Variations of the carbon isotopic ratio in atmospheric CO₂ over the last 250 years recorded in an ice core from H15, Antarctica

Kenji Kawamura[1], Takakiyo Nakazawa[1], Toshinobu Machida[2],
Shinji Morimoto[3], Shuhji Aoki[1], Misa Ishizawa[4],
Yoshiyuki Fujii[3] and Okitsugu Watanabe[3]

[1] *Center for Atmospheric and Oceanic Studies, Graduate School of Science,*
Tohoku University, Sendai 980-8578
[2] *National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba 305-0053*
[3] *National Institute of Polar Research, Kaga 1-chome, Itabashi-ku, Tokyo 173-8515*
[4] *Frontier Research System for Global Change, Institute for Global Change Research,*
3137-25 Showa-machi, Kanazawa-ku, Yokohama 236-0001

Abstract: Variations of $\delta^{13}C$ in atmospheric CO₂ were reconstructed for the period of 1724 to 1961 by analyzing a high-accumulation ice core drilled at H15, Antarctica. Measured values of $\delta^{13}C$ were corrected for the gravitational enrichment which occurred in the firn, on the basis of the analytical results of $\delta^{15}N$ in N₂ in the core. From the vertical profile of $\delta^{15}N$ calculated using a diffusion model for the firn, it was suggested that the air in the layer shallower than 17 m depth was mixed well with the atmosphere over the firn surface. The average value of $\delta^{13}C$ during the period 1724–1775 was found to be -6.67 ± 0.11‰. $\delta^{13}C$ decreased secularly from this value to -7.33‰ in 1961, and its trend was enhanced especially after the late 19th century, corresponding to the long-term increase of the CO₂ concentration. CO₂ fluxes estimated by deconvolution analysis of the reconstructed CO₂ concentrations with the box-diffusion model accounted for the observed variations of $\delta^{13}C$ fairly well. It was also suggested that a dip of $\delta^{13}C$ found at the end of the 18th century was attributable to terrestrial biospheric CO₂ emissions enhanced under high air temperatures.

1. Introduction

The atmospheric CO₂ concentration has been increasing for the last 200 years due to human activities (Neftel *et al.*, 1985; Friedli *et al.*, 1986; Etheridge *et al.*, 1996). Causes of such a concentration increase have to be clarified quantitatively not only for predicting future levels of the atmospheric CO₂ concentration but also for limiting or reducing CO₂ emissions into the atmosphere. For this purpose, it is useful to elucidate temporal variations of $\delta^{13}C$ in atmospheric CO₂, in addition to those of its concentration. Therefore, precise and systematic measurements of $\delta^{13}C$ in atmospheric CO₂ were begun for the first time by Keeling *et al.* (1989) at Mauna Loa and the South Pole in 1977 and then extended to various places of the world (Nakazawa *et al.*, 1993a; Francey *et al.*, 1995; Keeling *et al.*, 1995; Trolier *et al.*, 1996; Nakazawa *et al.*, 1997).

For better understanding of the global carbon cycle, it is also important to know the history of atmospheric $\delta^{13}C$ over a long time before its direct atmospheric measurement.

The analysis of air occluded in bubbles in polar ice cores is the most promising method for estimation of $\delta^{13}C$ in atmospheric CO_2 in the past. Indeed, several studies have tried to analyze Antarctic cores for reconstructing variations of atmospheric $\delta^{13}C$ during the period from the last ice age to the modern industrialized era (Friedli *et al.*, 1986; Siegenthaler *et al.*, 1988; Leuenberger *et al.*, 1992; Machida *et al.*, 1996; Indermühle *et al.*, 1999; Francey *et al.*, 1999). On the other hand, it has also been pointed out by previous studies that there are some difficulties in deducing precisely the temporal variations of air components from the ice core analysis. For example, the time resolution of the obtained data is rather coarse, since finite time is required so that bubbles are closed off in ice due to the snow-ice transition process. In addition, molecular diffusion of air in the firn affects the age of air in ice, and heavier air components are enriched in air enclosed in ice due to the effect of gravitational separation in the firn (Craig *et al.*, 1988; Schwander, 1989). Therefore, more data from well-examined analyses of high quality ice cores are required to clarify detailed variations of atmospheric $\delta^{13}C$ in the past.

In this study, we collected a high quality ice core at site H15 in a high accumulation area of Antarctica, and then analyzed it for $\delta^{13}C$ in CO_2, in addition to the CO_2 concentration. To estimate the degree of gravitational separation of isotopically different CO_2 in the firn, we also measured $\delta^{15}N$ in N_2 in air extracted from the ice core samples. In this paper, we will give the results obtained from the H15 core and discuss the temporal variations of $\delta^{13}C$ in atmospheric CO_2 over the last 250 years.

2. Experimental Procedures

Details of the ice core used in this study have been described elsewhere (Machida *et al.*, 1995). Therefore, only a brief description of the core will be given here. A 120 m long ice core of high quality was drilled at H15, Antarctica (69°05'S, 40°47'E, 1057 m a.s.l.) in 1991, using a mechanical drill. The annual mean air temperature at the drilling site is $-20.5°C$. The age of the ice core was estimated by using an average annual accumulation rate of 260 kg m^{-2} year^{-1}, which was determined from the signal peaks of ECM (Electronic Conductivity Measurements) corresponding to volcanic eruption events such as Tambora in 1815. The uncertainty of the ice age determined by this method was estimated to be less than 5 years, at least for the depth range shallower than 65 m, by comparing with the timing of the respective volcanic eruptions. Considering that bubbles in the H15 ice core are generally sealed off at 50 m depth corresponding to an ice age of 135 years BP and that the effect of time delay caused by molecular diffusion in the firn amounts to about 6 years for CO_2 at H15 (Schwander, 1989; Etheridge *et al.*, 1992), the age difference between the air and the ice was found to be about 129 years. For the age of air trapped in the H15 ice core, we note that the increase trends of the CO_2 concentrations deduced from the Siple core (Friedli *et al.*, 1986) and the DE 08 core (Etheridge *et al.*, 1996) are in close agreement with those from the H15 core (Kawamura *et al.*, 1997; Nakazawa *et al.*, 1993b; Machida *et al.*, 2000 (in preparation)), as described below. This fact implies that the dating of the air from these 3 ice cores were done with almost the same uncertainty.

For analys of $\delta^{13}C$ in CO_2, a dry extraction system installed in a cold room of

$-20°C$ was used to extract air from the ice core samples (Nakazawa *et al.* 1993c). For each air extraction, an ice sample of about 350 g was used. The ice sample was placed in the stainless-steel chamber of the extraction system after its contaminated surfaces were removed using a bandsaw and a cutter knife. The extraction system was then evacuated for more than 2 hours to remove contaminated room air from its inside, as well as to sublimate the ice surfaces for further cleaning of the sample. After evacuation, the sample was milled by an ice cutter into fine powder, and the released air was cryogenically collected into a stainless-steel sample tube with a volume of 25 cm^3 cooled by liquid helium, after passing it through a glass trap held at $-100°C$. The air sample was first analyzed for the CO_2 concentration by using a gas chromatograph after laying the tube in our laboratory for 1 or 2 days to ensure the mixing of air components in the tube. Then, CO_2 was extracted cryogenically from the remaining air in the tube for a mass spectrometer analysis. The CO_2 extraction procedures were the same as those described in Nakazawa *et al.* (1993a).

The mass spectrometer used in this study was a Finnigan MAT delta-S. $\delta^{13}C$ is defined in the form

$$\delta^{13}C(‰) = \left[\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1 \right] \times 1000. \tag{1}$$

Here, $(^{13}C/^{12}C)_{sample}$ and $(^{13}C/^{12}C)_{standard}$ represent the ratios of ^{13}C to ^{12}C for the sample and the standard, respectively. Our standard system for isotope measurements comprised primary, secondary, working and check gases. The primary standard gas was CO_2 produced by reacting NBS-18 ($\delta^{13}C = -5.029‰$ and $\delta^{18}O = -23.035‰$ with respect to PDB), distributed by the International Atomic Energy Agency, Vienna, with 100% phosphorous acid at 25°C (IAEA, 1995; Nakazawa *et al.*, 1993a). The secondary, working and check gases were CO_2 extracted from the atmosphere. The working standard gas was used as a reference of the mass spectrometer for analyses of the samples, but its $\delta^{13}C$ value was found to change gradually after being introduced into a bellow of the mass spectrometer. Therefore, we measured the check gas with a known value of $\delta^{13}C$ before and after analyzing the samples, to correct the drift in $\delta^{13}C$ of the working gas. Since N_2O contained in the air samples cannot be removed from CO_2 by the extraction method used in this study, its contribution was corrected by the procedures described in Nakazawa *et al.* (1993a, 1997).

For analysis of $\delta^{15}N$ in N_2 occluded in the ice samples, we used a wet method to extract the air (Nakazawa *et al.*, 1993c, d). The ice sample of about 150 g was put in the stainless-steel chamber of the wet extraction system after removing its contaminated surfaces. After more than 2 hours of evacuation, the sample was melted and the released air was collected in a sample tube of 5 ml volume cooled by liquid helium. $\delta^{15}N$ in N_2 in the extracted air, defined as

$$\delta^{15}N(‰) = \left[\frac{(^{15}N^{14}N/^{14}N^{14}N)_{sample}}{(^{15}N^{14}N/^{14}N^{14}N)_{surface}} - 1 \right] \times 1000, \tag{2}$$

was measured against our working standard gas, using another Finnigan MAT delta-S mass spectrometer. Here, the subscript "surface" means the present-day tropospheric

air.   Since our working standard was prepared by purifying the atmosphere in a heavily industrialized area, its $\delta^{15}N$ was determined prior to use, on the basis of the air samples collected using aircraft at 0-1 km height over Syowa Station (69°S, 39°E, 21 m a.s.l.), Antarctica between February 1994 and January 1995, which showed no appreciable seasonal variation of $\delta^{15}N$ in N_2.

It is essential for the ice core analysis to assess the uncertainties arising from various facets of the procedure, such as the air extraction from ice cores, the store of air in the sample tubes, the extraction of CO_2 from air samples, and the mass spectrometry. Therefore, we performed the following tests prior to analyses of the H15 core.   An Antarctic ice core was milled in the chamber of the dry extraction system and then the system was evacuated for more than 1 hour.   After evacuation, about 50 m*l* of a mixture of air and CO_2 with known value of $\delta^{13}C$ was injected into the chamber, and the mixture gas was then collected in the sample tube by almost the same procedure as actual air extraction from an ice core.   The $\delta^{13}C$ value of CO_2 was measured by using the mass spectrometer 1 or 2 days after its recovery.   For $\delta^{15}N$, milled Antarctic ice was put in the chamber of the wet system, and after 1 hour of evacuation, the air sample of known $\delta^{15}N$ value was introduced into the chamber, and then the air sample was transferred to the sample tube, melting the ice.   The air sample was analyzed for $\delta^{15}N$ 1 or 2 days after collection.   These procedures were repeated several times both for $\delta^{13}C$ and $\delta^{15}N$.   The experimental precisions of our ice core analysis, thus estimated, were 0.05‰ for $\delta^{13}C$ of CO_2 and 0.02‰ for $\delta^{15}N$ of N_2.

3.   Results and Discussion

Heavier air components are expected to be enriched in air in the firn, relative to the atmosphere, due to gravitational separation.   If the air is completely in diffusive equilibrium throughout the whole layer of firn, the gravitational enrichment of a given air component can be described by the barometric equation (Schwander, 1989)

$$\frac{P_z}{P_0} = \exp(\frac{mgz}{RT}), \tag{3}$$

where P_z and P_0 are partial pressures of the air component at a certain depth z (m) and the surface, respectively; m (kg mol^{-1}) is the molecular weight of the air component; g is the acceleration of gravity (9.81 m s^{-2}); R is the gas constant (8.314 J mol^{-1} K^{-1}); and T (K) is the temperature at the site.   If a well-ventilated layer exists in the upper part of the firn or if the snow accumulation rate is extremely high, the fractionation of air components occurring in the firn is expected to be smaller than the value given by eq. (3).   In addition, if the past environmental conditions such as accumulation rate and temperature are different from those at present or if there are any thick melt layers in the firn, it is difficult to estimate the gravitational fractionation straightforwardly from eq. (3).   For more precise estimation of the magnitude of the gravitational separation effect in the firn, it is crucial to measure $\delta^{15}N$ in N_2 in ice.   Since the isotopic ratio of atmospheric N_2 is thought to have been constant over a long time, $\delta^{15}N$ in N_2 in ice should be affected only by the effect of the gravitational separation in the firn.
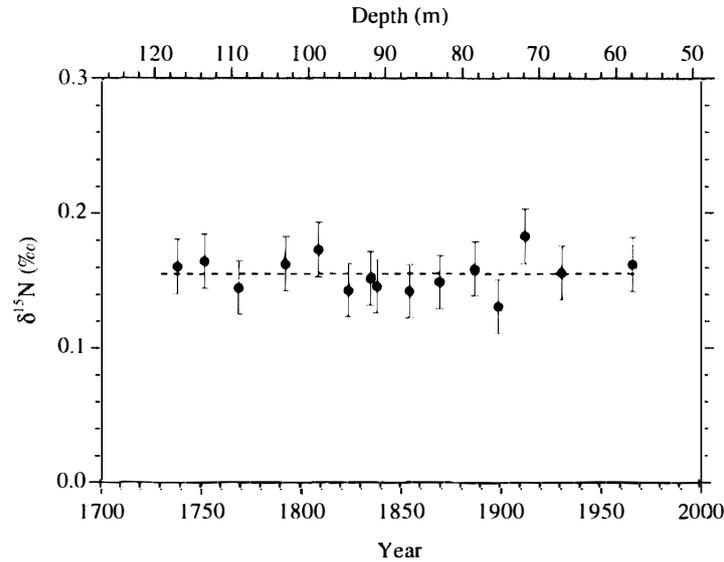
Fig. 1. Measured values of $\delta^{15}N$ in N_2 in air extracted from the H15 ice core.   The error bars represent the measurement uncertainty of $\pm 0.02‰$, and dashed line means the average of measured values.

Therefore, we measured $\delta^{15}N$ in N_2 in air extracted from 15 ice samples covering the whole length of the H15 core.   The results are shown in Fig. 1.   All the measured values of $\delta^{15}N$ were positive, showing an average value of $+0.155 \pm 0.013‰$.   Fairly constant values of $\delta^{15}N$ imply that the mixing of air in the firn at H15 was not greatly changed at least for the last 250 years.   By comparing with the average value of measured $\delta^{15}N$, it was found that the gravitational enrichment of $\delta^{15}N$ calculated from eq. (3) was overestimated by about $0.08‰$.

There are two possibilities for accounting for the difference between the measured and calculated values of $\delta^{15}N$.   If air in the uppermost part of the firn is mixed well with the atmosphere due to convection driven by wind and pressure fluctuations, the diffusive layer of the firn becomes thin, and consequently, $\delta^{15}N$ of N_2 at the close-off depth is expected to be smaller than prediction by eq. (3).   In this regard, Bender et al. (1994) suggested, from their analytical results of the firn air collected at Vostok, Antarctica, that the air was mixed well in the layer shallower than 13 m below the surface .   If the snow accumulation rate is extremely high, vertical advection of ice prevents the firn column from reaching perfect diffusive equilibrium (Trudinger et al., 1997).   In this case, the rate of change in $\delta^{15}N$ with respect to depth is expected to be smaller than the theoretically predicted value.   Such a phenomenon was found at Law Dome (DE08-2), Antarctica, where the accumulation rate is $1100 \, kgm^{-2} \, yr^{-1}$ (Trudinger et al., 1997).

To examine the cause of the difference between the measured and calculated values of $\delta^{15}N$ in ice at site H15, the vertical profile of $\delta^{15}N$ in the firn was calculated using a one-dimensional diffusion model (Schwander et al., 1993), on the assumption that the relationship between porosity and diffusivity at the site agrees with that at Siple Station (Schwander et al., 1988).   The result indicated that the rate of change in $\delta^{15}N$ with respect to depth obtained from the model calculation was almost the same as that expected from eq. (3), except for a few meters in the bubble close-off region where the

rates from the model were smaller than that from the equation. The $\delta^{15}N$ value calculated for the bubble close-off depth was close to that expected from eq. (3). This implies that downward advection of ice due to snow accumulation does not substantially prevent nitrogen molecules from reaching diffusive equilibrium at H15. We also found that the value of $\delta^{15}N$ calculated by the model for the close-off depth is in good agreement with the average of values obtained from the ice core samples, by assuming that the air in the uppermost layer of the firn with a thickness of 17 m is mixed with the atmosphere over the surface, and air components are moved by molecular diffusion below that depth. To confirm this result, analysis of firn air from various depths at the site is required.

The CO_2 concentrations derived from the H15 core have been outlined in Nakazawa *et al.* (1993b) and Kawamura *et al.* (1997), and their detailed results will be published elsewhere (Machida *et al.*, 2000 (in preparation)). Briefly speaking, the atmospheric CO_2 concentration level obtained from the ice core showed a "background" value of 279.1 ± 1.3 ppmv from 1724 to 1780, and then increased with time to 317.4 ppmv in 1961, showing a rapid increase of about 7 ppmv in the late 18th century when the climate recovered from the Little Ice Age. The CO_2 concentrations from the H15 ice core are in excellent agreement with those obtained by analyzing the ice core from Siple, Antarctica (Neftel *et al.*, 1985; Friedli *et al.*, 1986), with the exception of values in the late 18th century when the H15 core showed higher concentrations by up to about 6 ppmv than the Siple core did. Compared with the results of the H15 core, the Siple core shows the CO_2 concentrations lower by less than 2 ppmv before 1780 and higher by less than 1.5 ppmv between 1850 and 1900. After 1900, the results from the two cores are in excellent agreement with each other, the difference being within 1 ppmv. The results from the H15 core are also very close to those from the Law Dome cores, including a rapid increase in the late 18th century (Etheridge *et al.*, 1996). Between 1720 and 1880, the results from the Law Dome cores are almost the same as those from the H15 core or lower by 2 ppmv at most. For the period 1880–1940, the CO_2 concentrations from the Law Dome cores are higher by only 1–2 ppmv than those from the H15 core.

The values of $\delta^{13}C$ in CO_2 obtained from the H15 core are summarized in Table 1 and also shown in Fig. 2, together with the results from our direct atmospheric measurements at Syowa Station (our unpublished data). In this figure, the measured values of $\delta^{13}C$ are shifted down by 0.16‰ for correcting the gravitational separation in the firn in accordance with the analytical results of $\delta^{15}N$ in N_2. It is expected that the ages of $^{12}CO_2$ and $^{13}CO_2$ at the same depth in the firn are different due to their slightly different diffusivities. This leads to another modification of $\delta^{13}C$ from the original atmospheric value, since $\delta^{13}C$ in atmospheric CO_2 has been changing rapidly, especially for the last 100 years. Trudinger *et al.* (1997) pointed out for the firn air at DE08-2 that the diffusion correction shifted up the $\delta^{13}C$ values by about one third of the gravitational correction. Francey *et al.* (1999) also found from the Law Dome cores that the diffusion correction of $\delta^{13}C$ was about 0.1‰ at the depth corresponding to the air age of 1970 and less than 0.01‰ for the pre-industrial era. In spite of their indications, the $\delta^{13}C$ values from the H15 core were not corrected for the diffusion effect, because the firn air at the site was not available for us. However, the diffusion

Table 1.   Measured values of $\delta^{13}C$ in CO_2 obtained from the H15 ice core.

Age of air (Year)	δ^{13}C (‰)	Age of air (Year)	δ^{13}C (‰)	Age of air (Year)	δ^{13}C (‰)
1724	−6.63	1804	−6.85	1901	−6.87
1735	−6.76	1809	−6.98	1906	−7.04
1737	−6.76	1818	−6.83	1914	−7.10
1739	−6.55	1826	−6.83	1919	−6.96
1744	−6.53	1832	−7.00	1936	−7.15
1746	−6.59	1834	−7.04	1939	−7.16
1756	−6.62	1842	−6.88	1952	−7.31
1766	−6.74	1848	−6.78	1961	−7.33
1775	−6.83	1870	−6.85		
1780	−6.98	1879	−6.80		
1790	−7.05	1884	−6.79		
1799	−7.05	1892	−6.77		
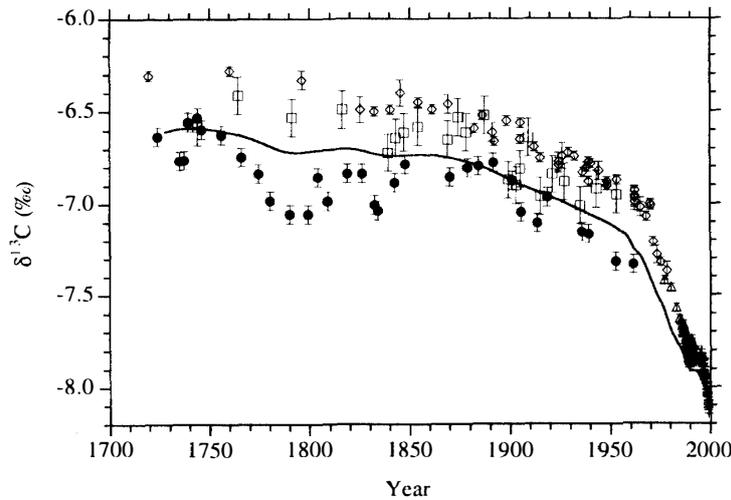
Fig. 2.   Variation of $\delta^{13}C$ in atmospheric CO_2 during the last 250 years deduced from the H15 ice core (solid circles).   The results from the Siple core, the Law Dome core and the Law Dome firn air are also plotted by open squares, open diamonds and open triangles, respectively, in addition to annual mean $\delta^{13}C$ values from direct atmospheric measurements at Syowa Station by pluses. The error bars represent the measurement uncertainties of individual values.   The values of atmospheric $\delta^{13}C$ calculated using the box-diffusion model are given by the solid line.

correction of δ^{13}C for the H15 core would be much less than those for the Law Dome cores, since the close-off depth is shallower by about 20 m than at Law Dome and the diffusive layer of the firn becomes thin by the existence of the well-mixed surface layer with a thickness of 17 m.

The value of δ^{13}C was somewhat variable between 1726 and 1775 when the CO$_2$ concentration was fairly constant at about 280 ppmv, with an average of -6.67 ± 0.11 ‰, and then lowered to some extent until about 1900 after showing an appreciable dip around 1790 when the CO$_2$ concentration showed high values.   From the beginning of

the 20th century, $\delta^{13}C$ began to decrease rapidly toward the value of $-7.33‰$ in 1961, corresponding to the enhanced long-term increase of the CO_2 concentration.

The $\delta^{13}C$ values obtained in this study are compared in Fig. 2 with those from the Siple core (Friedli *et al.*, 1986) and the Law Dome core (Francey *et al.*, 1999). The data from the Siple core are plotted after subtracting 0.1‰ for the correction of their increase during the air extraction procedure and gravitational separation (Leuenberger *et al.*, 1992). The $\delta^{13}C$ values from the Siple core and the Law Dome core are systematically higher than those from the H15 core, but a similar temporal variation can be seen in the results from the three cores, especially after the mid-19th century for which the differences from the results of the H15 core are about 0.2 and 0.3‰ for the Siple core and the Law Dome core, respectively. Such a similarity of variation suggests that the systematic discrepancy in the results from these cores may be due to different analytical techniques, including standards of $\delta^{13}C$ measurements, and/or different qualities of the ice cores employed by the respective groups. To make its causes clear, inter-laboratory analyses of the same ice core sample are required. It is also seen from Fig. 2 that the $\delta^{13}C$ value of the H15 core was temporarily but clearly low around 1790 when the H15 core showed a clear bump of the CO_2 concentration, the respective differences from those of the Siple core and the Law Dome core being 0.5 and 0.7‰. In this connection, it should be noted that the data around 1790 were obtained at quite different dates and we confirmed no intrusion of contaminated room air into the air samples during their extraction procedures. Therefore, such a dip of $\delta^{13}C$ may suggest that high CO_2 concentrations are probably due to enhanced release of biospheric CO_2 through respiration of living plants and oxidation of organic matter in soil under high air temperatures when the climate recovered from the Little Ice Age. As described later, terrestrial biospheric CO_2 is isotopically lighter than atmospheric CO_2. Another possible cause of the $\delta^{13}C$ dip may be attributable to temporarily reduced quality of the ice core for $\delta^{13}C$, although the reason is unknown at this stage. With respect to the reason why the CO_2 concentration was lower in the Little Ice Age than before and after that period, Trudinger *et al.* (1999) suggested, from their box-diffusion model study of the results from the Law Dome core, that the CO_2 concentration decrease and the $\delta^{13}C$ increase during the Little Ice Age could be explained by the terrestrial biospheric response to lowered temperatures.

To examine the long-term variation of $\delta^{13}C$ in CO_2 derived from the H15 core, the values of atmospheric $\delta^{13}C$ were calculated by the procedures described in Nakazawa *et al.* (1997). Year-by-year total emissions of CO_2 since 1725 were first estimated by a single deconvolution method in which a box-diffusion model was applied to the variations of the CO_2 concentration obtained by smoothing the data from the H15 core and direct atmospheric measurements at the South Pole and Mauna Loa (Keeling and Whorf, 1999). After this procedure, the non-fossil (biospheric) CO_2 flux for each year was derived by subtracting the contribution of fossil fuel consumption (Marland *et al.*, 1999) from the total emission. The total emission and biospheric flux of CO_2, thus obtained, are shown in Fig. 3, together with the ocean uptake, fossil fuel emission and atmospheric increase. Then, the values of $\delta^{13}C$ in atmospheric CO_2 were calculated by using the box-diffusion model again, on the basis of $\delta^{13}C$ of fossil fuel CO_2 (Andres *et al.*, 1996) and the isotopic fractionation effects of CO_2 exchange between the atmosphere
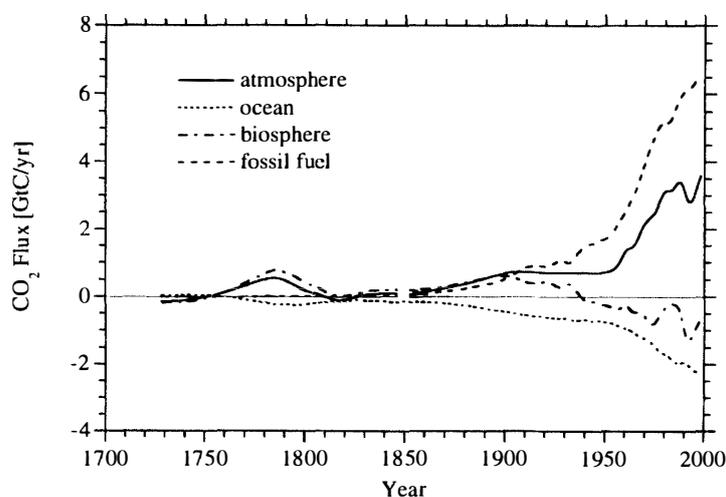
Fig. 3.   *Biospheric and oceanic CO_2 fluxes estimated by applying the box-diffusion model to the CO_2 concentration record obtained from the H15 ice core analyses and the direct atmospheric measurements at the South Pole and Mauna Loa.   The atmospheric CO_2 increase and CO_2 emissions from fossil fuel consumption are also plotted.*

and the terrestrial biosphere and between the atmosphere and the ocean, in addition to biospheric fluxes of CO_2 obtained above and fossil fuel CO_2 emissions.   An initial value of $\delta^{13}C$ was set to be $-6.6\%_0$ for 1725.   The atmospheric $\delta^{13}C$ values calculated by this procedure are also given in Fig. 2.

The calculated values of $\delta^{13}C$ agree relatively well with the results of the H15 core analyses and the direct atmospheric measurements, except in the late 18th century.   As can be understood from Fig. 3, the calculated long-term decreasing trend of $\delta^{13}C$ is attributable to emissions of both biospheric and fossil fuel CO_2 before the 19th century and then mostly to fossil fuel consumption.   In this regard, the $\delta^{13}C$ values of biospheric and fossil fuel CO_2 are about $-25\%_0$ and -24 to $-41\%_0$, respectively (Keeling et al., 1989; Tans, 1981), which are much lower than the atmospheric values of -6.5 to $-8\%_0$. A small dip of $\delta^{13}C$ was found in the late 18th century, corresponding to the rapid increase of the CO_2 concentration of about 7 ppmv.   However, the calculated values of $\delta^{13}C$ are considerably different from the measured values.   Such a large difference may suggest that the release of biospheric CO_2 was much larger than that derived by the above-mentioned single deconvolution procedure, and excess CO_2 was absorbed by the oceans.   It is well known that atmospheric $\delta^{13}C$ is affected significantly by CO_2 exchange between the atmosphere and the terrestrial biosphere but scarcely by that between the atmosphere and the ocean (Nakazawa et al., 1997).   Regarding the differences between the calculated and measured $\delta^{13}C$ values in the late 18th century, we found that the calculated values were not largely affected by the degree of the stiffness of the spline fitting to the CO_2 concentration data.

In this study, general features of temporal variations of $\delta^{13}C$ in atmospheric CO_2 over the last 250 years were revealed and their causes were discussed.   However, further analyses of high quality ice cores from high accumulation areas, as well as an intercomparison of isotope measurement techniques used by different groups, are still

needed to obtain more detailed and precise variations of atmospheric $\delta^{13}C$ in the past.

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