongly depends on the errors of these corrections. Thus, the total coefficient of absorption can be obtained from two independent sets of empirical data, which gives the possibility to check the agreement of all suppositions made within the theory of perturbations (expansions in small parameters).

Then, we shall assume that all empirical data in (24) and (25), apart from $\Delta\delta^{13}C_a$, are known rather accurately. We shall consider the right-hand parts of this formula as functions of $\Delta\delta^{13}C_a$-variations in the shift of the relative $^{13}C_a$ concentration in the atmosphere for the whole period of anthropogenic disturbances, starting from the 17th century [23]. Apart from the observational data, (24) and (25) include both the values independent of time ($'\sigma$, ζ, k_a, $\overset{*}{\varkappa}$) and the values varying in time ($\delta^{13}C$, x_a). The latter vary systematically, starting from 1958. In general, it would be worthwhile calculating the $\varkappa$ coefficient for each year of measurements with the relevant values of variables, making sure that $\varkappa$ is independent of time, and then calculating the average value of $\varkappa$, as had been done for the $\varkappa$ coefficient, fig. 2. However, only $\Delta\delta^{13}C_a$ averages for the last two decades have been published. Therefore, we use their averages for the last 25 years of observations (1958-1982) as independent of time. Thus, the following empirical data, included in (24) and (25), were used: $\dot{\delta}^{13}C_a = -0.04\%_0\,y^{-1}$ [24-27], $m_{a0} = (590 \pm 20)\,Gt\,C$, $(280 \pm 10)\,p.p.m.$ [28], $\dot{\bar{x}}_a = 0.0042\,y^{-1}$ [20], $\bar{x}_a = 0.21$ [20], $\overline{\Delta\delta^{13}C} = -(0.5 \pm 0.1)\%_0$ [29], where the bar denotes an averaging for the 25-year period of observations (1958-1982); $\overset{*}{\varkappa} = 0.70 \pm 0.2$ (20), $^{13}\sigma_f = {}^{13}\sigma_b = (18 \pm 2)\%_0$ [1, 18, 30], $c^+ = 0.9 \pm 0.1$ [18, 31], $c^- = -0.5 \pm 0.05$ [18, 32], $\zeta = 10 \pm 1$ [14, 33], $K = 0.075 \pm 0.003$ (22).

Substituting these quantities to formulae (24) and (25), we can obtain the coefficients $\overset{*}{\varkappa}_b$ and $\varkappa$ as functions of variations of $\Delta\delta^{13}C_a$ in the atmosphere:

$$(26) \quad \overset{*}{\varkappa}_b = \frac{0.20 + 0.076\,\Delta\delta^{13}C_a}{-0.42\,\Delta\delta^{13}C_a - 0.20},$$

$$(27) \quad \varkappa = -0.22\,\Delta\delta^{13}C_a - 0.093.$$

From the Le Chatelier condition $\overset{*}{\varkappa}_b \geqslant 0$ we obtain that $\Delta\delta^{13}C_a$ must be limited by the

inequality

(28) $$0.5‰ \leqslant -\Delta\delta^{13}C_a \leqslant 2.6‰.$$

The Le Chatelier conditions for $\varkappa$ (15), (16), (21) and (27) lead to the following constraints:

(29) $$1.3‰ \leqslant -\Delta\delta^{13}C_a \leqslant 4.9‰.$$

Combining the constraints (28) and (29), we obtain that the Le Chatelier principle for the land and oceanic biota is fulfilled if $\Delta\delta^{13}C_a$ is confined to

(30) $$1.3‰ \leqslant -\Delta\delta^{13}C_a \leqslant 2.6‰.$$

Then we shall find the limits of variations of dimensionless coefficients of total absorption by the ocean, $\varkappa$ (27), the absorption by the land biota of rare isotopes $\overset{*}{x}_b$ (26) and the exchange coefficient k_a (17):

(31) $$0.19 \leqslant \varkappa \leqslant 0.47, \quad 0.29 \leqslant \overset{*}{x}_b \leqslant 0, \quad 0.076\,y^{-1} \leqslant k_a \leqslant 0.11\,y^{-1}.$$

The minimum $\varkappa = \varkappa_{\min}$ corresponds to the absence of biogenic absorption of carbon by the ocean: $\varkappa^+ = 0$. To this corresponds the minimum value of the exchange coefficient k_a, which practically contradicts all available minimum estimates of this coefficient[11-13, 19]. Besides, a maximum $\overset{*}{x}_b$ value, which is at the limit of the estimates made in[1] using a model of land biota, corresponds to the $\varkappa_{\min}$ value. The largest value of $\varkappa$ corresponds to $\overset{*}{x}_b$ close to zero, and to a value of the exchange coefficient k_a agreeing with previous estimates[1, 12, 15].

Upon determining the limits of variations of the principal constants of carbon cycle, one can estimate the rates of absorption of carbon by the ocean and of carbon release from land biota. For this purpose we use five-year averages 1978-1982 (to smooth the annual fluctuations) of the increase of carbon concentration in the atmosphere: $\dot{m}_a = x_a m_{a0} = 140\,Gt\,C$ [20], of the rate of fossil carbon emission $\dot{m}_f = -5.1\,Gt\,C/y$ [21], and of the rate of the carbon accumulation in the atmosphere $\dot{m}_a = 3.4\,Gt\,C/y$ [20]. The rate of the carbon absorption by the ocean is estimated with the formula $\dot{m}_s = k_s m_a$; the rate of reduction of the carbon content in the land biota is then calculated from the equation of balance

$$\dot{m}_s + \dot{m}_a + \dot{m}_f + \dot{m}_b = 0.$$

The emissions of carbon from the reservoirs f and b correspond to negative $\dot{m}_f$ and $\dot{m}_b$.

Then in the absence of biological absorption of carbon by the ocean at $\varkappa = \varkappa_{\min}$ (31) we have

(32) $$\begin{cases} \varkappa = 0.19; \quad \overset{*}{x}_b = 0.29; \quad k_a = 0.076\,y^{-1}, \\ -\Delta\delta^{13}C_a = 1.3‰, \quad k_s = 0.014\,y^{-1}, \\ \dot{m}_s = \dot{m}_s^- = 2.0\,Gt\,C/y, \quad \dot{m}_s^+ = 0, \quad \dot{m}_b = -0.3\,Gt\,C/y. \end{cases}$$

In another extreme case (31), compatible with the Le Chatelier condition, we have

(33) $$\begin{cases} \varkappa = 0.47; \quad \overset{*}{x}_b = 0; \quad k_a = 0.11\,y^{-1}, \quad -\Delta\delta^{13}C_a = 2.6‰, \\ k_s = 0.05\,y^{-1}, \quad \dot{m}_s = 7.1\,Gt\,C/y, \quad \dot{m}_s^- = 1.9\,Gt\,C/y, \\ \dot{m}_s^+ = 5.2\,Gt\,C/y, \quad \dot{m}_b = -5.4\,Gt\,C/y, \end{cases}$$

where the contribution of organic and inorganic absorption by the ocean is calculated using the ratio: $m_s^+/m_s^- = x^+/(x^-/\zeta)$, x^+ and x^- have been obtained from (11). The quantities in (33) are close to those obtained in [19].

Estimates (32) and (33) were obtained based on the Le Chatelier principle, without using empirical data for $\Delta\delta^{13}C_a$. Now we shall consider these data. The published data for $\Delta\delta^{13}C_a$, averaged over 1958-1982, are as follows: $-\overline{\Delta\delta^{13}C_a} = 0.5\%_0$ in tree rings of total statistics, including the trees standing separately and the trees in the forest [18]; $-\overline{\Delta\delta^{13}C_a} = 0.9\%_0$ in ice cores [15] and in some tree rings [34]; $-\overline{\Delta\delta^{13}C_a} = 1.3\%_0$ in specially chosen individual trees, starting from the mid-XIX century, corresponding to the beginning of fossil fuel burning, which does not correspond to the beginning of anthropogenic disturbance of the biosphere [35]; $-\overline{\Delta\delta^{13}C_a} = 1.9\%_0$ for the global-scale statistics of the separately growing trees, starting from the XVI century [23], including the whole period of the substantial anthropogenic disturbance of the biosphere.

The minimum values $-\overline{\Delta\delta^{13}C_a} < 0.5\%_0$ contradict the Le Chatelier principle. They give a value of total coefficient x (27) either close to zero or negative, $i.e.$ the ocean practically does not absorb CO_2 from the atmosphere, despite the observed growth of the carbon concentration in the atmosphere. It means that the CO_2 concentration in the ocean increases at the same rate (or higher) as in the atmosphere due to the conversion of part of organic carbon into inorganic. The ocean biota, hence, responds to increasing CO_2 concentration in the environment by ejecting CO_2 into the environment. Such biota violates the Le Chatelier principle and is unstable, which does not correspond to its persistent existence during the millennia. At $x = 0$ both in the ocean and in the atmosphere the CO_2 concentration increases in the absence of a carbon flux across the interface. At $x < 0$ the ocean becomes a source of the CO_2 emission to the atmosphere.

The data for ice cores and tree rings in the interval $0.5\%_0 \leqslant -\overline{\Delta\delta^{13}C_a} \leqslant 1.3\%_0$ contradict the Le Chatelier principle, too. These data correspond to $x > 0$ at $x^+ < 0$. It means that the ocean absorbs CO_2 from the atmosphere but carbon is accumulated in the ocean faster than it is transported across the interface (this happens due to CO_2 release from organic stores of the ocean).

All the data which reveal breaking of the constraints (30) obtained from the Le Chatelier principle, should be considered incorrect since they do not adequately simulate $-\overline{\Delta\delta^{13}C_a}$ variations in the atmosphere. The data for ice cores, apparently, underestimate the $\overline{\Delta\delta^{13}C_a}$ values because of the considerable impact of diffusion inside the cores [36], which is, practically, absent in organic substances of tree rings. With increasing CO_2 concentration and decreased $^{13}C/^{12}C$ ratio in the past atmosphere the diffusion ought to have led to an overestimation of CO_2 concentration and to an underestimation of the $^{13}C/^{12}C$ ratio compared to their true values in the atmosphere of respective times. At the same time, the pre-industrial value of CO_2 concentration in the atmosphere is apparently correctly reproduced by the data of ice cores, since it has been constant during the last thousand years [28]. Variations of CO_2 concentration in air bubbles of ice cores formed more than 500 years ago agree even now with other data on the pre-industrial CO_2 concentration in the atmosphere. The data for ice cores formed now agree with direct present-day measurements of CO_2 concentration in the atmosphere. The CO_2 concentrations in ice cores of the intermediate interval [15] are strongly overestimated compared to the atmospheric CO_2 concentration of that time [20]. It follows from the fact that an extrapolation of the observed present-day exponential CO_2 growth to the time period before 1958 leads to much lower CO_2 concentrations than in ice cores.

The correct value of the pre-industrial $^{13}C/^{12}C$ ratio may be obtained through measurements of this ratio in older parts of ice cores until this ratio stops decreasing and stabilizes at a certain level, like an absolute value of CO_2 concentration. For this purpose the ice cores $(50 \div 1000)$ years old have to be used.

An inadequacy of the data of tree rings[31, 34] with $-\overline{\Delta\delta^{13}C_a} = < 1.3\%o$ is apparently connected either with incorrect reproduction of atmospheric $^{13}C/^{12}C$ ratio in the trees surrounded by forest or with inadequate statistics of the trees measured. Note that among 60 trees used in the global-scale statistics[23], there are trees in which $-\overline{\Delta\delta^{13}C_a}$ reaches maximum values in (30) compatible with the Le Chatelier principle. Therefore, further broadening of the statistics of the investigated trees may raise the $-\Delta\delta^{13}C_a$ values and, respectively, total and biological coefficients of absorption of carbon by the ocean up to adequate maximum values (33).

The empirical value $-\overline{\Delta\delta^{13}C_a} = 1.3\%o$ [32] agrees with the Le Chatelier principle in the absence of biological absorption of carbon by the ocean. The characteristics of carbon cycle compatible with this value are given in (32). These values correspond to i) too small a value of the exchange coefficient k_a, which contradicts the estimates of this coefficient from direct measurements[11, 12, 16] and based on different models of the ocean[14, 15, 34]; ii) too low a rate of carbon emission from the land biota, which contradicts the estimates of this rate from the data of land use and deforestation[17, 22]; iii) too high a value of the $\overset{*}{x}_b$ coefficient of absorption of rare isotopes of carbon by the land biota, which contradicts model estimates made in[1]; iv) the value $-\overline{\Delta\delta^{13}C_a} = -1.3\%o$ was obtained with the choice of the initial time for variations in the ratio $^{13}C/^{12}C$ in the atmosphere connected with the beginning of fossil fuel burning period which does not coincide with the beginning of anthropogenic disturbance of the biosphere and anthropogenically induced decrease of the $^{13}C/^{12}C$ ratio in the atmosphere.

All these arguments are dismissed in case of observed maximum value $-\overline{\Delta\delta^{13}C_a} = 1.9\%o$ which we shall take as the most reliable empirical value at the present time. For this value we obtain from (11), (17), (20), (26) and (27) the following characteristics of the contemporary global carbon cycle:

$$(34) \quad \begin{cases} x = 0.32; \quad \overset{*}{x}_b = 0.1; \quad k_a = 0.094\,\text{y}^{-1}; \quad -\overline{\Delta\delta^{13}C_a} = 1.9\%o; \\ k = 0.030\,\text{y}^{-1}; \quad \dot{m}_s = 4.2\,\text{Gt C/y}; \quad x^-/\zeta = 0.23; \quad x^+ = 0.24; \\ \dot{m}_s = 2.1\,\text{Gt C/y}; \quad \dot{m}_s^- = 2.1\,\text{Gt C/y}; \quad \dot{m}_b = -2.5\,\text{Gt C/y}. \end{cases}$$

As is seen from (34), the biological and physico-chemical absorption of carbon by the ocean coincide, i.e. the oceanic biota, in accordance with the Le Chatelier principle, effectively compensates the disturbance of carbon concentration in the atmosphere.

If the land biota were not disturbed by man and preserved its natural state, it ought to have followed the Le Chatelier principle. In this case an increase of CO_2 in the atmosphere would have led to the absorption of CO_2 by the land biota from the atmosphere. With small x_a, by analogy with the ocean, we could write

$$(35) \qquad\qquad\qquad \dot{x}_b = k_b x_a.$$

For the an undisturbed land biota $k_b = k_{b0} > 0$. At the present time ($x_a = 0.23$, and $\dot{x}_b = -0.0042\,\text{y}^{-1}$) we have $k_{b0} = -0.018\,\text{y}^{-1}$ [36].

Thus, the present value of the absorption coefficient for the land biota, including

man, turns out to be negative. It means that the present land biota is strongly disturbed, unstable and violates the Le Chatelier principle.

Due to high land productivity, the value of the undisturbed coefficient k_b could have been several times larger than the coefficient for the ocean. We believe that the oceanic biota is weakly disturbed and the present k_b value coincides with its undisturbed value. The undisturbed biosphere could have more effectively liquidated environmental pollutions than it happens now.

This consideration makes it possible to assess the temporal change of the coefficient $k_b = \dot{x}_b/x_a$ (35), which characterizes the state of land biota. Figure 3 demonstrates the time dependence of k_b on the assumption that the relative rate of variations in the difference $k_{b0} - k_b$ coincides with the relative rate of the growth of population on the Earth. The present value of k_b is given in [36]. Undisturbed values of biotic coefficients of absorption of carbon for land and ocean are considered proportional to their total primary productivities which approximately coincide. Therefore, it is assumed that $k_{b0} = k_s^+ = k_s(k^+/k) \approx k_s/2$ (see (4)). It is seen from fig. 3 that the transition of k_b across zero takes place in the middle of the current century. It means that as far back as the last century and the beginning of this century the near-surface part of the biosphere had functioned as an exclusively effective absorber of all anthropogenic pollutions.
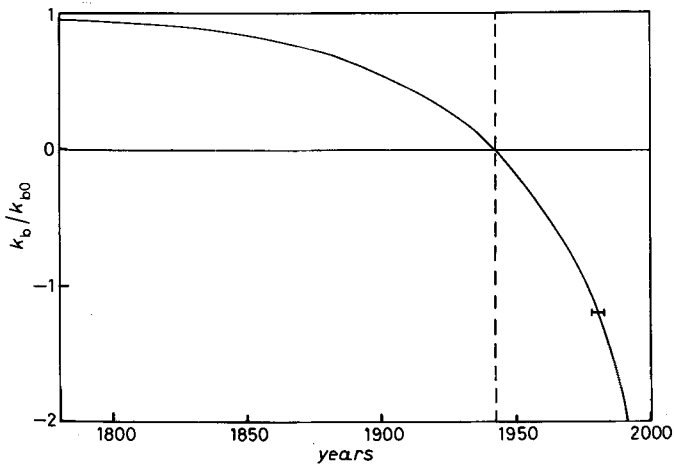

Fig. 3. – Violation of the Le Chatelier principle in land biota. The biotic response to the environmental disturbance is determined from the equation: $\dot{m}_b = k_b m_a$ (35); $\dot{m}_b$ is the rate of the change of biotic biomass, m_a is the variation of carbon mass in the atmosphere. The realization of the Le Chatelier principle corresponds to satisfying the condition $k_b > 0$ (upper semi-plane). The solid line represents the equation $z \equiv (k_{b0} - k_b)/k_{b0} = \exp[\alpha(t - t_0)]$, $k_{b0} > 0$ is an undisturbed value of the k_b coefficient (which coincides with the calculated coefficient of the biological absorption of carbon by the ocean); the parameters $t_0 = 1941$ (the year of changing the sign of k_b (the dashed vertical line) and $\alpha = 0.02\,\mathrm{y}^{-1}$ (it coincides with the average observed relative rate of growth of the world population) have been found from conditions: $z(1980) = 2.2$ (observed value [36], marked by the symbol ——), $z(1825) = 0.1$ (supposed value).

7. – Conclusion.

The approach developed here based on an expansion in series over small parameters makes it possible to assess variations in the carbon cycle on the basis of the

available empirical data without using models of the structure of the ocean and land biota.

The use of the Le Chatelier principle enables one to select observational data which do not contradict the observed stability of the atmosphere-ocean-biota system. The data selected in accordance with the Le Chatelier principle point to the normal response of the oceanic biota directed towards a compensation of environmental disturbances. A further analysis of variations in the concentration of ^{13}C isotope in tree rings and ice cores can lead to a conclusion about the substantial increase of the biotic and total absorption of carbon by the ocean.

The biota can maintain the environment in a steady state in the presence of external disturbances due to the transition of excess inorganic substances, residing in the environment, into low-active organic forms (for instance, either into dissolved organic matter in the ocean or into organic carbon in soil and tree stems). And, on the contrary, with the shortage of inorganic substances in the environment the biota can replenish them disintegrating low-active organic supplies. As a result of these processes, the CO_2 concentration in the atmosphere and ocean can return to a pre-industrial value after cessation of disturbances [1, 19]. In the absence of the response of biota, that can transform excess atmospheric CO_2 into organic forms, all the carbon released to the atmosphere would, practically, forever remain in the environment upon being re-distributed between the ocean and the atmosphere [14].

The absorption of carbon by the oceanic biota as a response to increased CO_2 concentration in the atmosphere, with concentrations of other biogens (nitrogen, phosphorus) being constant, can result from the synthesis by phytoplankton of primary organic product not containing N, P, which, then, is excreted from aquatic plants, enlarging, thereby, the supply of dissolved organic matter in the ocean (at the same time, the ratios C/N, C/P in dissolved organic matter can increase) [19].

It should be noted that there has been no evidence, so far, for the response of the ocean to the growth of CO_2 concentration in the atmosphere on a global scale, and it is very difficult to obtain such evidence from observations. The authors only state that the available observational data do not contradict such a possibility [19].

The results obtained show that the land biota can completely control the environmental state, maintaining it in the state acceptable for life. As is known, the possible rate of environmental changes (concentrations of biologically active compounds) as a result of synthesis or decomposition of organic substances by the biota exceeds by four orders of magnitude the rate of its change due to geophysical and cosmic processes (volcanic activity, filtration of substances from the Earth's mantle, fluxes of cosmic particles, etc.). Under normal conditions both the synthesis and decomposition completely compensate each other in natural biota, which is an indication of ecological equilibrium. With the help of a very small disbalance between the rates of synthesis and decomposition at a relative level of about 10^{-4} the natural (anthropogenically undisturbed) biota can compensate the effect of any abiotic factors on the environment. There is no requirement for environmental stability in the absence of biota. It is quite possible that the existing environment on the lifeless Earth would not be stable and would not follow the Le Chatelier principle. The evolution of the environment on the dead Earth could lead the planet to the state of Mars or Venus, where life is impossible. The current attempts to construct models with a stable carbon cycle without consideration of biota are qualitatively incorrect. In such models the stability of temperature is explained by abiotic stability of the existing CO_2 concentration, which regulates the greenhouse effect.

It is still unclear what is an explanation to the existing CO_2 concentration level, which provides the temperature regime acceptable for life. The instability of the water cycle of a dead planet is completely ignored, although its impact on the greenhouse effect is known to be an order of magnitude stronger than the impact of carbon dioxide. Neglecting the biotic effect on the environment in the consideration of geophysical processes means rejecting quantitatively basic terms when taking into account negligible (10^{-4}) secondary terms.

The strongly disturbed biota looses its stability and stops following the Le Chatelier principle. Apparently, this has happened, on a global scale, with the land biota, which, instead of compensating the environmental distortion, has become itself one of its basic pollutants (34). Probably, before the mid-XX century, the land biota had preserved its stability and had been a more effective cleaner of the environment than the ocean. At present, slightly disturbed oceans still compensate the environmental disturbances.

It must be emphasized (although it may seem a paradox) that breaking the balance of the biota through substituting the anthropogenic biotic complexes (crops, secondary forests, aquacultures, etc.) for natural biota biosphere is much more harmful for the environment compared to complete destruction of the biota. In the first case, when the connection between the synthesis and decomposition breaks, biological processes of the environmental destruction take place, which are four orders of magnitude stronger compared to geophysical processes which take place in the second case, in the absence of the biota.

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