

Variations in the Global Content of Organic Carbon in the Oceanic and Land Biota

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Summary. — The net absorption of CO₂ by the global ocean is shown to linearly depend on the increment in atmospheric CO₂ starting from its stationary preindustrial level. The respective proportionality coefficient is inferred from the data on ¹³C and ¹⁴C variations in tree rings, and its value corresponds to a small disturbance in the biospheric carbon.

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1. — Introduction

Man's activity leads to the redistribution of carbon between the four active reservoirs: atmosphere, land surface biota, fossil fuel and ocean. The problem is that, while the variations of the atmospheric and fossil fuel carbon content are known to a high degree of accuracy⁽¹⁻⁴⁾, the data on such variations in the land surface biota and in the ocean cited by various sources differ by as much as an

(¹) C. D. KEELING, R. B. BACASTOW and T. P. WHORF: *Measurements of the concentration of carbon dioxide at Mauna Loa Observatory, Hawaii*, in *Carbon Dioxide Review*, edited by W. C. CLARK (Clarendon Press, New York, N. Y., 1982), p. 377.

(²) J. A. WATTS: *The carbon dioxide question: data sampler*, in *Carbon Dioxide Review*, edited by W. C. CLARK (Clarendon Press, New York, N. Y., 1982), p. 431.

(³) G. MARLAND and R. M. ROTT; *Tellus B*, **36**, 232 (1984).

(⁴) W. D. KOMHYR, R. H. GAMMON, T. B. HARRIS and L. S. WATERMAN: *J. Geophys. Res.*, **90**, 5567 (1985).

order of magnitude^(5,6). Traditionally the net absorption of inorganic carbon by the ocean is calculated according to various models⁽⁷⁻⁹⁾. So far these models have postulated low oceanic carbon absorption in organic form: the oceanic cell production is limited by the availability of such nutrients as N and P and, therefore, cannot increase with increasing concentration of inorganic carbon in the ocean. However, an increase in extracellular organic excretions containing neither N nor P is possible even at constant concentrations of these nutrients^(10,11). The respective productivity may reach the maximum observed productivity of the ocean and exceed the absorption of inorganic carbon considerably. Direct global measurements of change of oceanic productivity and variations both in the organic and inorganic oceanic carbon are not feasible yet⁽¹²⁾.

In this paper the total net oceanic absorption of carbon in organic and inorganic form is obtained from the data of the change of carbon isotopes (¹²C, ¹³C, ¹⁴C) ratios in the atmosphere, ocean and tree rings. The approach used in the present study does not demand for any particular models of the inner structure of the ocean: there is no need to stratify the ocean into layers of different mixing properties to specify its primary productivity and destructivity, etc.

2. - Variables and notations.

Indices and symbols.

i(= a, f, l, s, Σ) lower right «reservoir» index standing for recent state: a atmosphere, f fossil fuel, b land surface biosphere, s ocean, Σ total dissolved inorganic carbon, Σ CO₂, in the surface layer of the ocean. The index i=s is omitted for any variable denoting the surface layer of the ocean.

⁽⁵⁾ R. H. HOUGHTON, J. E. HOBBIE, J. M. MELILLO, B. MOORE, B. J. PETERSON, G. R. SHAVER and G. M. WOODWELL: *Ecol. Monogr.*, **53**, 235 (1983).

⁽⁶⁾ W. C. CLARK, K. H. COOK, G. MARLAND, A. W. WEINBERG, R. M. ROTTY, P. R. BELL, J. A. ALLISON and C. L. COOPER: *The carbon dioxide question: Perspectives for 1982*, in *Carbon Dioxide Review*, edited by W. C. CLARK (Clarendon Press, New York, N. Y., 1982), p. 3.

⁽⁷⁾ C. D. KEELING: *The carbon dioxide cycle*, in *Chemistry of the Lower Atmosphere*, edited by S. RASOOL (Plenum Press, New York, N. Y., 1983).

⁽⁸⁾ H. OESCHGER, U. SIEGENTHALER, H. SCHOTTERER and A. GUGELMAN: *Tellus*, **27**, 160 (1975).

⁽⁹⁾ T.-H. PENG, W. S. BROECKER, H. D. FREYER and S. TRUMBORE: *J. Geophys. Res.*, **88**, 3609 (1983).

⁽¹⁰⁾ V. G. GORSHOV: *Nuovo Cimento C*, **5**, 209 (1982).

⁽¹¹⁾ V. G. GORSHOV: *Nuovo Cimento C*, **9**, 902 (1986).

⁽¹²⁾ R. H. GAMMON: *Global ocean carbon research program*, Committee on Climatic Changes and the Ocean, Seventh Session, Paris, First draft (1986).

i0 indicates the preindustrial stationary state.

\pm upper right indices denoting *a*) mass of organic (+) and inorganic (-) carbon in the ocean, *b*) production (+) and destruction (-) of organic carbon in any reservoir.

ν (= 13, 14) upper left index denoting rare carbon isotopes; usually omitted in the case $\nu = 12$: $^{12}\text{C} \equiv \text{C}$.

\equiv is the identity symbol: it introduces new dependent variables.

Basic measurable variables.

m_i, m_s^\pm change of carbon mass during the industrial era ($i = a, f, b$), Gt C.

$\dot{m}_i \equiv dm_i/dt$ rate of change of carbon mass, Gt C y^{-1} .

P_i^\pm production (+) or destruction (-) of organic carbon, Gt C y^{-1} .

$[\text{CO}_2]_a, [\text{CO}_2] - \text{CO}_2$: mean global concentrations in the atmosphere (*a*) and surface layer of the ocean (without lower index), g C m^{-3} .

$[\Sigma\text{CO}_2]$ mean global concentration of total dissolved inorganic carbon (including carbonate and bicarbonate ions) in the surface layer of the ocean, g C m^{-3} .

$\delta[\text{CO}_2]_a \equiv [\text{CO}_2]_a - [\text{CO}_2]_{a0}$, $\delta[\text{CO}_2] \equiv [\text{CO}_2] - [\text{CO}_2]_0$, $\delta[\Sigma\text{CO}_2] \equiv [\Sigma\text{CO}_2] - [\Sigma\text{CO}_2]_0$ change of carbon concentration during the industrial era.

${}^\nu M_{a0}$ preindustrial carbon mass in the atmosphere.

${}^\nu x_i$ relative change of carbon mass and concentration so that ${}^\nu x_i \equiv {}^\nu m_i / {}^\nu M_{a0}$, $i = a, b, f$; ${}^\nu x_{i0} = 0$.

${}^\nu x_s^\pm \equiv {}^\nu m_s^\pm / {}^\nu M_{a0}$ relative change of organic (+) and inorganic (-) carbon mass in the ocean.

$$(1) \quad {}^\nu x_a \equiv \delta[{}^\nu\text{CO}_2]_a / [{}^\nu\text{CO}_2]_{a0}, \quad {}^\nu x \equiv \delta[{}^\nu\text{CO}_2] / [{}^\nu\text{CO}_2]_0, \quad {}^\nu x_\Sigma \equiv \delta[\Sigma {}^\nu\text{CO}_2] / [\Sigma {}^\nu\text{CO}_2]_0.$$

${}^\nu r$ is the ${}^\nu\text{C}/^{12}\text{C} \equiv {}^\nu\text{C}/\text{C}$ ratio and

${}^\nu\sigma$ the isotopic fractionation correction (${}^\nu a \equiv 1 + {}^\nu\sigma$ is the usually used isotopic fractionation factor^(7,13)) so that

$$(2) \quad \begin{cases} {}^\nu r_a \equiv [{}^\nu\text{CO}_2]_a / [\text{CO}_2]_a, \\ {}^\nu r_b \equiv {}^\nu P_b^+ / P_b^+, \quad {}^\nu\sigma_b \equiv {}^\nu r_a / {}^\nu r_b - 1 = {}^\nu r_{a0} / {}^\nu r_{b0} - 1, \end{cases}$$

(13) U. SIEGENTHALER and K. O. MÜNNICH: $^{13}\text{C}/^{12}\text{C}$ fraction during CO_2 transfer from air to sea, in *Carbon Cycle Modelling*, edited by B. BOLIN, SCOPE 16 (Wiley, Chichester, 1981) p. 249.

$$(3) \quad \begin{cases} {}^{\nu}r_f \equiv {}^{\nu}\dot{m}_f/\dot{m}_f = {}^{\nu}m_f/m_f, & {}^{\nu}\sigma_f \equiv {}^{\nu}r_{a0}/{}^{\nu}r_f - 1, & \nu = 13, \\ {}^{\nu}r^- \equiv [{}^{\nu}\text{CO}_2]/[\text{CO}_2], & {}^{\nu}r^+ \equiv {}^{\nu}P_s^+/P_s^+, \end{cases}$$

$$(4) \quad {}^{\nu}\sigma^+ \equiv {}^{\nu}r^-/{}^{\nu}r^+ - 1 = {}^{\nu}r_0^-/{}^{\nu}r_0^+ - 1,$$

$$(5) \quad {}^{\nu}r_{\Sigma} \equiv [\Sigma {}^{\nu}\text{CO}_2]/[\Sigma \text{CO}_2], \quad {}^{\nu}\sigma^- \equiv {}^{\nu}r^-/{}^{\nu}r_{\Sigma} - 1 = {}^{\nu}r_0^-/{}^{\nu}r_{\Sigma 0} - 1.$$

3. - Absorption of atmospheric CO₂ by the ocean.

The net absorption flux \dot{m}_s of carbon passing through the ocean-atmosphere interface is determined by the air-sea difference in relative variations of CO₂ concentration x_a and x (^{11,14,15}) (see sect. 2):

$$(6) \quad \begin{cases} \dot{m}_s = \frac{\beta[\text{CO}_2]_a - [\text{CO}_2]}{R_a} S & \text{or} & \dot{x}_a = k_a(x_a - x), \\ k_a \equiv (hR_a)^{-1}, & h \equiv V_a/\beta S, & V_a \equiv M_{a0}/[\text{CO}_2]_{a0}, \end{cases}$$

where the stationary-state condition, $\beta[\text{CO}_2]_{a0} = [\text{CO}_2]_0$, is taken into account, R_a and k_a are known resistance (^{11,14,15}) and exchange coefficients (^{7,8}) of CO₂ penetration through the air-sea interface, respectively, β the CO₂ solubility (⁷), V_a the atmospheric volume, S the area of the world ocean surface.

The relative uncertainty of the global mean for x_a is only a few per cent, since the atmosphere is intensely mixed (¹). But the global mean for x is unknown: the value of x varies both in time and space by more than $\pm x_a$ changing its sign (^{11,12,16,17}) and the relative uncertainty of the global mean for x is also of the order of $\pm x_a$. In order to exclude the value x from the consideration, let us consider the absorption of carbon by the oceanic waters.

The net carbon absorption by the ocean as a whole (including surface and deep layers) depends only on the dissolved CO₂ perturbation in the mixed surface layer. The total carbon absorption \dot{m}_s is the sum of absorption in organic \dot{m}_s^+ and

(¹⁴) M. L. WESLEY, D. R. COOK, R. L. HART and R. M. WILLIAMS: *J. Geophys. Res.*, 87, 8827 (1982).

(¹⁵) E. T. DEGENS, S. KEMPE and A. SPITZY: *Carbon Dioxide: a Biological Portrait. The Handbook of Environmental Chemistry*, Vol 1, part C, edited by O. HUTZIGER (Springer-Verlag, Berlin, 1984), p. 127.

(¹⁶) W. S. BROECHER, T. TAKAHACHI, H. J. SIMPSON and T.-H. PENG: *Science*, 206, 409 (1979).

(¹⁷) G. I. PEARMAN, P. HYSON and P. J. FRASER: *J. Geophys. Res.*, 88, 3581 (1983).

inorganic \dot{m}_s^- forms:

$$(7) \quad \dot{m}_s = \dot{m}_s^+ + \dot{m}_s^- \quad \text{or} \quad \dot{x}_s = \dot{x}_s^+ + \dot{x}_s^- .$$

The inorganic absorption \dot{m}_s^- is determined by the eddy diffusion and depends on the change in the total dissolved inorganic carbon $\delta[\Sigma \text{CO}_2]$ ^(7,8,11,12). The organic absorption \dot{m}_s^+ is determined by the change in the activity of biota and at constant concentrations of other nutrients may depend on the change in dissolved carbon dioxide $\delta[\text{CO}_2]$: The ratio ¹³C/C in ΣCO_2 is 9% higher and in the biota (16 ÷ 18)% lower than in dissolved gas ^(13,16). The ratio in the land biota which directly consume CO_2 from the air is also 18% less than in air ⁽⁹⁾. It follows from the biochemical universality that the oceanic biota principally absorb CO_2 instead of ΣCO_2 .

Since the stationary state exists, the values \dot{m}_s^+ and \dot{m}_s^- should turn to zero for zero x and x_Σ , respectively. At small increments of x and x_Σ we may use a linear approximation (the first term in the Taylor expression of \dot{m}_s^\pm over the powers of x and x_Σ)

$$(8) \quad \dot{m}_s^+ = (\delta[\text{CO}_2]/R^+)S \quad \text{or} \quad \dot{x}_s^+ = k^+x, \quad k^+ \geq 0,$$

$$(9) \quad \dot{m}_s^- = (\delta[\Sigma \text{CO}_2]/R_\Sigma^-)S \quad \text{or} \quad \dot{x}_s^- = k^-x_\Sigma, \quad k^- \geq 0,$$

$$(10) \quad k^\pm \equiv (hR^\pm)^{-1}, \quad R^- \equiv R_\Sigma / \phi_0, \quad \phi_0 \equiv [\Sigma \text{CO}_2]_0 / [\text{CO}_2]_0 \approx 200 .$$

Here, instead of the coefficient of direct proportionality k^\pm , we may use the constant resistance R^\pm of organic (+) and inorganic (-) carbon absorption by the oceanic waters ⁽¹¹⁾ that have the same dimensions as R_a .

Absorption of carbon by the ocean has a buffering character and we have ^(7,11)

$$(11) \quad x/x_\Sigma = \zeta \approx 10 \quad \text{or} \quad x_\Sigma = x/\zeta .$$

Here ζ is the empirically known buffer factor ^(7,8). Finally, from (7)-(11) we have

$$(12) \quad \dot{x}_s = kx, \quad k \equiv k^+ + k^-/\zeta > 0, \quad (k \equiv (hR)^{-1}, \quad R^{-1} \equiv (R^+)^{-1} + (R^- \zeta)^{-1}) .$$

Excluding the value x from (6) and (12), we obtain

$$(13) \quad \dot{x}_s = k_s x_a,$$

$$(14) \quad k_s \equiv (k_a^{-1} + k^{-1})^{-1}, \quad k_s \leq k_a, \quad k_s \leq k \quad (k_s \equiv (hR_s)^{-1}, \quad R_s \equiv R_a + R),$$

$$(15) \quad x = (k_s/k) x_a \leq x_a .$$

⁽¹⁶⁾ P. M. WILLIAMS and L. I. GORDON: *Deep Sea Res.*, 17, 19 (1970).

Equation (13) may be written independently of the general point of view. The ocean interacts only with the atmosphere and \dot{x}_s depends only on x_a . At a small x_a we may use a Taylor expansion of \dot{x}_s over the powers of x_a . Since there existed a stationary preindustrial state the first term of that expansion is (13). The values of constant resistances R^\pm (15) may be obtained in the models^(8,11). In the previous work the resistance R^- was obtained in boxes or box-diffusion models^(8,9,11) and R^+ was supposed to be equal to infinity in^(8,9) and to mean global resistance $R_p \approx R_a$ of the gross ocean productivity in⁽¹¹⁾. But the maximal observed ocean productivity is ten times larger than the global ones^(19,20). Hence we know only that $0.1 R_a \leq R^+ < \infty$. In the present work we shall obtain the values of the two independent combinations of R^+ and R^- and the value of k_s (13) from the data on the two carbon isotopes ^{13}C and ^{14}C .

4. - Change of the carbon rare-isotope content in biomass.

In this section the reservoir index $i = b$ or s and the index $+$ for biomass are omitted. To derive the value \dot{m} , let us introduce the function $b(\tau)$ which describes the distribution of the primary production and of biomass with the turnover (or residence) time τ :

$$(16) \quad \begin{cases} b(\tau) \equiv P(\tau)/P, & \tau \equiv M(\tau)/P(\tau), \\ \int_0^\infty b(\tau) d\tau = 1, & \int_0^\infty b(\tau) \tau d\tau = \bar{\tau} \equiv M/P. \end{cases}$$

Here $P(\tau)$ and $M(\tau)$ are the densities (per unit size $d\tau$) of organic production and biomass for a given τ ; P , M and $\bar{\tau}$ are, respectively, the total production, biomass and mean turnover time. The rate of biomass change $\dot{M}(\tau)$ is equal to the difference in production $\dot{P}^+(\tau)$ and destruction $\dot{P}^-(\tau)$:

$$(17) \quad \dot{M}(\tau) = \dot{P}^+(\tau) - \dot{P}^-(\tau),$$

$$(18) \quad \dot{P}^+(\tau) = P^+(\tau) \dot{r}(t),$$

$$(19) \quad \dot{P}^-(\tau) = P^-(\tau) \begin{cases} \dot{r}(t - \tau), & t - \tau > t_0, \\ \dot{r}(t_0), & t - \tau < t_0. \end{cases}$$

⁽¹⁹⁾ R. H. WHITTAKER and G. E. LIKENS: *The biosphere and man*, in *Primary Productivity of the Biosphere*, edited by H. LIETH and R. WHITTAKER (Springer-Verlag, Berlin, 1975), p. 305.

⁽²⁰⁾ O. G. N. DE VOOG: *Primary production of aquatic environments*, in *The Global Cycle*, edited by B. BOLIN, E. T. DEGENS, S. KEMPE and R. KETNER (J. Wiley & Sons, New York, N. Y., 1979), p. 259.

Here ${}^v r(t) \equiv {}^v P^+ / P^+$ is the recent ${}^v C/C$ ratio in the production, t_0 is the start of the perturbation. Let us introduce the increments of variables

$$(20) \quad \begin{cases} {}^v r(t - \tau) = {}^v r - \tau({}^v r - {}^v r_0) / T, & {}^v r \equiv {}^v r(t), \quad {}^v r_0 \equiv {}^v r(t_0), \quad T \equiv t - t_0, \\ P^\pm(\tau) \equiv P_0(\tau) + p^\pm(\tau), \quad M(\tau) \equiv M_0(\tau) + m(\tau), \quad \dot{M}_0(\tau) = 0. \end{cases}$$

TABLE. I - The distribution of biomass and primary production vs. turnover times.

i	Land i = b					Ocean i = s				
	1	2	3	4	total	1	2	3	4	total
M_n , Gt C	1	50	500	1500	2100	0.3	4	0	2000	2000
P_n , Gt C y^{-1}	20	50	10	1	80	30	40	0	0.7	70
$b_n = P_n / P$	0.25	0.62	0.12	0.012	1	0.4	0.6	0	0.01	1
$\tau_n = M_n / P_n$, y	0.05	1	50	1500	25	0.01	0.1	—	3000	29

Note: $P = \sum_{n=1}^4 P_n$ is the gross and $\sum_{n=2}^4 P_n$ the net primary production. Biomass M_n and production P_n are labelled as follows: $n = 1$: consumption during plant respiration; $n = 2$: metabolically active and $n = 3$ metabolically passive (wood) parts of plants consumed by heterotrophs; $n = 4$: humus. $b(\tau) = \sum_{n=1}^4 b_n / \tau_n \cdot \exp[-\tau / \tau_n]$, $\sum_{n=1}^4 b_n = 1$, $\sum_{n=1}^4 b_n \tau_n = \bar{\tau}$. $b(\tau)$ does not depend on the ratio $\tau / \bar{\tau}$. Sources cited:

Continents: $P - P_1$ ⁽²¹⁾, $P_1/P = 0.3$ ⁽¹⁹⁾, τ_1 ⁽²²⁾; $M_2 + M_3$ ^(21,23), $P_2 + P_3$ ^(21,23), τ_2 ^(19,22), τ_3 ⁽⁵⁾, M_4 ^(21,23), τ_4 ⁽²⁴⁾.
 Ocean: $P - P_1$ ⁽²¹⁾, $P_1/P = 0.4$ ⁽¹⁹⁾, τ_1 ⁽²²⁾, M_2 ⁽¹⁹⁾, P_2 ^(10,11,19,25), M_4 ⁽²⁶⁾, τ_4 ⁽²⁷⁾.

It follows from the sum rule (16) that the data for land from^(23,25) lead to an unrealistically large value of $P - P_1 = 130$ Gt C y^{-1} and of $P = 200$ Gt C y^{-1} as well as $\bar{\tau} \approx 10$ y and $\tau_4 \approx 100$ y which are too low⁽²⁴⁾.

⁽²¹⁾ G. L. AJTAY, P. KETNER and P. DUVIGNEAUD: *Terrestrial primary production and phytomass*, in *The Global Carbon Cycle*, edited by B. BOLIN, SCOPE 13 (Wiley, Chichester, 1979), p. 129.

⁽²²⁾ V. G. GORSHKOV: *Ecology*, 1, 1 (1982), in Russian.

⁽²³⁾ J. S. OLSON, J. A. WATTS and L. J. ALLISON: *Carbon in live vegetation of mayor world ecosystem* (Unites State Department of Energy, TR004, 1983).

⁽²⁴⁾ O. A. CHYCHAGOVA: in *Evolution and Age of Soils* (Puschyno, USSR, 1986), p. 75, in Russian.

⁽²⁵⁾ V. G. GORSHOV: *Oceanology*, 24, 453 (1984), in Russian.

⁽²⁶⁾ M. KOPPER and E. T. DEGENS: *Organic carbon in the ocean: nature and cycling*, in *The Global Carbon Cycle*, edited by B. BOLIN, E. T. DEGENES, S. KEMPE and P. KETNER (J. Wiley & Sons, New York, N. Y., 1979), p. 451.

⁽²⁷⁾ R. M. WILLIAMS, M. C. STEINHOUSE, E. U. DRUFFEL and M. KOIDE: *Nature (London)*, 276, 698 (1978).

⁽²⁸⁾ W. R. EMMANUEL, G. G. KILLOUGH and J. S. OLSON: *Modelling the circulation of carbon in the world's terrestrial ecosystems*, in *Carbon Cycle Modelling*, edited by B. BOLIN, SCOPE 16 (Wiley, Chichester, 1981).

⁽²⁹⁾ W. R. EMMANUEL, G. G. KILLOUGH, W. M. POST and H. H. SHUGART: *Computer implementation of a globally averaged model of world carbon cycle*, U. S. Department of Energy, DOE/NBB-0062 (1984).

Here $P_0(\tau)$ is the stationary value of production and destruction. To obtain the total change in biomass for isotopes, ${}^v\dot{M}$, we integrate (17) over $d\tau$. Then in the linear approximation we have

$${}^v\dot{m} = {}^v\dot{m}_1 + {}^v\dot{m}_2,$$

$$(21) \quad {}^v\dot{m}_1 = \dot{m} {}^v r \approx \dot{m} {}^v r_0 \quad \dot{m} = p^+ - p^-,$$

$$(22) \quad {}^v\dot{m}_2 = P_0({}^v r - {}^v r_0) \alpha = P_0[{}^v r(t) - {}^v r(t - \bar{\tau})] A,$$

$$(23) \quad \alpha \equiv \frac{1}{T} \int_0^T \tau b(\tau) d\tau + \int_{\bar{\tau}}^{\infty} b(\tau) d\tau, \quad A \equiv \alpha T / \bar{\tau}.$$

The first term (21) is determined by the biotic reaction to the change in the ambient CO_2 . The second term (22) is present if only the environmental rare-isotope concentration changes, so that the total CO_2 is unperturbed and there is no biotic reaction, the ratio ${}^v\text{C}/\text{C}$ in the biota gradually catches up with its new environmental value. The respective biota-environment fluxes of rare isotopes, ${}^v\dot{m}_2$, remain appreciably large for about 1 y only. The isotopes commence to flow immediately after the disturbance and remain high, while the isotope composition changes in the metabolically active part of the biota which has a high turnover rate and low mass. A few years later these fluxes rapidly dwindle and a slow process of change of the isotopic composition in the massive part of the biota of low activity (wood, soil humus, dissolved oceanic organic matter) starts in its turn.

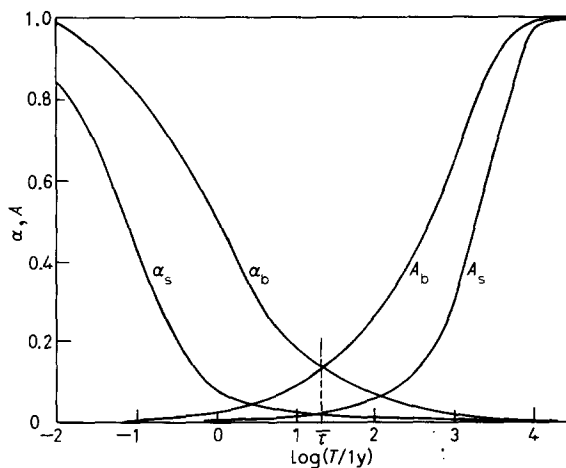


Fig. 1. - Reduction coefficients for biospheric absorption of carbon rare isotopes. $T \equiv t - t_0$ is the time lapse from the start of the perturbation t_0 ; $\bar{\tau}$ is the average turnover time for biomass. The values of α and $A \equiv \alpha T / \bar{\tau}$ are plotted according to data from table I.

The model of the distribution function, $b(\tau)$, corresponding to the empirical data for land and oceanic biota is presented in table I. For almost every empirical value presented in table I only its order of magnitude is certain (it is known to a factor of about 2). Practically, however, this does not affect the confidence level of the data in fig. 1 and of any further result in the present study.

The plots of α and A as calculated using the data in table I are presented in fig. 1. It may be seen that $\alpha < 0.2$ for $T > 0.5$ y for ocean and $T > 5$ y for land. The values of α , A and consequently ${}^v\dot{m}_2$ remain small if $\tau_4 \gg T \gg 1$ y. This is an intrinsic property independent of the model chosen. Also the factor $A \sim 1$ (see (23)) if $T \gg 1000$ y $\gg \bar{\tau}$ both for land and ocean. Therefore, τ in (19) must not be substituted by $\bar{\tau}$ (see above) if $T \leq 100$ y (cf. expression (23) from⁽⁸⁾).

5. - Absorption of the carbon rare isotopes by the ocean.

The value of the α_s for the oceanic biota is very small (fig. 1), so the rate of biomass change ${}^v\dot{m}_s$ is governed by the first term ${}^v\dot{m}_1$ (21). Therefore, we have for rare isotopes (see sect. 2 and (8))

$$(24) \quad {}^v\dot{m}_s = {}^v\dot{m}_s^+ + {}^v\dot{m}_s^- \quad \text{or} \quad {}^v\dot{x}_s = {}^v\dot{x}_s^+ + {}^v\dot{x}_s^-,$$

$$(25) \quad {}^v\dot{m}_s^+ = (\delta[\text{CO}_2]/R^+)S {}^v r_0^+ \quad \text{or} \quad {}^v\dot{x}_s^+ = {}^v k^+ x,$$

$$(26) \quad {}^v k^+ \equiv ({}^v h {}^v R^+)^{-1}, \quad {}^v R^+ \equiv R^+ \frac{{}^v r_0^-}{{}^v r_0^+} \equiv R^+(1 + {}^v \sigma^+), \quad {}^v h \equiv V_a {}^v \beta S,$$

$$(27) \quad {}^v\dot{m}_s^- = (\delta[\Sigma {}^v \text{CO}_2]/R_\Sigma)S \quad \text{or} \quad {}^v\dot{x}_s^- = {}^v k^- {}^v x_\Sigma,$$

$$(28) \quad {}^v k^- \equiv ({}^v h {}^v R^-)^{-1}, \quad {}^v R^- \equiv R_\Sigma {}^v \phi_0 \equiv R^-(1 + {}^v \sigma^-), \quad {}^v \phi_0 \equiv \frac{[\Sigma {}^v \text{CO}_2]_0}{[{}^v \text{CO}_2]_0},$$

$$(29) \quad \phi' \phi \equiv ([{}^v \text{CO}_2]/[\text{CO}_2])/([\Sigma {}^v \text{CO}_2]/[\Sigma \text{CO}_2]) \equiv {}^v r^- / r_\Sigma \equiv 1 + {}^v \sigma^-.$$

Note that the biotic reaction (25) depends on the value of x but not on ${}^v x$: the biota cannot sense the change in rare isotopes. Here the magnitude of the resistance R_Σ is determined by the eddy diffusion and hence is the same for any carbon isotope. The ratio (29) is available from the empirical data⁽¹⁸⁾. It may be shown⁽²⁰⁾ that, to a relative error of about 10^{-2} , the correction ${}^v \sigma^-$ does not depend on x . Since ${}^v \sigma^-$ is constant, we obtain from (29) and (11) the Bolin-

⁽²⁰⁾ V. G. GORSHOV: *Antropogenic disturbance of the global carbon cycle*, Leningrad Nuclear Physics Institute, Preprint No. 1241 (1986), p. 1.

Ericsson equation (7)

$$(30) \quad {}^v x_{\Sigma} = {}^v x - x + x/\zeta.$$

From (30) we obtain that *a*) the buffering effect is absent for the rare isotopes if only the rare isotopes are perturbed in the ocean, *i.e.* ${}^v x_{\Sigma} = {}^v x$ at $x = 0$ (compare to eqs. (11)), *b*) the rare isotopes are strongly perturbed if only the natural isotope is perturbed in the ocean and there is no direct perturbation of the rare isotopes (Bolin-Ericsson effect), *i.e.* ${}^v x_{\Sigma} \approx x$ at $x \neq 0$ and ${}^v x_{\Sigma} \ll {}^v x$ (the latter inequality follows from the large value of ${}^v \phi$ (28), (29), (10)). According to (30), it is convenient to introduce the differential variables (8)

$$(31) \quad {}^v z \equiv {}^v x - x, \quad {}^v z_i \equiv {}^v x_i - x_i, \quad i = a, b, f, s.$$

The correction on fractionation ${}^v \sigma_{\beta}$ for ${}^v \beta \equiv \beta(1 + {}^v \sigma_{\beta})$ and ${}^v h$ is far smaller than the correction ${}^v \sigma^{\pm}$ (13), so we may neglect it. Introducing (30) into (27) and subtracting (7) from (24) term, by term, we obtain

$$(32) \quad {}^v \dot{z}_s = k^- {}^v z - ({}^v \sigma^+ k^+ + {}^v \sigma^- k^- / \zeta) x.$$

The net absorption flux of the carbon rare isotopes passing through the ocean-atmosphere interface is similar to (6). The fractionation correction ${}^v \sigma_a$ for ${}^v R_a \equiv R_a(1 + {}^v \sigma_a)$ is also small in comparison with ${}^v \sigma^{\pm}$ (13), so we may neglect it together with those for ${}^v \beta$ and ${}^v h$. Thus we obtain

$$(33) \quad {}^v \dot{z}_s = k_a ({}^v z_a - {}^v z).$$

Excluding the value ${}^v z$ from (32) and (33) and using (15), we have

$$(34) \quad {}^v \dot{z}_s = k_s^* {}^v z_a - {}^v \sigma k_s x_a,$$

$$(35) \quad k_s^* \equiv [k_a^{-1} + (k^-)^{-1}]^{-1} \quad (k_s^* \equiv (hR^*)^{-1}, \quad R^* \equiv R_a + R^-),$$

$$(36) \quad {}^v \sigma \equiv (k_s^*/k^- k) ({}^v \sigma^+ k^+ + {}^v \sigma^- k^- / \zeta),$$

$$(37) \quad 0 \leq k_s \leq k_a, \quad 0 \leq k_s^* \leq k_a.$$

Here k is determined in (12). It may be seen from eq. (35) that the value k_s^* remains the same for ^{13}C and ^{14}C . The restrictions (37) follow from the positiveness of R^+ and R^- or k^+ and k^- .

Relationships (6), (12), (13), (32)-(43) may be visualized as «Ohm law for electrical circuitry» (fig. 2). The values x and ${}^v z$ play the role of circuitry potentials and the resistance R_i the role of loads.

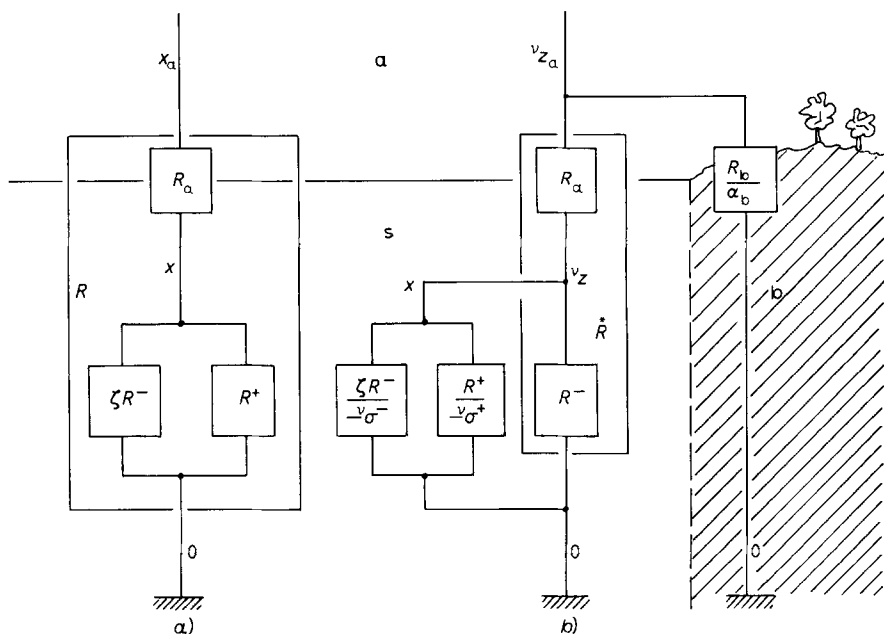


Fig. 2. – Oceanic absorption of carbon. a) Absorption of the principal isotope, ^{12}C : x_a and x are the relative variations of CO_2 concentration in the atmosphere and ocean, respectively; R^+ , R^- and R_a the resistances to organic (R^+) and inorganic (R^-) carbon absorption by ocean and penetration of CO_2 through the air-sea interface (R_a); ζ is the buffer factor. b) Absorption of rare isotopes: vz_a and vz , respectively, atmospheric and oceanic variations of $\delta^{13}\text{C}$; $v\sigma^+ > 0$, $v\sigma^- < 0$ fractionation corrections for resistances $vR^\pm \equiv R^\pm(1 + v\sigma^\pm)$; $R_b \equiv (h k_{b0})^{-1}$ (41) is the effective resistance to absorption CO_2 by land biota.

6. – Budget equation for carbon isotopes.

The equation of budget of carbon may be written in the forms⁽¹¹⁾ (see sect. 2 for notations)

$$(38) \quad \begin{cases} \dot{m}_a + \dot{m}_f + \dot{m}_b + \dot{m}_s = 0 & \text{or} & \dot{x}_a + \dot{x}_f + \dot{x}_b + \dot{x}_s = 0, \\ \dot{x}_i \equiv \dot{m}_i / M_{a0}, & & M_{a0} = (570 \pm 20) \text{ Gt C }^{(11)}. \end{cases}$$

For rare isotopes the budget equations (38) may be written in differential variables, cf. (31):

$$(39) \quad v\dot{z}_a + v\dot{z}_f + v\dot{z}_b + v\dot{z}_s = 0.$$

To interpret their physical meaning we recall that in the atmosphere

$$(40) \quad \left\{ \begin{array}{l} {}^{\nu}r_a \equiv \frac{[{}^{\nu}\text{CO}_2]_{a0} + \delta[{}^{\nu}\text{CO}_2]_a}{[\text{CO}_2]_{a0} + \delta[\text{CO}_2]_a} = {}^{\nu}r_{a0}(1 + {}^{\nu}z_a), \\ i.e. \\ {}^{\nu}z_a = ({}^{\nu}r_a - {}^{\nu}r_{a0})/{}^{\nu}r_{a0} = \Delta\delta{}^{\nu}C_a = \Delta\delta{}^{\nu}C_b. \end{array} \right.$$

In accordance with the common definition, $\delta{}^{\nu}C_a \equiv {}^{\nu}r_a/{}^{\nu}r_s - 1$; ${}^{\nu}r_s$ is the ratio of the isotope concentration as given by the international standards⁽³¹⁾. The differences $\Delta\delta{}^{\nu}C_a$ may be substituted by $\Delta\delta{}^{\nu}C_b$ for tree rings (40). The latter relation is a consequence of the constancy of ${}^{\nu}\sigma_b$ ^(9,13), see (1).

We have for fossil fuel (see (3), (31))

$$(41) \quad {}^{\nu}\dot{z}_f \equiv -{}^{\nu}\sigma_f \dot{x}_f.$$

The land biota yield (we account for both terms in (20) and (21), see also (2))

$$(42) \quad \begin{aligned} {}^{\nu}\dot{z}_b &= -{}^{\nu}\sigma_b \dot{x}_b + k_b {}^{\nu}z_a, \\ k_b &\equiv \alpha_b k_{b0}, \quad k_{b0} \equiv P_0/M_{a0} = (0.14 \pm 0.03) \text{ y}^{-1}. \end{aligned}$$

For the definition of α_b see (22) and fig. 1. The value of k_{b0} was calculated from data in table I.

Using (13), (34), (40)-(42), we express the budget equations (38), (39) as follows:

$$(43) \quad \dot{x}_a = -\dot{x}_f - \dot{x}_b - k_s x_a,$$

$$(44) \quad {}^{\nu}\dot{z}_a = {}^{\nu}\sigma_f \dot{x}_f + {}^{\nu}\sigma_b \dot{x}_b - K {}^{\nu}z_a + {}^{\nu}\sigma k_s x_a,$$

$$(45) \quad K \equiv k_s^* + k_b.$$

7. - Retrieval of constant k_s^* form the data on ^{14}C .

The half-life of ^{14}C is 5730 y and ^{14}C may be seen as a stable isotope for a time period of the order of 100 y. The fossil carbon does not contain ^{14}C , *i.e.* ${}^{14}\sigma_f = 1$. At

⁽³¹⁾ M. STUIVER and H. POLLACH: *Radiocarbon*, 19, 355 (1977).

the same time $^{14}\sigma_b \sim ^{14}\sigma \leq 3 \cdot 10^{-2}$. Therefore, the second and fourth terms in the right-hand side of (44) may be omitted in the case $\nu = 14$. As a result we have

$$(46) \quad \Delta \delta^{14}C_b = \dot{x}_f - K \Delta \delta^{14}C_b \quad \text{or} \quad \Delta \delta^{14}C_b = x_f - K \int_{t_0}^t \Delta \delta^{14}C_b dt'.$$

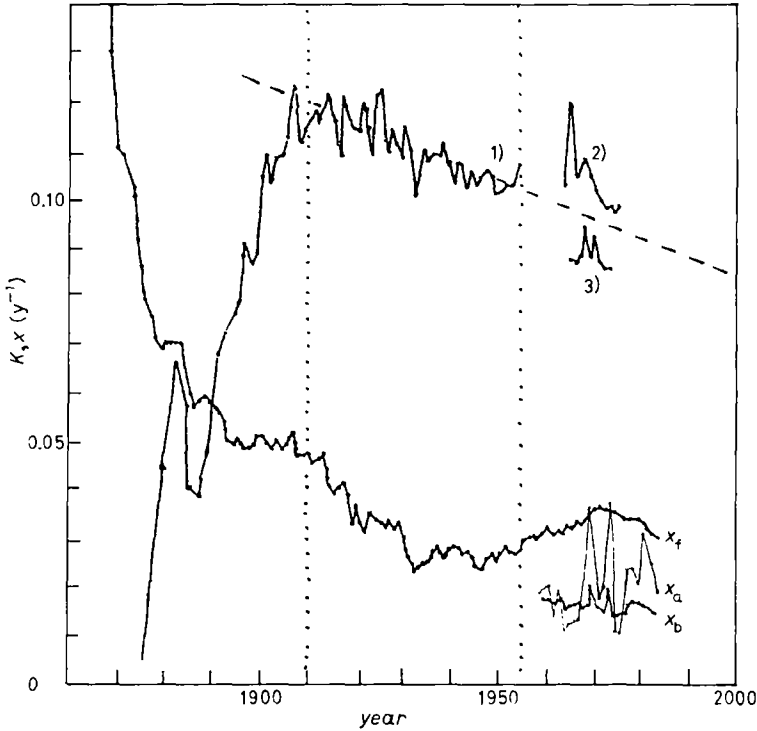


Fig. 3. - The coefficient K (46) for absorption of carbon isotopes from the atmosphere. Broken lines interconnect experimental annual averages. 1) are the values of K as obtained from the magnitude of the Suess effect⁽³²⁾. Prior to $t_1 = 1910$ y (dash-dots) the input from fossil fuel is impossible to trace against the natural fluctuations. This is also the case after $t_2 = 1953$ y when atmospheric nuclear tests commenced on full scale. The dotted line presents the point-to-point linear regression over the interval $[t_1, t_2]$ plotted according to the equation $K = (0.101 \pm 0.008) y^{-1} [1 - (0.17 \pm 0.016) \cdot (t - t_2) / \Delta t]$. Here $\Delta t \equiv t_2 - t_1 = 44$ y and the errors correspond to standard deviations. Extrapolating this regression forward up to $t_3 = t_2 + \Delta t = 1998$ y we may assess $K = (0.10 \pm 0.02) y^{-1}$ over the whole interval $[t_1, t_3]$. 2), 3) are the values of K as yielded by the data on atmospheric nuclear tests Nordcapp and Mas Palomas stations, respectively, after⁽³³⁾. Relative rates of carbon variation in the i -th reservoir $x_i \equiv \dot{m}_i / m_i$, $i = f, a, b$ are plotted after x_f ⁽²⁸⁾, x_a Mauna Loa⁽⁷⁾, x_b budget equation (43) with k_b borrowed from (56). Averages for (1958-1980) are as follows: $\bar{x}_f = (0.034 \pm 0.021) y^{-1}$, $\bar{x}_a = (0.019 \pm 0.0073) y^{-1}$, $\bar{x}_b = (0.017 \pm 0.0014) y^{-1}$. Note that \bar{x}_f is almost twice as large as \bar{x}_a .

⁽³²⁾ M. STUIVER and P. D. QUAY: *Earth Planet. Sci. Lett.*, 53, 349 (1981).

⁽³³⁾ R. NYDAL and K. LÖVSETH: *J. Geophys. Res.*, 88, 3621 (1983).

Equation (46) makes it possible to retrieve the coefficient K from the empirical data. The measurements of $\Delta\delta^{14}\text{C}_b$ variations in tree rings⁽³²⁾ and x_f in fossil fuel emissions^(2,3) yield the following value of K (see fig. 3) (and⁽³⁰⁾ for details):

$$(47a) \quad K = (0.10 \pm 0.020) \text{y}^{-1}.$$

It may be obtained also from the data on variations of $\delta^{14}\text{C}_a$ in the atmosphere following nuclear tests⁽³³⁾. An all-station average yields (see⁽³⁰⁾ for details)

$$(47b) \quad K = (0.085 \pm 0.016) \text{y}^{-1}.$$

Both values (47a), (47b) lie within their standard deviation limit. Within this limit they are of the order of k_{b0} (42). Therefore, if $T > (3 \div 5) \text{y}$, then the time-dependent value of k_b may be neglected in (45), (46) since α_b is small (42), cf. fig. 1. Hence within the error limit of (47a), (47b) we may consider

$$(48) \quad K = k_s^*.$$

8. - Retrieval of the constant k_s from the data on ^{13}C .

The air-sea penetration constant for CO_2 , k_a , is measured directly⁽¹⁴⁾. According to^(11,15) its value is

$$(49) \quad k_a = (0.11 \pm 0.023) \text{y}^{-1}.$$

Within the error limit the constants k_a , k_s^* do not differ from each other. We deduce that $k_a < k^-$, see (35).

For ^{13}C all the terms in (44) are of the same order of magnitude. This equation may then be used to retrieve the constant k_s from the empirical data. The isotopic fractionation corrections for ^{13}C have the following values^(9,13,18,34):

$$(50) \quad {}^{13}\sigma_b \approx {}^{13}\sigma_f = (18 \pm 1)\text{‰}, \quad {}^{13}\sigma^- = -9\text{‰}, \quad {}^{13}\sigma^+ = (16 \pm 2)\text{‰}.$$

The measurements of x_a started only in 1958⁽¹⁴⁾. On the other hand, decadal means of $\delta^{13}\text{C}_b$ are available⁽³⁵⁻³⁷⁾. Thus we have only two points at which to apply

⁽³⁴⁾ I. G. ENTING and G. I. PEARMAN: *Description of one-dimensional global carbon cycle model*, CSIRO Aust. Div. Atmos. Phys. Techn., Paper No. 42 (1982), p. 1.

⁽³⁵⁾ H. D. FRAYER and N. BELACY: *J. Geophys. Res.*, 88, 6844 (1983).

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⁽³⁷⁾ E. R. DRUFFEL and L. M. BENAVIDES: *Nature (London)*, 321, 58 (1986).

eq. (44) and present only two (1960-1980) bidecadal averages of the measured variables. According to direct atmospheric measurement data⁽³⁸⁻⁴⁰⁾, $\delta^{13}C_a = -3.0 \cdot 10^{-5} y^{-1} (-0.03\% y^{-1})$. Using the data from Mauna Loa^(1,4) and the data on M_{a0} (38)^(11,41), we obtain $\bar{x}_a = 0.21$, $\bar{x}'_a = 0.0040 y^{-1}$. There exist two statistics for $\Delta\delta^{13}C$. For free-standing tree (FST) we have $\overline{\Delta\delta^{13}C_b} = 1.55 \cdot 10^{-3} (-1.55\%)$ ⁽³⁵⁾; on the other hand, the total tree population (TTP), including forest trees, yields $\overline{\Delta\delta^{13}C_b} = -0.5 \cdot 10^{-3} (-0.5\%)$ ^(9,36). The latter data were obtained also in the ocean⁽³⁷⁾, $\Delta\delta^{13}C_a = -1.1\%$ for ice core data⁽⁴¹⁾.

Expressing the variables k^- and k^+ in $^{13}\sigma$ (36) through k_s (14) and k_s^* (35), we finally obtain from the budget equation (44) the following relationship:

$$(51) \quad Z \equiv k_s/k_a = \frac{1 - \gamma a Y}{1 - b Y}, \quad Y \equiv \frac{\zeta}{c^+ - c^-}, \quad X \equiv \frac{k_a}{k_s^*} - 1,$$

$$(52) \quad \gamma \equiv \frac{K}{k_s^*}, \quad c^\pm \equiv \frac{^{13}\sigma^\pm}{^{13}\sigma_b}, \quad b \equiv 1 + X(1 - c^+),$$

$$(53) \quad a \equiv \frac{-\delta^{13}C_b - K\Delta\delta^{13}C_b - ^{13}\sigma_b \dot{x}'_a}{^{13}\sigma_b K x_a}.$$

For relative variables Z and X (51), (53) the restrictions (37) have the form

$$(54) \quad 0 \leq Z \leq 1, \quad X \geq 0.$$

Expressions (51)-(53) are valid for all the values of α_b or γ . In the case $\alpha_b \ll 1$, $\gamma = 1$, fig. 1, all the variables in (53) are known from empirical data:

$$(55) \quad \begin{cases} X = 0.1^{+0.3}_{-0.1} & \text{or} & 0 \leq X \leq 0.4, \\ c^+ = 0.9 \pm 0.1, & c^- = -0.5 \pm 0.06, & \zeta = 10 \pm 1, \\ a = a_1 = 0.30 \pm 0.04 \text{ (FST)}, & a = a_2 = 0.024 \pm 0.006 \text{ (TTP)}, \end{cases}$$

$$a = a_3 = 0.18 \text{ (ice core data}^{(41)}).$$

⁽³⁸⁾ H. S. GOODMAN: *The $^{13}C/^{12}C$ ratio of atmospheric carbon dioxide at the Australian baseline station Cape Grim*, in *Carbon Dioxide and Climate: Australian Research*, edited by G. I. PEARMAN (CSIRO, Melbourne, 1980).

⁽³⁹⁾ C. D. KEELING, W. G. MOOK and P. P. TANS: *Nature (London)*, **277**, 121 (1979).

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⁽⁴¹⁾ O. SIEGENTHALER, H. OESCHGER: *Tellus B*, **39**, 140 (1987).

From (51), (55) we have

$$(56) \quad \begin{cases} Z \equiv k_s/k_a = a \leq 0.30, & k_s \leq 0.033y^{-1}, \\ k^-/\zeta k_a \equiv 1/X\zeta \geq 0.25, \\ k^+/k_a \equiv Z/(1-Z) - 1/X\zeta \leq 0.18, \\ k^+/(k^-/\zeta) \leq 0.72. \end{cases}$$

Thus the inorganic carbon absorption (k^-/ζ) by the ocean is larger than the biotic one (k^+). The result (56) contradicts the presence of large biotic carbon absorption by the ocean ($k^+ \gg k^-/\zeta$)⁽¹¹⁾. For ice core data⁽⁴¹⁾ we have $k_s = 0.02y^{-1}$ and $\dot{m}_b = 0.8\text{Gt C/y}$ (at $\dot{m}_a = 3\text{Gt C/y}$ ⁽⁴⁾, $\dot{m}_t = 5\text{Gt C/y}$ ⁽³⁾, $m_a = 140\text{Gt C}$ ⁽⁴¹⁾) in good agreement with the result of the box and outcrop diffusion models⁽⁴¹⁾.

* * *

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● RIASSUNTO (*)

Si dimostra che l'assorbimento netto di CO_2 da parte di tutti gli oceani dipende linearmente dall'aumento di CO_2 nell'atmosfera, a cominciare dal suo livello pre-industriale stazionario. Il rispettivo coefficiente di proporzionalità si deduce dai dati sulle variazioni di ^{13}C e ^{14}C negli anelli degli alberi, e il suo valore corrisponde ad una piccola perturbazione del carbonio della biosfera.

(*) Traduzione a cura della Redazione.

Возмущение глобального круговорота углерода: изменение содержания углерода в наземной и океанической частях биосферы.

Резюме. — С помощью данных по изменению отношения $^{13}\text{C}/^{12}\text{C}$ и $^{14}\text{C}/^{12}\text{C}$ в атмосфере и древесных кольцах показано, что выбросы углерода в атмосферу из наземной части и поглощение углерода из атмосферы океанической частью биосферы не превосходят выбросы ископаемого топлива. Углеродосодержание биосферы в целом остается практически неизменным.