The attenuation of fast atmospheric CH_4 variations recorded in polar ice cores

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[1] To reconstruct fast atmospheric trace gas variations from polar ice cores it has to be considered that their amplitudes are attenuated during the enclosure process in the ice. Relevant processes for the attenuation are the molecular diffusion in the open pores of the firn column and the gradual bubble close off in the depth of the transition from firn to ice. These processes depend mainly on temperature and accumulation rate and lead e.g. to a strong attenuation for cold sites with low accumulation rates. With a diffusion and enclosure model it is possible to calculate the attenuation for a single event and to compare ice core records from different sites. We investigate the atmospheric methane (CH_4) variation during the cold event 8200 years ago and calculate that its amplitude as recorded in the EPICA Dome C ice core is attenuated to a magnitude between 34% and 59%. *INDEX TERMS:* 1610 Global Change: Atmosphere (0315, 0325); 1863 Hydrology: Snow and ice (1827); 3210 Mathematical Geophysics: Modeling. **Citation:** Spahni, R., J. Schwander, J. Flückiger, B. Stauffer, J. Chappellaz, and D. Raynaud, The attenuation of fast atmospheric CH_4 variations recorded in polar ice cores, *Geophys. Res. Lett.*, *30*(11), 1571, doi:10.1029/2003GL017093, 2003.

1. Introduction

[2] Reconstruction of the past atmospheric trace gas composition can be achieved by analysing the air enclosed in bubbles of polar ice cores. The air is not enclosed directly beneath the snow surface but at a depth of 50 to 150 m, depending on the site. The range of the firn-ice transition results from different local properties, mainly temperature and accumulation rate. In the firn the air exchanges with the atmosphere through the open pore system by molecular diffusion [*Schwander*, 1989]. Therefore, the air isolated in bubbles is younger than the surrounding ice and has not a discrete age, but an age distribution. In addition, most bubbles are formed at the transition from firn to ice over a depth interval of about 15 m, which makes the age distribution even wider. Hence, fast variations in the atmospheric mixing ratio of trace gases are smoothed in the firn column and recorded in the bubbles as attenuated signals. This fact is important in the context of the question whether greenhouse gas changes similar in amplitude and duration as those driven today by anthropogenic activities could have been imprinted in the ice core record of the past. We investigate the smoothing effect on the atmospheric CH_4 variation about 8200 years before present (yr BP). The 8.2 kyr BP cooling event is probably the largest short-term temperature variation in the Northern Hemisphere in the relatively stable warm climate of the preindustrial Holocene. It is recorded in the isotopic ratios in Greenland ice cores, lasted there about 100–150 years and is calibrated as a temperature drop of 7.4 K over Greenland [*Leuenberger et al.*, 1999]. For an event of such short duration it is expected that the attenuation can be clearly observed and that it differs for different drilling sites.

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2. CH_4 Results at the 8.2 kyr BP Cold Event

[3] Our investigations are based on CH_4 measurements on the Greenland Ice Core Project (GRIP) ice core (72°34′N, 37°37′W, 3230 m a.s.l.) and the Dome Concordia (Dome C) ice core drilled in the frame of the European Project for Ice Coring in Antarctica (EPICA, 75°06′S, 123°21′E, 3233 m a.s.l.). For the CH_4 measurements the air trapped in polar ice samples of ~40 g is extracted with a melt-refreezing method [*Flückiger et al.*, 2002]. Their analytical uncertainty (1σ) is 10 parts per billion by volume (ppbv) [*Chappellaz et al.*, 1997]. Additional to the existing records [*Blunier et al.*, 1995; *Chappellaz et al.*, 1997; *Flückiger et al.*, 2002] 15 and 13 new depth levels have been measured for GRIP and Dome C, respectively. For both records the mean age resolution is 54 yr between 9 and 7 kyr BP and 36 yr between 8.5 and 7.6 kyr BP. Figure 1 shows the measured CH_4 data together with the $\delta^{18}O$ values of the ice from the GRIP and the Dome C cores. The variation in $\delta^{18}O$ of ice and $\delta^{15}N$ of air [*Leuenberger et al.*, 1999], proxies for air temperature changes, parallel the CH_4 in the GRIP record within the given data resolution. There is no $\delta^{18}O$ variation in the Dome C record and, therefore, no evidence for a significant cooling in Antarctica. In the GRIP record the CH_4 decreases from a level of about 660 to 580 ppbv in only 110 yr, and the event lasts for approximately 300 yr. To unveil the CH_4 minimum in the Dome C record we use a spline according to *Enting* [1987] with a cut-off period of 200 yr. Taking into account the relative uncertainty of the two independent gas age scales (200 yr), the obtained minimum is synchronous in time with the GRIP minimum. The amplitude of the CH_4 drop in Dome C is only about half of the GRIP amplitude and shows not such a sharp CH_4 change. As the atmospheric lifetime of CH_4 (~10 yr for the Holocene) [*Chappellaz et al.*, 1997] is several times longer than the interhemispheric mixing time (~1 yr), changes in the atmospheric CH_4 mixing ratio on time scales of several years or longer are globally very similar in shape. In the following we compare the observed

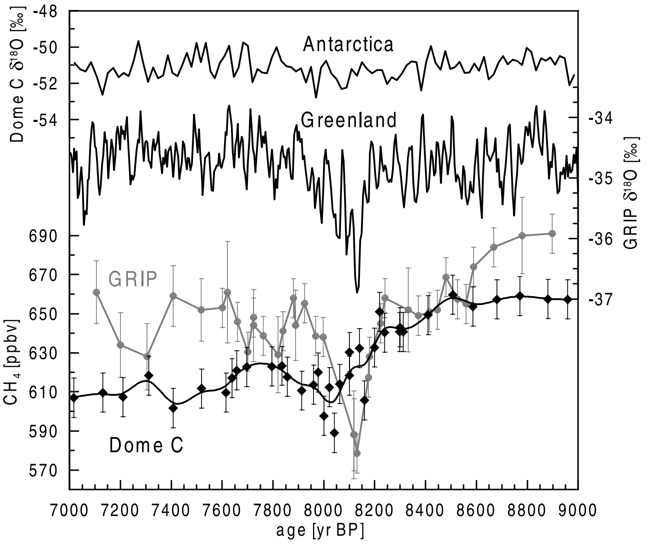

Figure 1. Comparison of $\delta^{18}O$ measured along the Dome C [*Stenni et al.*, 2001] and the GRIP [*Dansgaard et al.*, 1993] ice core (top curves) and the CH_4 from Dome C (black diamonds) [*Flückiger et al.*, 2002] and GRIP (connected grey circles) [*Blunier et al.*, 1995; *Chappellaz et al.*, 1997] for the time period of the 8.2 kyr BP event. The spline through the Dome C data (bottom curve) was calculated with a cut-off period of 200 yr [*Enting*, 1987]. The time scales for the ice and the enclosed air, in years before 1950 AD, are based on the time scale by *Schwander et al.* [2001] for Dome C and on *Johnsen et al.* [1995] and *Schwander et al.* [1997] for GRIP adapted to 1950 AD, respectively.

attenuation found in the Dome C record with results of a one dimensional diffusion and enclosure model.

3. The Diffusion and Enclosure Model

[4] The time of the gas exchange in the firn by diffusion and the bubble close off process are mainly affected by the mean temperature and the annual accumulation rate of the site. Both, the temperature and the accumulation rate in Central Greenland (−31°C, 209 kg/m^3/yr) are higher than at Dome C (−54°C, 27 kg/m^3/yr) [*Schwander et al.*, 1993, 2001]. In the GRIP ice core the firn-ice transition is at shallower depths and bubbles are occluded during a much shorter time interval. Several models have been presented to assess the diffusion in firn air [*Rommelaere et al.*, 1997; *Schwander et al.*, 1993; *Trudinger et al.*, 1997]. For this study we have used a modified version of the one dimensional box model of *Schwander et al.* [1993]. A continuous bubble close off function has been implemented in this model to calculate the age distribution of air in bubbles at a given depth. In order to calculate the diffusivity for each box the depth profile of the closed porosity s_c is needed. As a first estimate for s_c, defined as the ratio between the volume of sealed-off pores and the bulk volume of the ice, we use the equation from *Schwander* [1989]:

$$s_c = \begin{cases} s \cdot \exp\left[75 \cdot \left(\frac{\rho(z)}{\rho_{co}} - 1\right)\right] & , \quad 0 < \rho(z) < \rho_{co} \\ s & , \quad \rho(z) > \rho_{co} \end{cases} \qquad (1)$$

where s is the total porosity, $\rho(z)$ the density at depth z, and ρ_{co} the density at the depth where the air is completely enclosed in bubbles. The open porosity $s_o = s - s_c$ is then used for the parameterisation of the depth profile of the effective diffusivitiy

$$D_{eff} = \frac{D_0}{1 + 0.5 \cdot (1 - s_o) \cdot \left(\alpha + (1 - \alpha) \cdot s_o^{-\beta}\right)} \qquad (2)$$

where D_0 is the molecular diffusion coefficient of the considered gas in air. The coefficients are corrected for the temperature and the pressure of the site and given relative to CO_2 in *Schwander et al.* [1993]. The denominator of (2) characterises the tortuosity of the firn. For $s_o \rightarrow 1$ it approaches the theoretical value of $1 + 0.5 \cdot (1 - s_o)$ [*Maxwell*, 1881]. The free parameters α and β in the following hyperbolic factor allow to fit experimental data. For present conditions the parameters have been determined for GRIP ($\alpha = 0.78$, $\beta = 2.5$) [*Schwander et al.*, 1993]. In order to estimate α and β for Dome C we use the Southern Hemisphere CH_4 evolution of the past 100 yr, reconstructed from atmospheric measurements at South Pole [*Dlugokencky et al.*, 2001] and the mesurements on Law Dome ice core [*Etheridge et al.*, 1998], and calculate the expected CH_4 mixing ratios in the present firn column. The best correlation with firn air measurements [*Bräunlich et al.*, 2001] is found for $\alpha = 0.90$, $\beta = 2.5$ and $\rho_{co} = 836 \pm 5$ kg/m^3. This close off density agrees well with $\rho_{co} = 839$ kg/m^3 estimated from the temperature of the site [*Martinerie et al.*, 1994]. It is assumed that β has been constant over time and possible changes of the firn tortuosity during the 8.2 kyr BP event, when temperature and accumulation rate varied in Greenland, are attributed to changes in parameter α.

[5] Bubble formation is a continuous process in the firn with an increasing rate as the firn-ice transition is approached. The amount of air that is separated from the open pore system in a small depth interval is calculated in function of the change in the ratio of the closed porosity to the total porosity. With this approach in the model 80% of the moles of the air are ultimately trapped in a depth region between 63 and 71 m for GRIP and between 89 and 101 m for Dome C. Because the diffusion process is decoupled from the trapping process, the effective diffusion ceases above the close off depth and leads to the so called non-diffusive zone [*Schwander et al.*, 1997]. In every time step a fraction of air is added to the closed pore space with the mixing ratio in the open pores at this depth. An individual layer reaches finally the close off depth where no open pores are left. There, the mixing ratio of the considered gas in the enclosed air doesn't change anymore and is recorded as time series in the bubbles of the ice. Equation (1) is considered as a good mean for the closed porosity over several layers, although the close off process is erratic, e.g. air tight layers can already occur at shallower depths and isolate deeper but still permeable ones from the open pore system.

4. CH_4 Age Distribution in the Bubbles

[6] The physical processes in the firn depend on various local parameters of the site. The main parameters for GRIP and Dome C used in the model (Table 1) are calculated as a mean over the gas age interval from 9 to 7 kyr BP. Maximum and minimum values are taken as the means plus, minus the

Table 1. Parameters Used for the Diffusion and Enclosure Model for the Climatic Conditions at 8.2 kyr BP at Dome C (DC) and GRIP

Parameter, Unit		Values			
9 to 7 kyr BP	Site	*min*	*mean*	*max*	Ref
Acc. rate, $kg/m^2/yr$	DC	29.9	31.5	32.9	a
	GRIP	195.0	202.3	209.5	b
Surface temperature, °C	DC	−54.0	−53.5	−53.0	a
	GRIP	−33.0	−31.2	−29.4	b
Close off density, kg/m^3	DC	831	836	841	e
	GRIP	809	811	813	b
Surface density, kg/m^3	DC	295	335	375	c
	GRIP	300	340	380	d
Tortuosity (α)	DC	0.86	0.90	0.94	e
	GRIP	0.62	0.78	0.94	d

[a]*Schwander et al.* [2001].
[b]*Leuenberger et al.* [1999].
[c]*J. P. Steffensen*, personal communication [2003].
[d]*Schwander et al.* [1993].
[e]this study.

standard deviation (1σ) over this period for the accumulation rate, the surface temperature, and the close off density. The modelled density profile is varied to envelop the density measurements, including variations in surface density. It is assumed that parameter α depends as a first approximation linearly on temperature and accumulation rate. As there is no possibility to directly assess the temperature dependence of α in the structural change of the GRIP firn, we apply a large uncertainty (±20%) for α. Its uncertainty is estimated to be ±4% at Dome C, since the variations of temperature and accumulation rate are about 5 times smaller than at GRIP (Table 1). Figure 2 shows the expected CH_4 age distributions in the completely closed off bubbles of the GRIP and the Dome C ice cores using the conditions for the 8.2 kyr BP event. The best guess is calculated with the mean values and the range of solutions with all extreme values. In order to estimate the error range, individual error sources are assumed to be correlated such that the resulting error is highest, i.e. larger than in the case of independent error sources. Realistic age distributions are, therefore, within

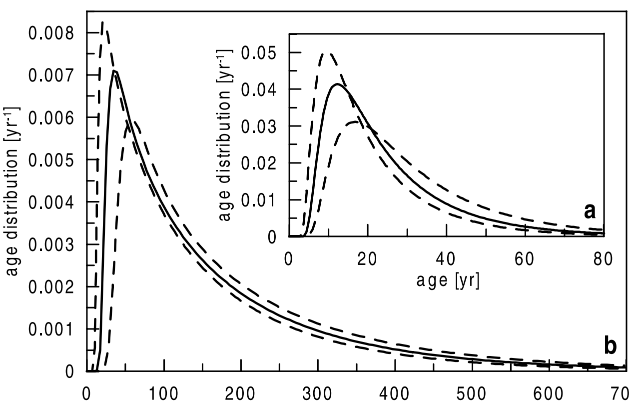

Figure 2. Modelled CH_4 age distribution for (a) GRIP and (b) Dome C at the depth where the air is completely enclosed in bubbles using the conditions during the 8.2 kyr BP event (Table 1). The solid line represents the best guess and the dashed lines the range of solutions. The age distributions are normalised to have an area of 1. Note the different scales in the two parts of the figure.

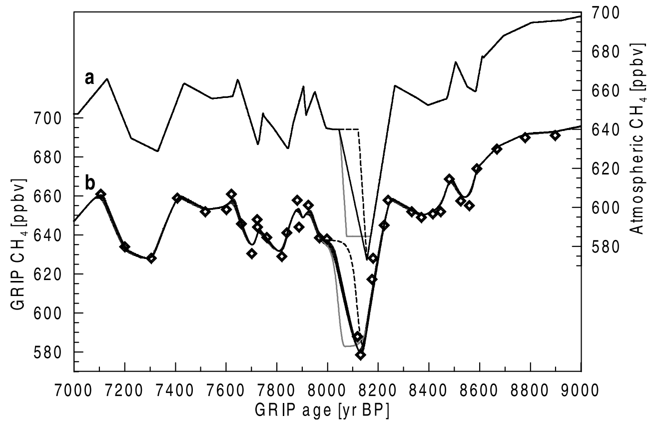

Figure 3. (a) Possible Northern Hemisphere CH_4 variations shown as the scenarios S1 (solid black line), S2 (solid grey line) and S3 (dashed black line). (b) Modelled CH_4 evolutions for the GRIP ice core assuming the three scenarios with the corresponding line styles. The thickness of the black line marks the range of solutions for S1. All model runs for GRIP lie within the 1σ uncertainty (10 ppbv) of the CH_4 measurements (diamonds) from Figure 1.

these limits. The distribution is about 7 times wider for Dome C than for GRIP. The mean age of the CH_4 molecules since they have exchanged with the atmosphere is 25 yr, but the most probable age is 12 yr for GRIP. The corresponding ages for Dome C are 171 yr and 34 yr, respectively.

5. The Expected Dome C CH_4 Record

[7] The model can be applied to calculate the expected CH_4 variation recorded in the Dome C ice core for the 8.2 kyr BP event. As an input for the model the original atmospheric CH_4 variation has to be estimated by deconvoluting the signal recorded in the GRIP core. A good approximation of the atmospheric variation is achieved by simply stretching the amplitude of the GRIP variation. Using this signal, referred as scenario 1 (S1), as an input to the diffusion and enclosure model set up for the GRIP site, the model results and the GRIP data are in good agreement, if the stretching factor is 1.13 (±0.02). We tested two additional atmospheric scenarios for the longest (S2) and the shortest (S3) possible duration of the event within the CH_4 data (Figure 3). For these scenarios the slopes of the CH_4 rise are chosen as 2 ppbv/yr, similar to the fastest increase observed in ice cores at the end of the Younger Dryas. The three differently reconstructed atmospheric signals representing the Northern Hemisphere CH_4 variation are used as an input to the model set up for Dome C. While the recorded CH_4 variation in GRIP ice shows about 88% of the atmospheric amplitude in S1, the calculated amplitude for Dome C is attenuated to 44%, 59% and 34% in S1, S2, and S3, respectively (Figure 4). The comparison of the modelled variation and the spline through the CH_4 measurements are in good agreement when taking the interhemispheric difference into account [*Chappellaz et al.*, 1997]. Therefore, the smaller CH_4 amplitude for the 8.2 kyr BP event in the Dome C ice core, compared to the amplitude in the GRIP core can be fully explained by differences in the enclosure and diffusion processes at the two sites. The uncertainties of the used Dome C parameters

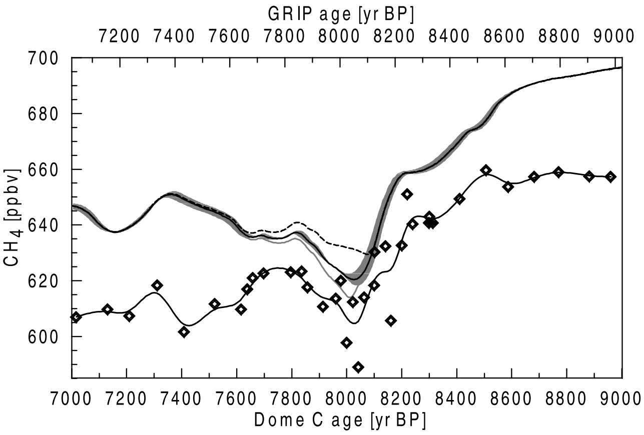

Figure 4. Comparison between the spline through the Dome C CH_4 data (bottom curve and diamonds) from Figure 1 and the modelled CH_4 variations (three top curves) for the same core calculated from the assumed scenarios with the corresponding line styles (Figure 3). The shaded area marks the range of solutions for S1. The GRIP age scale has been displaced by 25 yr against the Dome C age in order to match the minimum of the spline trough the data and the modelled variation from S1.

have only a small influence on the results as indicated with the range of solutions for S1.

[8] Assuming that the calculated smoothing is correct, the interhemispheric CH_4 difference has changed through the 8.2 kyr BP event for all three scenarios. The difference is smaller during the event (8.5 to 7.6 kyr BP) than before and after the event. A source calculation [*Chappellaz et al.*, 1997] indicates that the atmospheric CH_4 drop was mainly due to a reduction of CH_4 sources in mid to high northern latitude.

6. Conclusions

[9] The factor of attenuation for the cold event 8200 yr ago in the Dome C record is calculated to be 34% to 59%. The model is able to reproduce the attenuated CH_4 variation as observed in the measurements. For warm sites with high accumulation rates like GRIP the width of the CH_4 age distribution originates mainly from the diffusive mixing, whereas the gradual bubble close off broadens the age distribution only to a minor degree [*Schwander et al.*, 1993]. On the other hand for sites with cold temperature and low accumulation rates like Dome C the model results show that the width of the age distribution is mainly governed by the bubble close off process and has to be considered when reconstructing the evolution of the past atmosphere. To reach for example 95% of the amplitude of an atmospheric CH_4 variation in the Dome C ice core, the event has to last for at least 500 yr for Holocene conditions, while in the GRIP ice core events lasting 62 yr are recorded with the same attenuation. Based on our model results we can conclude that fast atmospheric CH_4 variations, e.g., with increasing rates similar to the anthropogenic CH_4 increase over the last 200 yr and an immediate decrease, are not erased in low accumulation-rate ice cores, but that very detailed measurements are required to detect them. Therefore, models as presented in this study will improve the interpretation of climatic events in trace gas records measured along ice cores from sites with low accumulation rates.

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