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Scientific note

Reconstruction of past atmospheric CH_4 concentration from the firn air data at Dome Fuji

Satoshi Sugawara[1], Kenji Kawamura[2], Shuji Aoki[2], Takakiyo Nakazawa[2] and Gen Hashida[3]

[1] *Institute of Earth Science, Miyagi University of Education, Sendai 980-0845*
[2] *Center for Atmospheric and Oceanic Studies, Tohoku University, Sendai 980-8578*
[3] *National Institute of Polar Research, Kaga 1-chome Itabashiku, Tokyo 173-8515*

***Abstract*:** Air samples were collected from different depths of the firn layer at Dome Fuji in December 1998 and analyzed for CH_4 concentrations. The age distribution of CH_4 in the firn was calculated by using a one-dimensional numerical model, and then the inverse method was applied to reconstruct variations of atmospheric CH_4 in the past. The age distribution function was calculated by including processes of molecular diffusion, downward air advection and bubble trapping in the snow-ice transition zone. Once the age distribution function is calculated, the vertical distribution of CH_4 in the firn layer can be reconstructed by a linear combination of the age distribution functions weighted by the atmospheric CH_4 concentrations in the past. Therefore, the most plausible past atmospheric record of CH_4 can be derived iteratively so that its observed profile in the firn layer was reproduced well. In order to check the calculation scheme, the estimated variation of atmospheric CH_4 was compared with direct measurements in the Antarctic region. They were in good agreement with each other, even for rapid slowing down of the secular increase observed in the 1990's.

key words: CH_4, firn air, Dome Fuji

1. Introduction

It is well known that the concentration of atmospheric CH_4 has increased rapidly over the last 200 years due to human activities such as rice agriculture, raising of ruminants, landfills, fossil fuel production and biomass burning; current concentration levels are more than double the pre-industrial values (Craig and Chou, 1982; Rasmussen and Khalil, 1984; Stauffer *et al*., 1985; Steele *et al*., 1992; Nakazawa *et al*., 1993a; Sugawara *et al*., 1994; Etheridge *et al*., 1998; Dlugokencky *et al*., 1998). Atmospheric CH_4 is one of the most important greenhouse gases that pass solar radiation but strongly absorb long-wave radiation emitted from the earth's surface. Therefore, increase of CH_4 concentration will enhance the greenhouse effect of the earth's atmosphere and bring about additional warming of the surface-troposphere system. Atmospheric CH_4 also has an important role in the chemical system. The major sink for atmospheric CH_4 is reaction with hydroxyl radicals (OH) in the atmosphere, which affects the oxidizing capacity in the troposphere by controlling OH.

For predicting future levels of atmospheric CH_4 concentration and for evaluating strategies for limiting or reducing future emission of this gas into the atmosphere, it is indispens-

able to determine the budget of the present CH_4 cycle on the earth's surface quantitatively. For this purpose, the background concentration of atmospheric CH_4 has been measured for air samples taken from fixed stations on land, ships and aircraft (Khalil and Rasmussen, 1983; Steele *et al*., 1992; Dlugokencky *et al*., 1994; Sugawara *et al*., 1994). Firn air measurement is also an effective way to elucidate past variations of atmospheric trace gases. It is well known that air in firn of polar ice sheets is older than the surface atmosphere (Schwander, 1989; Schwander *et al*., 1988, 1993). Therefore, it is possible to estimate temporal variations of atmospheric constituents for the last few decades from their vertical distributions in firn. The age of each air constituent in firn is expressed by statistical distribution depending on depth, because the mixing of firn air is controlled mainly by molecular diffusion. Taking this into account, use of an inverse method and the age distribution should be effective for the reconstruction of past changes of atmospheric constituents. For this purpose, we applied a one-dimensional diffusion model to the CH_4 concentration in firn air at Dome Fuji, Antarctica. Air samples were analyzed precisely not only for CH_4 concentration, but also for a number of other gas concentrations and isotopic ratios, at Tohoku University. Therefore, it should be possible to estimate past atmospheric changes of various species and isotopes. In this study, we focus on reconstruction of the CH_4 concentration, and assess its validity by comparing with direct measurements.

2. Model descriptions

We developed a one-dimensional diffusion model assuming that the firn structure was homogeneous horizontally. The basic process of air movement in firn was the same as proposed originally by Schwander *et al*. (1993) and used subsequently by Trudinger *et al*. (1997) and Rommelaere *et al*. (1997). It was assumed that the molecular diffusion flux in the open pore space arises from the gradient of trace gas quantity and the gravitational effect

$$F = -D\left[s\frac{\partial}{\partial z}\left(\frac{c}{s}\right) - \frac{mgc}{RT}\right]. \tag{1}$$

Here, D denotes the diffusion coefficient of the trace gas molecule to be considered. This coefficient is not a pure molecular diffusion coefficient, but an effective value for the tortuous space in the firn layer. Therefore, it is called 'effective diffusivity' to distinguish it from the pure diffusion coefficient. The variables s, c and T represent the open porosity, the trace gas quantity (mol m^{-3}) and the firn temperature (K), respectively. The constants m, g, and R are the mass number of the trace gas (kg mol^{-1}), the acceleration of gravity (m s^{-2}), and the gas constant (J mol^{-1} K^{-1}), respectively. The vertical advection flux of the trace gas, which is caused by air trapping at the close-off zone and downward bulk motion of firn, is also important, especially for sites with large accumulation rates. Schwander *et al*. (1993) assumed a successive shifting down of discretely divided firn layers, while Trudinger *et al*. (1997) introduced a coordinate system which moves downward at the vertical velocity of firn. In this study, we adopted an expression by Rommelaere *et al*. (1997). Mass conservation of the trace gas is given by

$$\frac{\partial c}{\partial t} + \frac{\partial (vc)}{\partial z} + \frac{\partial F}{\partial z} + rc = 0, \tag{2}$$

for the open pore space and

$$\frac{\partial c_b}{\partial t} + \frac{\partial (v_f c_b)}{\partial z} - rc = 0, \tag{3}$$

for bubbles. Here, c and c_b are the trace gas quantities in the open pore space and bubbles (mol m^{-3}), respectively. The vertical velocity of air in the open pore space (m s^{-1}), v, is distinguished from that of firn itself, v_f. At the transition zone where the open pore air is gradually trapped into bubbles, mass conservation is calculated by using the bubble trapping rate, r (s^{-1}). This simply means that a portion of the trace gas quantity in the open pore space, rc, is added to bubbles. A mathematical expression of the bubble trapping rate is given by Rommelaere *et al.* (1997) to be

$$r = -v_f \frac{s_t}{s} \frac{\partial}{\partial z}\left(\frac{s}{s_t}\right), \tag{4}$$

where s_t is the total porosity. The total porosity was calculated from the firn density data (Dome-F Ice Core Research Group, 1998) using the equation

$$s_t = 1 - \frac{\rho}{\rho_{ice}}, \tag{5}$$

where ρ and ρ_{ice} are the densities of firn and ice (kg m^{-3}), respectively. At the transition zone, the porosity should be divided into open and closed. In this study, the closed porosity, s_c, was calculated by using the empirical equation given by Schwander (1989)

$$s_c = s_t \exp\left(75\left(\frac{\rho}{\rho_{close}} - 1\right)\right), \tag{6}$$

where ρ_{close} is the density at the close-off depth (kg m^{-3}). Under the steady state condition for firn densification, the vertical velocity of firn, $v_f(z)$, is simply given by

$$v_f = \frac{a_s}{\rho}, \tag{7}$$

where a_s is the accumulation rate (kg m^{-2} s^{-1}). Equations (2) and (3) denote conservation of mass for the trace gas. However, the equations for the concentrations are preferable for more accurate calculation. The concentrations in the open pore space and bubbles, x and x_b, are expressed by

$$x = \frac{c}{c_{air}} \quad \text{and} \quad x_b = \frac{c_b}{c_{air,b}}, \tag{8}$$

respectively. Here, c_{air} and $c_{air,b}$ are the air quantities for the open pore space and bubbles (mol m^{-3}), respectively. The vertical profile of the air quantity in the open pore space was calculated from the barometric equation,

$$c_{air}(z) = c_{air,0} \exp\left(\frac{m_{air} g z}{RT}\right). \tag{9}$$

Here, the air quantity at the surface (mol m^{-3}), $c_{air,0}$ depends on the mean atmospheric pressure at the site. The air quantity in bubbles (mol m^{-3}), $c_{air,b}$, and vertical advection velocity of

open pore air (m s^{-1}), v, were determined by integrating the mass conservation equations of air in open and closed pores,

$$\frac{\partial(vc_{\mathrm{air}})}{\partial z}+rc_{\mathrm{air}}=0 \quad \text{and} \quad \frac{\partial(v_{\mathrm{f}}c_{\mathrm{air,b}})}{\partial z}-rc_{\mathrm{air}}=0. \tag{10}$$

The conservation equation for the concentration can be written by using eqs. (2), (3), (8), (9), and (10),

$$\frac{\partial x}{\partial t}=D\frac{\partial^2 x}{\partial z^2}+\alpha\frac{\partial x}{\partial z}+\beta x, \tag{11}$$

and,

$$\frac{\partial x_{\mathrm{b}}}{\partial t}=-v_{\mathrm{f}}\frac{\partial x_{\mathrm{b}}}{\partial z}+r\frac{c_{\mathrm{air}}}{c_{\mathrm{air,b}}}(x-x_{\mathrm{b}}), \tag{12}$$

where

$$\begin{aligned}\alpha &= -v+\frac{\partial D}{\partial z}+D\left[\frac{(m_{\mathrm{air}}-m)g}{RT}+\frac{1}{c_{\mathrm{air}}}\frac{\partial c_{\mathrm{air}}}{\partial z}\right] \quad \text{and}\\ \beta &= \frac{(m_{\mathrm{air}}-m)g}{RT}\left(\frac{\partial D}{\partial z}+\frac{D}{c_{\mathrm{air}}}\frac{\partial c_{\mathrm{air}}}{\partial z}\right).\end{aligned} \tag{13}$$

To solve the differential eq. (11) numerically, the Crank-Nicolson method (Crank, 1975) was applied. In this method, implicit and explicit differentiations in time domain were added with the same weight for stable calculation. Thus, we obtain a tridiagonal system of discrete variables of the concentration, which can be easily solved by using the Thomas algorithm (Hirsch, 1988). The upwind differential method was applied to solve eq. (12). In this method, the stability of the numerical integration is controlled by the Courant number

$$\mu=v_{\mathrm{f}}\frac{\Delta t}{\Delta z}, \tag{14}$$

which should be less than 1 for stable calculation. We set 1.0 day and 1.0 m for Δt and Δz, respectively, so that the Courant number became sufficiently small, *i.e.* less than 10^{-3}. In this connection, the vertical velocity of firn, v_{f}, is smaller than about 11 cm $year^{-1}$ at Dome Fuji. Since the accumulation is very small at Dome Fuji, as shown in Table 1, the bubble trapping at the close-off zone occurs slowly. Under such conditions, the advection velocity of air in the open pores becomes low.

Table 1. Geographical information on Dome Fuji and parameters used for model simulation.

Location	77°19′S, 39°42′E
Elevation (m a.s.l.)	3810
Sampling date	Dec. 13–25, 1998
Accumulation (kg m^{-2} yr^{-1})	32
Surface density (kg m^{-3})	300
Mean temperature (K)	215
Mean pressure (hPa)	600
Thickness of diffusive layer (m)	104

3. Effective diffusivity

In this study, we derived the effective diffusivity of CO_2 by using an iterative procedure so that the vertical profile of the CO_2 concentration observed in firn was well reproduced. For this purpose, the time series of CO_2 concentration for the past 273 years was constructed on the basis of data from analyses of an Antarctic H15 ice core for 1725–1957 (Nakazawa *et al.*, 1993b; Kawamura *et al.*, 1997) and *in situ* measurements at the South Pole for 1957–1984 (Keeling *et al.*, 1995) and Syowa Station for 1984–1998 (Aoki *et al.*, 2000; Morimoto *et al.*, 2003). Using the time series of the atmospheric CO_2 concentration and an initial guess for the effective diffusivity, the vertical distribution of the CO_2 concentration in firn was integrated from January 1725 to the date when the firn air was sampled at Dome Fuji. The vertical profile of the CO_2 concentration on the sampling date could be changed by employing different effective diffusivities. Therefore, the effective diffusivity was revised iteratively until the standard deviation of the concentration differences became smaller than 1 ppmv. The effective diffusivity at Dome Fuji estimated by this reconstruction method decreases slightly with increasing depth in the layer between 0 and 20 m and then steeply in the layer below 20 m. The effective diffusivity for CH_4 molecules was obtained by multiplying that for CO_2 molecules by a factor of 1.291 (Trudinger *et al.*, 1997).

The age distribution of CH_4 molecules in firn at Dome Fuji was calculated as a response function to an impulse given at the surface of the ice sheet. This calculation was done for 1000 years to obtain the age distribution of bubble air below the close-off zone as well, although the results for bubble air were not used in this study. The age distributions of CH_4, thus calculated, are shown in Fig. 1. The mean age in open pore air was estimated to be about 23 years at 104 m, just above the close-off depth.

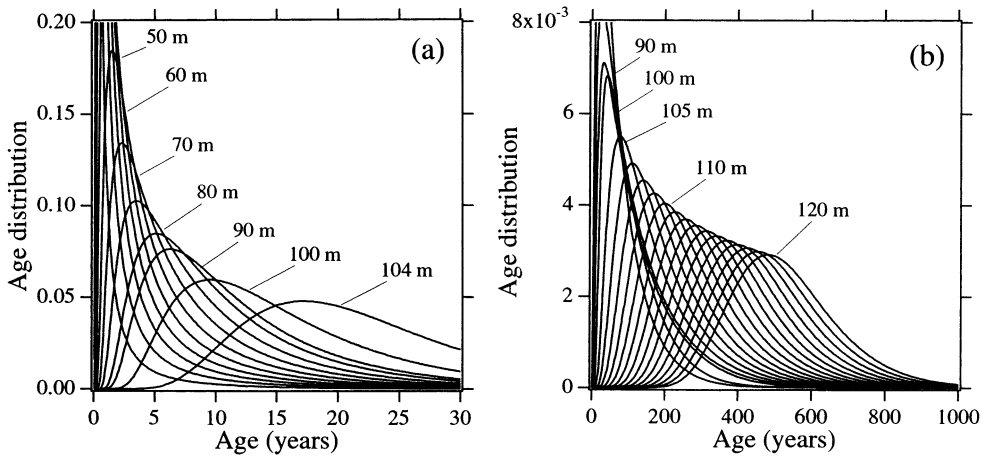

Fig. 1. Age distributions of CH_4 in (a) open pores and (b) bubbles at selected depths in firn at Dome Fuji.

4. Reconstruction method

As mentioned above, the past variation of the atmospheric CH_4 was reconstructed

inversely from its measured values in firn at Dome Fuji, using an iterative procedure. Before starting the iteration, the CH_4 concentrations observed in firn were rearranged in the time domain by calculating the mean ages from the age distributions of CH_4 at the respective depths, for use as a first guess of the atmospheric CH_4 in the past. The iterative procedure consisted mainly of the following three steps. First, the vertical profile of the CH_4 concentration in firn was calculated by using its age distribution and the first guess of the atmospheric CH_4 variation history. Second, the profile of the CH_4 concentration, thus calculated, was compared with that fitted to the observed values, and then the differences between the calculated and observed CH_4 concentrations were obtained. Finally, the initially guessed values of the atmospheric CH_4 concentration were revised by slightly adjusting the respective values in proportional to the differences obtained in the second step. These steps were repeated until the standard deviation of the differences reached its minimum value, which was less than 7.0 ppbv.

5. Results and discussion

Air was sampled at 14 different depths ranging from 10 to 104 m in firn at Dome Fuji. At the same time, two samples were also collected at the surface of the ice sheet. Details of the experimental air sampling procedure and the CH_4 concentration data in firn at Dome Fuji have been described elsewhere (Kawamura, 2000). Since systematic measurements of the atmospheric CH_4 concentration have been carried out in the Antarctic region since the 1980s (Dlugokencky *et al.*, 1994, 1998; Aoki *et al.*, 1992), the results reconstructed in this study can be compared with those from direct observations. The data from the Law Dome ice core (Etheridge *et al.*, 1998) were also used for the atmospheric CH_4 concentrations during the period 1700–1950, to initialize the vertical CH_4 distribution in firn. The CH_4 concentrations reconstructed from the Dome Fuji data are shown in Fig. 2, together with the results of direct atmospheric measurements at the South Pole by NOAA/CMDL (available on their website, http://www.cmdl.noaa.gov/) and Syowa Station by NIPR and Tohoku University (our unpublished data). Both data sets were corrected for the difference between the concentration scales employed by NOAA/CMDL and NIPR-Tohoku University. As seen in this fig-

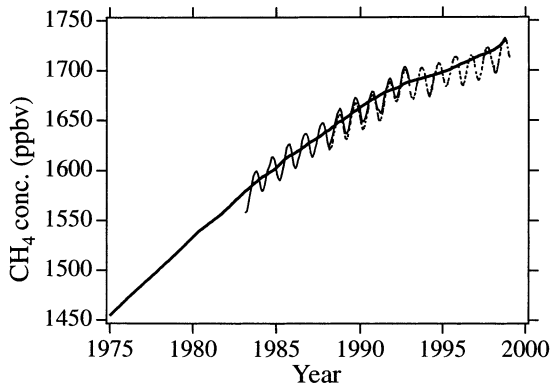

Fig. 2. Variations of the atmospheric CH_4 concentration reconstructed from its vertical profile observed in firn at Dome Fuji (thick solid line) and observed directly at the South Pole (thin line) and Syowa Station (dashed line).

ure, the variations of the atmospheric CH_4 concentration estimated in this study are in good agreement with those from the direct measurements at the Antarctic stations; the present result is always within the observed range of the concentration including the seasonal cycle. It is also obvious that not only the monotonic CH_4 increase during the 1980s, but also the stagnation of the increasing trend during the 1990s, was reconstructed well by using the present method. The CH_4 variations estimated in this study are slightly higher than those from direct measurements during the last 5 years. This discrepancy may be attributed to relatively higher CH_4 concentrations observed at depth shallower than 30 m in the firn. In this zone, the seasonal variations of the atmospheric CH_4 concentration should be propagated downward. Therefore, the vertical air sampling interval should be shorter in the shallower zone for more precise reconstruction.

6. Conclusions

A one-dimensional diffusion model was developed based on the theoretical formulation proposed by Schwander *et al.* (1993) and Rommelaere *et al.* (1997). The effective diffusivity in firn at Dome Fuji was estimated, so that the vertical CO_2 profile in firn was reproduced well by using the atmospheric CO_2 concentration history at the surface of the ice sheet. The iteration method was developed for reconstructing the past variations of atmospheric components from their vertical profiles observed in firn. This method was applied to the CH_4 data, and the result obtained was found to be consistent with direct atmospheric measurements in the Antarctic region. For better understanding of the CH_4 cycle on the Earth's surface, combined analyses of the long-term variations of the CH_4 concentration and its $\delta^{13}C$ and δD in the atmosphere are required. The method developed in this study should contribute significantly to such analyses.

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