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Measurements of concentration, $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios of tropospheric carbon dioxide over Switzerland

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ABSTRACT

In 1982, we collected air sample profiles approximately monthly from aircraft at altitudes up to about 7 km and analyzed them for CO_2 concentration and stable isotope composition. The following seasonally detrended mean values were obtained per 1 January, 1982: 338 ppm, $\delta^{13}C = -7.72‰$, $\delta^{18}O = -0.6‰$ (versus PDB); isotopic results are corrected for N_2O contribution. CO_2 results are discussed in terms of vertical eddy diffusion and of a mean annual vertical flux. Assuming a two-component mixture between background air and biospheric CO_2, $\delta^{13}C$ of the biospheric component is $-26.2‰$, in good agreement with other northern hemisphere results. $\delta^{18}O$ varies seasonally, but with relatively much scatter. The oxygen isotopic composition of CO_2 is determined by exchange with vegetation, soils and ocean; these processes are discussed in detail.

1. Background

In continuation of tropospheric CO_2 concentration measurements over Switzerland (Zumbrunn et al., 1983), we collected air samples from an airplane at different altitudes in 1982, at about monthly intervals. The 10 profiles extended to an altitude of about 7 km a.s.l. The main purpose was to get information about annual means and seasonal variations of CO_2 concentration, $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios. The results are presented here and discussed with respect to atmospheric mixing and surface sources and sinks of CO_2.

2. Experimental methods

The air samples were taken from a small aircraft, Pilatus Porter. Evacuated 1 l glass-bottles with O-ring valves (Louwers-Hapert) were filled with ambient air through a flexible teflon tube mounted on one wing of the airplane. In the laboratory, the CO_2 concentration was first determined with an infra-red laser spectrometer (IRLS) (Zumbrunn et al., 1983), with a precision of 0.8 ppm.

For the mass-spectrometric isotope analysis, CO_2 was extracted cryogenically in a glass vacuum line. The air sample of typically 500 ml STP was first expanded, after freezing out water vapour at dry ice temperature, into a 10 l volume and then pumped slowly with constant flow through a liquid nitrogen trap where CO_2 was frozen out quantitatively. Amounts of air and CO_2 were determined volumetrically, so the CO_2 concentration could be calculated with a precision of 1.3 ppm. These concentration values were systematically higher by about 4 ppm than the laser spectrometer results, although comparisons of standard gas measurements with both methods did not show such deviations. The reason for this difference is not clear. The presence of other condensable gases or incomplete removal of water vapour cannot be ruled out, although the latter should contribute only about 0.6 ppm if the saturation vapour pressure at $-77°C$ is achieved in the cool trap. The CO_2 data presented below are the laser spectrometer results.

The CO_2 sample, typically 150 μl STP, was transferred to a triple-collector mass-spectrometer, type MAT 250, where $\delta^{13}C$ and $\delta^{18}O$ were measured simultaneously. To obtain reliable results, it is essential to keep the extraction and

separation systems and the gas containers thoroughly clean from organic vapours and water. We tested the whole procedure with a standard gas. The results indicate an overall precision of extraction and mass-spectrometric analysis of 0.06‰ for $\delta^{13}C$ and 0.3‰ for $\delta^{18}O$.

3. Results

The raw data set was prepared for further analysis in the following way: first, obvious outliers were excluded. Then a constant secular trend was subtracted, normalizing all data to January 1, 1982. For CO_2, an annual increase of 1.5 ppm/yr is assumed; for $\delta^{13}C$ the assumed trend is -0.032 permil/yr, as obtained from a model of the global carbon cycle (Siegenthaler and Oeschger, 1987). Isotopic results were corrected for the influence of N_2O, as indicated by Mook and van der Hoek (1983); our own experiments with N_2O–CO_2 mixtures support their results. The $\delta^{13}C$ and $\delta^{18}O$ results were correspondingly corrected by adding 0.22‰ and 0.30‰, respectively. The whole following discussion is based on data detrended and corrected in this way.

In Table 1, annual mean and (half-)amplitude of the CO_2 concentration (trend-adjusted to 1/1/82) are listed together with the corresponding values of other stations. Annual mean and amplitude are calculated by means of a least square fit of a sine function at $h = 3$ km. The amplitude of 6.6 ppm is well comparable with the amplitude of 7 ppm at the station Schauinsland, FRG (48° N, 1200 m a.s.l) (Levin, 1987).

4. One-dimensional eddy diffusion

One-dimensional vertical mixing can be approximately described by eddy diffusion, as done by Bolin and Bischof (1970) and Machta (1974) for vertical CO_2 profiles. The CO_2 distribution $C(z, t)$ will be governed by the equation

$$\frac{\partial C(z,t)}{\partial t} = \frac{1}{\rho(z)} \cdot \frac{\partial}{\partial z}\left(\rho(z) \cdot K \frac{\partial C(z,t)}{\partial z}\right), \tag{1}$$

where K denotes the eddy diffusivity and $\rho(z)$ the density of air. We assume K constant. With $\rho = \rho_0 e^{-z/z_0}$, $\rho_0 = 1.29$ kg m^{-3}, $z_0 = 9.1$ km; with a cosine-shaped source at the earth surface the solution of (1) is given by the real part of

$$C(z,t) = C_0(z) + C_1 \times \exp\left[-\left(\alpha - \frac{1}{2z_0}\right) z + i(\omega t + \varphi_0 - \beta \cdot z)\right] \tag{2}$$

C_0 denotes the annual mean CO_2 concentration, C_1 the seasonal amplitude at $z = 0$, $\omega = 2\pi$ yr^{-1}, φ_0 the phase at $z = 0$. α and β are real constants for which we obtain by inserting eq. (2) into eq. (1): $\alpha + i\beta = [(1/2z_0)^2 + i\omega/K]^{1/2}$. For estimating K, each profile was subdivided into 500 m intervals and a concentration value assigned to the center of each interval by interpolation. Then, a sine function was fitted through the observed data at each altitude interval, yielding mean value, amplitude and phase as a function of the altitude; the results are shown in Figs. 1a, b. Linear regression analyses of log (amplitude) and of phase versus altitude allow us to estimate all parameters of the harmonic term of eq. (2) (data above 6.5 km are excluded):

Table 1. *Parameters of tropospheric CO_2 derived from profiles taken over Switzerland and for two stations from other authors*

	Switzerland	Schauinsland (FRG)[1]	Mauna Loa
Annual mean CO_2 concentration (ppm)	337 ± 0.3	341	340.1[2]
Amplitude (ppm)	6.6	~7	3.3[2]
Annual mean $\delta^{13}C$	-7.72 ± 0.02		-7.59[3]
Regression end member $\delta^{13}C_1$ (‰)	-25.4 ± 0.6	-25.7	-24.9 ± 1.4[4]

Annual mean values are per January 1, 1982. $\delta^{13}C$ values are corrected for N_2O.
[1] Levin (1987); [2] C. D. Keeling, 1985, pers. comm.; [3] Mook et al. (1983); [4] M. Heimann, C. D. Keeling and W. G. Mook, 1985, pers. comm.

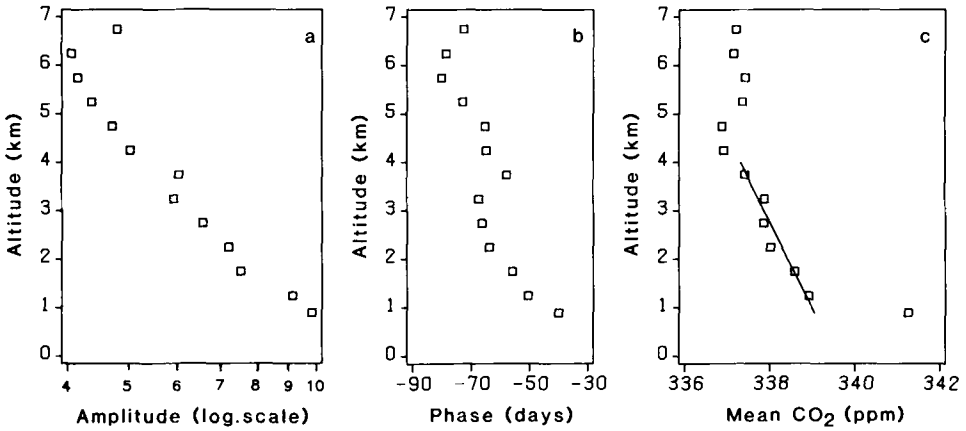

Fig. 1. (a) Amplitude (in ppm, log. scale), (b) phase (in days, $t = 0$ corresponds to 1/1/82), and (c) annual mean concentration (in ppm) of atmospheric CO_2 as a function of altitude (km). Values determined from sine fits, see text.

C_1 $= (11.2 \pm 0.3)$ ppm;
α $= 0.23 \pm 0.01$ km^{-1};
β $= 0.10 \pm 0.02$ km^{-1};
φ_0 $= -43° \pm 4°$;
K $= (1.94 \pm 0.16) \cdot 10^4$ cm^2 s^{-1} (from amplitude, i.e., from α and z_0);
K $= (9.0 \pm 3.7) \cdot 10^4$ cm^2 s^{-1} (from phase, i.e., from β and z_0);
$K_{mean} = (2.0 \pm 0.6) \cdot 10^4$ cm^2 s^{-1} (weighted with $1/\sigma^2$).

The indicated error limits denote the standard errors of the estimates. The large error limit for the second estimate of K stems from the large scatter of the phase versus altitude relation (Fig. 1b); the seasonal phase lag is apparently not as well defined in our data as the amplitude. If the calculation is carried out with the approximation of constant density, as e.g., done by Bolin and Bischof (1970), a larger value of K results; for our data, the result derived from the amplitude decrease would be $3.2 \cdot 10^4$ cm^2 s^{-1}.

Our result of $2 \cdot 10^4$ cm^2 s^{-1} is rather small compared to literature values. Machta (1974) found $5 \cdot 10^4$ cm^2 s^{-1}; other authors generally have given values of $1 \cdot 10^5$ to $3 \cdot 10^5$ cm^2 s^{-1} for the troposphere (see, e.g., Johnston et al., 1976). A possible reason is that the one-dimensional approach is a bad approximation, because the lower atmospheric layers are more strongly influenced by regional continental CO_2 sources and sinks than the upper layers. This leads to steeper gradients over the continent than in the case of horizontal homogeneity. The annual mean CO_2 concentration, $c_0(z)$, decreases with altitude (Fig. 1c), which indicates the existence of a net flux F of CO_2 into the atmosphere. Regression analysis on the C_0 data between 1000 and 4000 m altitude (solid line in Fig. 1c) yields a mean gradient of $-(0.56 \pm 0.8)$ ppm km^{-1}. The corresponding mean annual flux $F = -K\rho(dC_0/dz)$ is (15 ± 3) g C m^{-2} yr^{-1}, using $K = (2.0 \pm 0.6) \cdot 10^4$ cm^2 s^{-1} and a mean density of 0.87 kg m^{-3}. This should roughly correspond to the net release of fossil CO_2 over the continents in mid-latitudes. Rotty and Marland (1984) indicate a total global fossil CO_2 production of 5.1 Gt C in 1982, of which 89% are released in the latitude band 20° N to 60° N (Rotty, 1983). Our estimate for F corresponds to 0.93 Gt C yr^{-1} over the land area in this latitude band of $62 \cdot 10^{12}$ m^2, which is significantly lower, again indicating that our eddy diffusion coefficient may be too low. For obtaining a flux of 5.1 Gt C yr^{-1}, a K value of $9.5 \cdot 10^4$ cm^2 s^{-1} would have to be assumed.

The net CO_2 exchange between biosphere and atmosphere can be derived from the profiles of 8 March and 1 September, corresponding to the maximum and the minimum CO_2 content, respectively, of the atmosphere during the year. The difference of the column inventories corresponds to a withdrawal of 3.7 Gt C. Pearman and Hyson (1980) determined by means of a two-dimensional atmospheric model the net biospheric fluxes necessary to reproduce observed CO_2 concentration. According to their Table 5,

the net flux into the biosphere during the growing season is 3.8 Gt C in the belt 20–60°N, with which our estimate agrees well.

5. Carbon-13 results

The annual mean $\delta^{13}C$ value per 1 January, 1982, calculated by means of a least square fit of a sine function at $z = 3$ km, is -7.72 ± 0.02‰ (corrected for N_2O effect). This fits perfectly the latitude dependence of $\delta^{13}C$ in the northern hemisphere given by M. Heimann, C. D. Keeling and W. G. Mook (1985, personal communication) after correcting their values for the N_2O effect. Inter-laboratory comparison of results from isotope standard measurements indicates that our calibration agrees to better than 0.10‰ with that of Mook who measured the other data mentioned here.

Fig. 2 shows the seasonal variation of $\delta^{13}C$ (detrended), averaged over altitude from 2 km to the top of the profiles. Numerical data are given in Table 1. Under the assumption that this seasonal variation is only due to biospheric release and uptake of CO_2, i.e., mixing of atmospheric and biospheric CO_2 (with $\delta^{13}C_l$), the following relation should hold:

$$\delta^{13}C = M/C + \delta^{13}C_l \quad (3)$$

where C (CO_2 concentration) and $\delta^{13}C$ are observed values in the atmosphere, and $\delta^{13}C_l$ is the value for biospheric CO_2. Eq. (3) follows from the CO_2 and $^{13}CO_2$ balances for the addition of the seasonal biosphere signal (C_l, $\delta^{13}C_l$) to the mean annual (detrended) background CO_2 (C_a, $\delta^{13}C_a$):

$$C = C_a + C_l \quad (4)$$

$$C \cdot \delta^{13}C = C_a \cdot \delta^{13}C_a + C_l \cdot \delta^{13}C_l. \quad (5)$$

Inserting $C_l = C - C_a$ from eq. (4) into eq. (5) leads to eq. (3), with $M = C_a(\delta^{13}C_a - \delta^{13}C_l)$.

Fig. 3 shows the correlation of $\delta^{13}C$ with CO_2 concentration. Regression analysis of $\delta^{13}C$

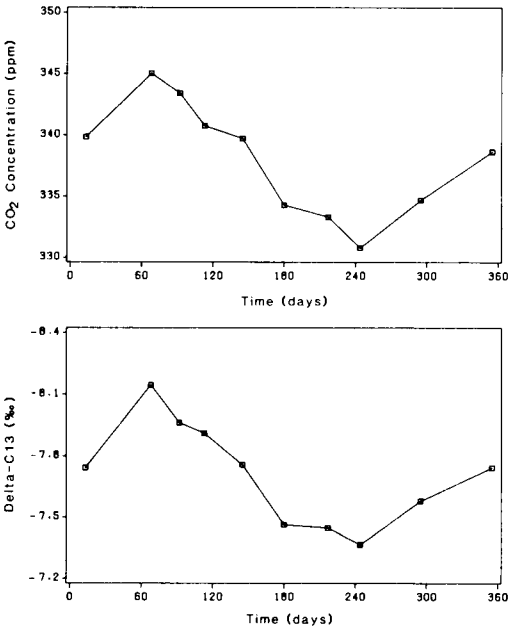

Fig. 2. Mean values for the interval 2 to 8 km of the CO_2 concentration (in ppm, top) and of $\delta^{13}C$ of CO_2 (‰ against PDB, N_2O corrected; bottom). All data are long-term detrended (see text). Horizontal axis: day of the year 1982.

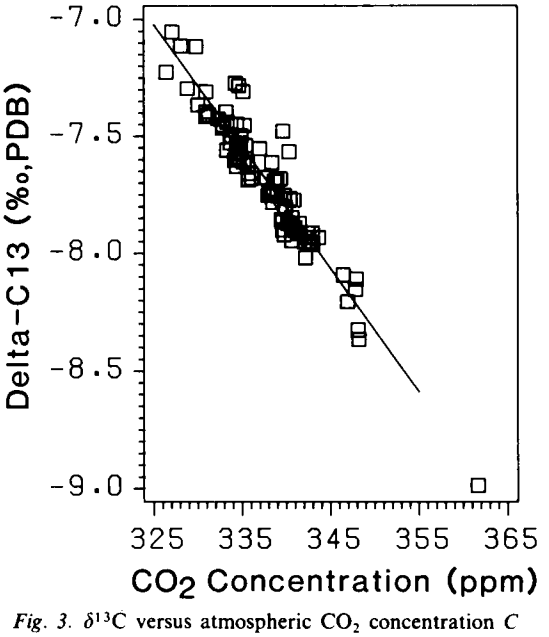

Fig. 3. $\delta^{13}C$ versus atmospheric CO_2 concentration C (in ppm) for the individual results (average value if two samples were taken at the same altitude) of all 10 profiles. All data are long-term detrended. Solid line: regression line of $\delta^{13}C$ against $1/C$. Standard deviation of residues: 0.09‰.

versus $1/C$ yields $M = 6024 \pm 216‰ \cdot$ppm, $\delta^{13}C_I = -25.5 \pm 0.6‰$ and a correlation coefficient $r = 0.95$. The value for $\delta^{13}C_I$ is in good agreement with the result of Levin (1987) for Station Schauinsland (FRG), $-25.7‰$, and with the mean $\delta^{13}C_I$ of four northern hemisphere stations (M. Heimann, C. D. Keeling and W. G. Mook, 1985, personal communication) of $-25.6 \pm 0.9‰$; it corresponds to the mean composition of plants. In principle, the oceanic contribution to the seasonal cycle should be corrected for; in the northern hemisphere the effect is, however, small, as seen by a simple estimate. If the northern hemisphere atmosphere is considered as a well-mixed reservoir (mass of air: M_{atm}), then its CO_2 concentration C varies, in response to exchange with the ocean according to

$$M_{atm} \frac{dC}{dt} = M_{atm}(C_s - C)/\tau_{as}. \quad (6)$$

The right-hand side is the net flux from the ocean, C_s the equilibrium partial pressure of CO_2, pCO_2, in surface water, and $\tau_{as} \approx 8$ yr is the atmospheric residence time of CO_2. If the seasonal part of C_s varies as $\sin \omega t (\omega = 2\pi\ \mathrm{yr}^{-1})$, then the atmospheric concentration is also found to vary sinusoidally, with an amplitude attenuated by the factor

$$[1 + (\omega\tau_{as})^2]^{-1/2} \quad (7)$$

and with a phase shift given by

$$\text{arc tg}\ (\omega\tau_{as}). \quad (8)$$

Numerically, this leads to an attenuation factor of 0.02 and a lag time of 18 days. The strong attenuation arises because the characteristic time for the seasonal signal, $\omega^{-1} = 0.16$ yr, is much smaller than the atmospheric residence time τ_{as} of CO_2. Weiss et al. (1982) observed surface water pCO_2 variations at 15–20°N and 14–17°S with peak-to-peak amplitudes of 21 and 16 ppm. If we assume that the average hemispheric half-amplitude is 20 ppm, which seems to be an upper limit, then the (half-) amplitude in the atmosphere would be 0.4 ppm. $\delta^{13}C$ in the atmosphere is essentially not affected by this oceanic CO_2, because there is an approximate $^{13}C/^{12}C$ equilibrium between atmosphere and surface ocean. After subtraction of the calculated oceanic seasonal signal from our CO_2 concentration results, regression analysis yields $\delta^{13}C_I = -25.6 \pm 0.7‰$, not significantly different from the previous value, which justifies the above regression calculations.

This regression analysis is based on the assumption that only the $\delta^{13}C$ data are affected with error, i.e., taking $1/C$ as an error-free variable. In reality, however, also the CO_2 data have errors. The precision of C is 0.8 ppm, that of $\delta^{13}C$ 0.06‰ (see above). A deviation of 0.8 ppm from, e.g., the annual mean value of 337 ppm corresponds, inserted into eq. (3) with $M = 6024‰ \cdot$ppm, to a $\delta^{13}C$ deviation of 0.04‰, which is comparable to the analytical error. This means that the uncertainty of the concentration data has a similar effect as that of the isotope data. Therefore, we also estimated $\delta^{13}C_I$ by means of a regression method given by Mandel (1964) for the case that both variables are subject to error. This yielded $-26.2‰$, slightly lower than the value obtained by the classical regression analysis.

Inoue and Sugimura (1985) calculated $\delta^{13}C_I$, based on eq. (3), from monthly sets of CO_2 and $\delta^{13}C$ data on samples of surface air collected in Japan. They obtained rather high $\delta^{13}C_I$ values, up to $-10‰$, for some months. By means of classical regression analysis, we also obtain relatively high values for some individual profiles. These high $\delta^{13}C_I$ results are always connected to low values of r, and they apparently reflect a bad correlation, rather than a special isotopic composition of the added CO_2. Applying the method of Mandel (1964) to the individual profiles, we mostly get values nearer to the result of $-26.2‰$ obtained for the set of all data. Apparently, the classical regression formulae give less reliable estimates for $\delta^{13}C_I$ if the concentration error is not negligible. Thus, there is no reason for invoking some isotopically special source of CO_2, but rather one must pay attention to the regression method used and to the statistical confidence limits of the estimated regression coefficients.

6. Oxygen-18 results

Mean values of $\delta^{18}O$ of atmospheric CO_2, averaged over altitude from 2 km to the top of each profile, are shown in Fig. 4. Excluding the suspicious January value of 0.4‰ (only 3 altitude

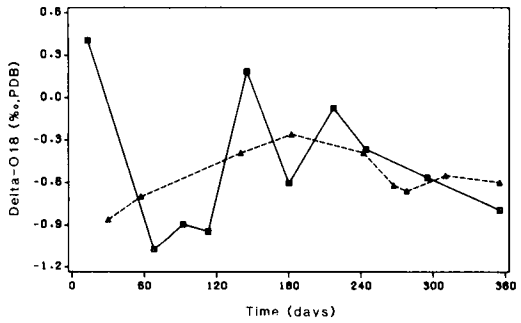

Fig. 4. Solid line: mean $\delta^{18}O$ values for the interval 2 to 8 km of CO_2 sampled in 1982 over Switzerland, ‰ against PDB and N_2O corrected. Full squares: outliers (see text). Dashed line: $\delta^{18}O$ of CO_2 sampled during 1981 at La Jolla, California (SIO), also N_2O corrected (Mook et al., 1983).

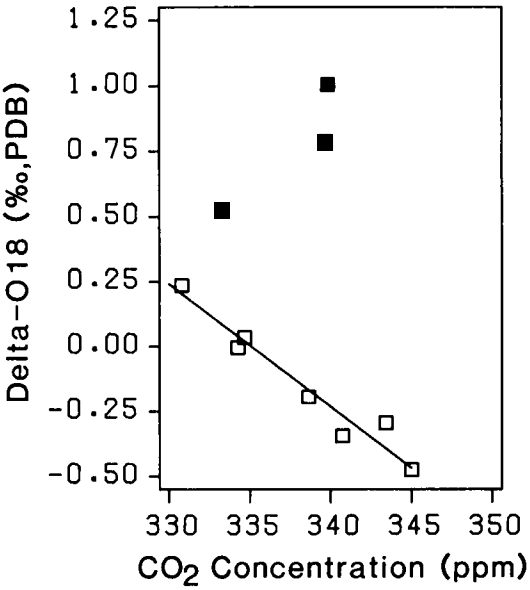

Fig. 5. $\delta^{18}O$ of atmospheric CO_2 (‰ against PDB, N_2O corrected) versus the (long-term detrended) CO_2 concentration C (in ppm), monthly mean values for the interval 2 to 8 km. Solid line: linear regression (see text). Full squares: outliers.

levels, large scatter of the individual results), the results are in the range of -1.08 to $+0.18$‰ with a mean of -0.58‰ (versus PDB). There is a relatively large scatter in the $\delta^{18}O$ data (standard deviation calculated from sample pairs: 0.3‰). A possible reason is isotopic exchange of CO_2 with a water film at the walls of the air sample flasks.

There is an indication of an annual cycle, with maximum values in summer. Such a seasonal variation is also suggested by data of Keeling (1961) and of Mook et al. (1983) (see data for La Jolla, California, 1982, dashed curve in Fig. 4). The annual mean $\delta^{18}O$ of our samples (-0.6‰) is in the range of the values observed by Keeling et al. (1984) at other northern hemisphere stations (~ -0.5 to -1‰).

Three out of the ten profiles (January, May and August; full squares in Figs. 4 and 5) have anomalously high $\delta^{18}O$ values if compared with a hypothesized smooth trend. We have no explanation for this, except the general observation of large scatter, possibly connected to sample storage. (The samples were all processed after storage of 1 to 20 days, except those of January that were stored for 28 days.) If these three profiles are excluded, an excellent correlation with CO_2 concentration C is observed for the profile mean values (mean values of all samples above 2000 m altitude), see Fig. 5. Linear regression of $\delta^{18}O$ against $1/C$ (solid curve in Fig. 5) yields, proceeding analogously as in eq. (3), $\delta^{18}O_1 = -16.4 \pm 1.6$‰, for the apparent composition of admixed/subtracted CO_2, assuming a two-component mixture; the correlation coefficient is 0.97. (Taking all 62 individual $\delta^{18}O$ and CO_2 results from the seven "well-behaved" profiles, the correlation coefficient is still 0.55, significantly different from zero.) Although three out of ten profiles do not follow it, the excellent $\delta^{18}O$–CO_2 correlation of the remaining seven suggests that the seasonal cycle of $\delta^{18}O$ may be due to admixture/removal of isotopically different CO_2.

7. Processes determining $\delta^{18}O$ of atmospheric CO_2

The oxygen isotopic composition of atmospheric CO_2 is influenced by a number of processes:

(1) exchange with the ocean;
(2) exchange and isotopic equilibration with cloud droplets;
(3) exchange with leaves and needles of plants; this includes not only assmilation, but all CO_2

that diffuses through the stomata into or out of the leaves;

(4) soil respiration; the amount of CO_2 produced in soils equals the net assimilation flux, i.e., (3) and (4) balance regarding CO_2 mass.

We will discuss these processes and show that exchange with the ocean and the biosphere are both important, while equilibration with cloud droplets is too slow to be of much influence. Processes (1) and (2) have been discussed by Bottinga and Craig (1968). The relative importance of the four processes depends on their corresponding exchange rate, which is inversely proportional to the atmospheric residence time with respect to the exchange flux considered. The residence times are approximately 8 years for (1) (e.g., Bolin et al., 1981) and 100 years for process (2), see below. The gross primary production of the land biosphere is ~ 110 Gt C yr^{-1} (Emanuel et al., 1981), corresponding to an atmospheric residence time of about 6 yr; the exchange time for processes (3) plus (4) must be smaller, since such CO_2 can also equilibrate isotopically with soil and leaf water that does not actually enter a biospheric carbon pool, i.e., is not included in the figure for the gross primary production.

The residence time of CO_2 with respect to isotopic equilibration with cloud droplets via the reaction $CO_2 + H_2O \rightleftarrows H_2CO_3$ (process (2)), is determined by the rate of hydration of CO_2 dissolved in the water droplets. It is given by the ratio of the amount of atmospheric CO_2, N_a, to the total hydration rate of atmospheric CO_2, F_h. Now

$$N_a = C\rho_a h_a A, \tag{9}$$

where $C = CO_2$ concentration, $h_a \approx 8000$ m is the equivalent height of the atmosphere, A the earth's surface area and ρ_a the density of air at sea-level. The hydration rate is given by

$$F_h = k \cdot C_{diss}\, m_w \cdot A = k \cdot s \cdot C \cdot 0.78 \rho_a m_w A, \tag{10}$$

where $k = 2.1 \cdot 10^{-3}$ s^{-1} is the rate constant for the hydration reaction at an estimated cloud temperature of 0°C (see review by Kern, 1960), C_{diss} = concentration of dissolved CO_2 in the water droplets, $m_w = 0.9$ kg m^{-2} is the mean liquid water content of the atmosphere (Bottinga and Craig, 1968), $s = 1.7 \cdot 10^{-3}$ m^3 kg^{-1} is the CO_2 solubility at 0°C, 0.87 = relative air density at 2000 m altitude (approximate mean cloud height). This yields

$$\tau_2 = N_a/F_h = 101 \text{ yr}. \tag{11}$$

Bottinga and Craig estimated an exchange time with atmospheric water of only about 3 days, but they assumed that the rate-limiting step is gas exchange which is determined by diffusion of CO_2 into the droplet's interior. While CO_2 exchanges rather rapidly with the droplets (characteristic diffusion time: $r^2/D \approx 0.02$ s for a droplet radius $r = 5$ μm and $D = 10^{-5}$ cm^2 s^{-1}), most of it is not equilibrated isotopically, because equilibration within a droplet proceeds with a characteristic time $k^{-1} \approx 470$ s. Thus, we conclude that equilibration with cloud droplets is of small influence for the oxygen isotope ratio of CO_2.

The other three processes proceed at comparable rates and must therefore all be considered. The $^{18}O/^{16}O$ ratios, R, of carbon dioxide and water is isotopic equilibrium with each other are related by

$$R(CO_2) = \alpha R(H_2O). \tag{12}$$

α is the equilibrium $^{18}O/^{16}O$ fractionation factor between CO_2 and water, depending on temperature (eq. (3) of Bottinga and Craig (1968)); $\alpha(25°C) = 1.0412$, $d\alpha/dT \approx -0.2‰/°C$. It is common to refer the isotopic composition of H_2O to the standard SMOW, that of CO_2 to the standard PDB, so that $R(CO_2) = [1 + \delta_{PDB}(CO_2)]R_{PDB}$ and $R(H_2O) = [1 + \delta_{SMOW}(H_2O)]\ R_{SMOW}$. Eq. (12) then yields

$$1 + \delta_{PDB}(CO_2) = \alpha[1 + \delta_{SMOW}(H_2O)] \times R_{SMOW}/R_{PDB}. \tag{13}$$

The term $R_{SMOW}/R_{PDB} = 0.96023$ accounts for the relation between the SMOW and PDB scales (Friedman and O'Neil, 1977). According to eq. (13), $\delta_{PDB}(CO_2) - \delta_{SMOW}(H_2O) = -0.21‰$ for isotopic equilibrium at 25°C. Bottinga and Craig (1968) estimated that in isotopic equilibrium with the ocean, average atmospheric CO_2 would have a $\delta^{18}O$ of 1.1‰ (versus PDB).

The seasonal sea surface temperature variations induce, via the temperature dependence of the fractionation factor, a $\delta^{18}O$ cycle in air-CO_2, the amplitude $\Delta\delta_a$ of which can be estimated as follows. For a typical temperature amplitude of 5°C for the temperate ocean, the

$\delta^{18}O$ amplitude for CO_2 in instantaneous equilibrium with surface seawater would be 1.0‰ (since $d\alpha/dT = -0.2‰/°C$). The atmospheric $\delta^{18}O$ amplitude can be estimated by the same one-box model consideration as given above for the ocean-induced concentration signal. The attenuation factor, given by eq. (7), is 0.02, and the atmospheric $\delta^{18}O$ variations originating from the oceanic temperature cycle have an amplitude of about 0.02‰. This is too small to be observed.

We conclude that the seasonal $\delta^{18}O$ cycle must be due to exchange with biosphere and soils. Nothing is known about direct $^{18}O/^{16}O$ fractionation effects for CO_2 during respiration and assimilation. However, such effects are masked by partial or full isotopic equilibration of the CO_2 with soil water or leaf water. We first discuss respiration. Plant materials have, in mid-latitudes, $\delta^{18}O \approx -14‰$ (Epstein et al., 1977) and atmospheric oxygen −16.9‰ (Kroopnick and Craig, 1976). (Both values refer to the standard PDB, and also all values quoted here for organic material.) Assuming that there is no isotope fractionation during the decomposition of organic matter, CO_2 from soil respiration should therefore have $\delta^{18}O \approx -15‰$. Before entering the atmosphere, it may, however, equilibrate with soil water with a value around −8‰ (versus SMOW) in mid-latitudes (e.g. Förstel and Hützen, 1982). Inserting this figure and $T \approx 12°C$ into eq. (8), we obtain $\delta^{18}O \approx -5‰$ for equilibrated soil CO_2.

The last process considered is the exchange with living parts of plants. We have studied the CO_2 exchange of leaves by means of a mechanistic model similar to that used by Farquhar et al. (1982) for explaining the $^{13}C/^{12}C$ ratio of plants. The calculations have to consider $^{18}O/^{16}O$ fractionation during CO_2 diffusion through the stomata and the CO_2 concentration within the intercellular space. They are not given here, because the result is not very conclusive in view of uncertainties about the degree of isotopic equilibration of CO_2 with leaf water, about the mean isotopic composition of leaf water and about the CO_2 concentration within the intercellular space. For the net flux from atmosphere to plants, we obtain $\delta^{18}O$ values between $\sim -20‰$ (for full equilibration with leaf water) and −4‰ (no equilibration).

In summary, we obtain an approximate range of −4 to −20‰ for the oxygen isotopic composition of the CO_2 exchange fluxes atmosphere-biosphere. This embraces the value of $\sim -16‰$ for admixed CO_2 estimated above from our data, but the uncertainty is of course very large. Nevertheless, this is more negative than $\delta^{18}O$ of air-CO_2, as is required if biospheric CO_2 is responsible for the observed seasonal cycle: addition of ^{18}O-depleted CO_2 leads to low $\delta^{18}O$ in winter, withdrawal to high $\delta^{18}O$ in summer.

We conclude that the main processes determining the oxygen isotope ratio of atmospheric CO_2 are exchange with vegetation and soils and exchange with the ocean, and that only the former can be responsible for the observed seasonal ^{18}O variation. The exchanges with the biosphere are quite complex and there remain several open questions. In order to answer them, it would be necessary to study experimentally the composition of soil CO_2 and the fractionation processes connected with assimilation and exchange of CO_2 with the live vegetation.

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REFERENCES

Bolin, B. and Bischof, W. 1970. Variation of the carbon dioxide content of the atmosphere in the northern hemisphere. *Tellus 22*, 431–442.

Bolin, B., Keeling, C. D., Bacastow, R. B., Björkström, A. and Siegenthaler, U. 1981. Carbon cycle modelling. In: *Carbon cycle modelling* (ed. B. Bolin). John Wiley & Sons, New York, 1–28.

Bottinga, Y. and Craig, H. 1968. Oxygen isotope

fractionation between CO_2 and water, and the isotopic composition of marine atmospheric CO_2. *Earth Planet. Sci. Lett. 5*, 285–295.

Emanuel, W. R., Killough, G. E. G. and Olson, J. S. 1981. Modelling the circulation of carbon in the world's terrestrial ecosystems. In: *Carbon cycle modelling* (ed. B. Bolin). John Wiley & Sons, New York, 335–353.

Epstein, S., Thompson, P. and Yapp, C. J. 1977. Oxygen and hydrogen isotopic ratios in plant cellulose. *Science 198*, 1209–1215.

Farquhar, G. D., O'Leary, M. H. and Berry, J. A. 1982. On the relationship between carbon isotope discrimination and the intercellular carbon dioxide concentration in leaves. *Aust. J. Plant Physiol. 9*, 121–137.

Förstel, H. and Hützen, H. 1981. $^{18}O/^{16}O$ ratio of groundwater in the Federal Republic of Germany. In: *Stable isotopes* (eds. H. L. Schmidt, H. Förstel and K. Heinzinger). Amsterdam: Elsevier, 173–178.

Friedman, I. and O'Neil, J. R. 1977. *Data of geochemistry* (ed. M. Fleischer). United States Government Printing Office, Geological Survey Professional Paper 440-KK.

Inoue, H. and Sugimura, Y. 1985. The carbon isotopic ratio of atmospheric carbon dioxide at Tsukuba, Japan. *J. Atmos. Chem. 2*, 331–344.

Johnston, H. S., Kattenhorn, D. and Whitten, G. 1976. Use of excess carbon-14 data to calibrate models of stratospheric ozone depletion by supersonic transports. *J. Geophys. Res. 81*, 368–380.

Keeling, C. D. 1961. The concentration and isotopic abundances of carbon dioxide in rural and marine air. *Geochim. Cosmochim. Acta 24*, 277–298.

Keeling, C. D., Carter, A. F. and Mook, W. G. 1984. Seasonal, latitudinal, and secular variations in the abundance and isotopic ratios of atmospheric CO_2, 2. results from oceanographic cruises in the tropical Pacific Ocean. *J. Geophys. Res. 89*, 4615–4628.

Kern, D. M. 1960. The hydration of carbon dioxide. *J. Chem. Educ. 37*, 14–23.

Kroopnick, P. and Craig, H. 1976. Oxygen isotope fractionation in dissolved oxygen in the deep sea. *Earth Planet. Sci. Lett. 32*, 375–388.

Levin, I. 1987. Atmospheric CO_2 in continental Europe—an alternative approach to clean air CO_2 data. *Tellus 39B*, 21–28.

Machta, L. 1974. Global scale atmospheric mixing. *Adv. Geophys. 18B*, 33–56.

Mandel, J. 1964. *The statistical analysis of experimental data*. John Wiley & Sons, New York, 288–292.

Mook, W. G. and van der Hoek, S. 1983. The N_2O correction in the carbon and oxygen analysis of atmospheric CO_2. *Isotope Geosci. 1*, 237–242.

Mook, W. G., Koopmans, M., Carter, A. F. and Keeling, C. D. 1983. Seasonal, latitudinal, and secular variations in the abundance and isotopic ratios of atmospheric carbon dioxide, 1. results from land stations. *J. Geophys. Res. 88*, 10915–10933.

Pearman, G. I. and Hyson, P. 1980. Activities of the Global Biosphere as reflected in atmospheric CO_2 records. *J. Geophys. Res. 85*, 4457–4467.

Rotty, R. M. 1983. Distribution of and changes in industrial carbon dioxide production. *J. Geophys. Res. 88*, 1301–1308.

Rotty, R. M. and Marland, G. 1984. Production of CO_2 from fossil fuel burning by fuel type, 1860–1982. Report NDP-006, Carbon Dioxide Information Center, Oak Ridge National Laboratory.

Siegenthaler, U. and Oeschger, H. 1987. Biospheric CO_2 emissions during the past 200 years reconstructed by deconvolution of ice core data. *Tellus 39B*, 140–154.

Weiss, R. F., Jahnke, R. A. and Keeling, C. D. 1982. Seasonal effect of temperature and salinity on the partial pressure of carbon dioxide in seawater. *Nature 300*, 511–513.

Zumbrunn, R., Friedli, H., Neftel, A. and Rauber, D. 1983. CO_2 measurements with an infrared laser spectrometer on flask samples collected at Jungfraujoch high-altitude research stations (3500 m a.s.l.) and with light aircraft up to 8000 m over Switzerland. *J. Geophys. Res. 88*, 6853–6857.