

CO₂-climate relationship as deduced from the Vostok ice core: a re-examination based on new measurements and on a re-evaluation of the air dating

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ABSTRACT

Interpretation of the past CO₂ variations recorded in polar ice during the large climatic transitions requires an accurate determination of the air-ice age difference. For the Vostok core, the age differences resulting from different assumptions on the firn densification process are compared and a new procedure is proposed to date the air trapped in this core. The penultimate deglaciation is studied on the basis of this new air dating and new CO₂ measurements. These measurements and results obtained on other ice cores indicate that at the beginning of the deglaciations, the CO₂ increase is either in phase or lags by less than about 1000 years with respect to the Antarctic temperature, while it clearly lags the temperature at the onset of the last glaciation.

1. Introduction

Important information on the link between CO₂ and climate has been deduced from the Vostok ice core, covering the last 160,000 years (Barnola et al., 1987). The study of the CO₂-climate relationship during some key periods, such as the large climatic transitions, is of special interest but requires (1) an accurate evaluation of the age difference between the air and the surrounding ice and (2) a more detailed CO₂ profile during these periods. We discuss here the different hypotheses concerning air trapping and present new results covering mainly the penultimate deglaciation and the beginning of the last glaciation.

2. Air-ice age difference

As the air bubbles do not close at the surface of the ice sheet but only near the firn ice transition (that is at about 90 m below the surface at Vostok), the air extracted from the ice is younger than the surrounding ice. To date the air with respect to the ice, in the case of Vostok, we pre-

viously assumed (Barnola et al., 1987) that: the pore closure occurs roughly in the firn density interval between 0.8 and 0.83 g cm⁻³, according to Schwander and Stauffer (1984); the air in the firn is well mixed with the atmosphere down to the bubble close off depth; the depth-density profile has remained unchanged over the last 160,000 years.

Since the close-off depth depends on temperature and accumulation rate, we have to assume that this depth has changed over the last climatic cycle at Vostok. We try here to estimate the influence of the past close-off depth on the age difference between the gas and the ice. This age difference, Δt , resulting from different assumptions, is plotted as a function of the age of the ice in Fig. 1. Four different cases have been calculated, two assuming a stationary close off depth (cases 1A and 2A) and two taking the changing close-off depth into consideration (cases 1B and 2B).

2.1. Constant close-off depth

In this case, Δt is the time required for an ice particle to reach the depth equivalent to 57.2 m of water, which corresponds to the mean density of

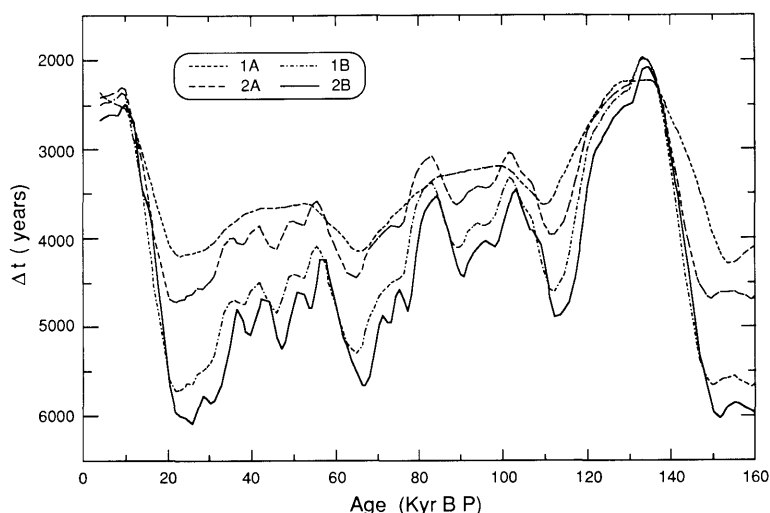


Fig. 1. Age difference between the air and the ice as a function of the age at Vostok. Curves 1A and 2A correspond to a constant trapping depth, curves 1B (Herron and Langway model) and 2B (Pimienta model) to a climate dependent trapping depth. These age differences have been established using accumulation rates from Lorius et al. (1985) for the curve 1A and accumulation rates deduced from the isotopic temperature profile of Jouzel et al. (1987) for curves 1B, 2A and 2B.

0.815 g cm^{-3} and is thus directly related to the past accumulation rate, $\lambda(t)$. Based on the idea that the accumulation rate is governed by the amount of water vapor above the inversion layer, $\lambda(t)$ depends on the temperature of formation of the precipitation and is derived from the past surface temperature following the procedure used to establish the Vostok chronology (Lorius et al., 1985), by the formula:

$$\lambda(t) = \lambda_0 (T_0^2 / T(t)^2) \exp(273k(1/T_0 - 1/T(t))), \quad (1)$$

where: λ_0 is the present-day accumulation rate ($2.2 \text{ g cm}^{-2} \text{ year}^{-1}$); $T(t)$ is the temperature in K just above the inversion layer at time t , and is related to the surface temperature $T_s(t)$ by $T(t) = 0.67T_s(t) + 88.9$ (Jouzel and Merlivat, 1984); T_0 is the present day inversion temperature (234 K); k is a constant equal to 22.5145.

In Fig. 1, the curves 1A and 2A show Δt as a function of age for different estimates of $\lambda(t)$. Curve 1A, which has been used by Barnola et al. (1987), is based on the accumulation rates from Lorius et al. (1985), while curve 2A is based on accumulation rates deduced with relation (1) from the isotopic surface temperature profile of Jouzel et al. (1987). The differences between the two results are

due to the fact that the accumulation rates of 1A have been evaluated using a very smoothed temperature curve and those of 2A using a detailed temperature profile. The maximum discrepancy is found during the coldest periods and is about 600 years. In both cases, Δt is equal to about 2500 years during the warm periods and increases up to 4500 years during the coldest periods. The width of the age distribution of the air, which is taken as the time required for a firn layer to densify from 0.80 g cm^{-3} to 0.83 g cm^{-3} , lies between about 300 years (warm periods) and 750 years (cold periods).

2.2. Climate dependent close-off depth

Δt is now the time required for an ice particle to reach the depth corresponding to the mean density of 0.815 g cm^{-3} . This depth changes with the temperature and the accumulation rate, the latter being linked to the temperature by relation (1). Two densification models, providing firn density profiles as a function of temperature and accumulation rate, are applied in this work to the past Vostok climatic conditions to estimate Δt . One of the models is from Herron and Langway (1980) and the other is derived from Pimienta (1987).

2.2.1. Herron and Langway model. This model has been derived empirically from the analysis of several Antarctic and Greenland ice core density profiles. It allows us to calculate firn density profiles, and thus Δt , if temperature, accumulation rate and surface firn density are known. It consists in two relations valid between the surface and a density of 0.55 g cm^{-3} and below 0.55 g cm^{-3} , respectively. In this work, the surface density is chosen so that the calculated depth of the 0.55 g cm^{-3} density is equal to the present-day 0.55 g cm^{-3} measured level. This surface density is then kept constant during the last climatic cycle. This model has to be applied to steady-state conditions in temperature and accumulation, so we have taken the mean climatic conditions prevailing during the transformation of the snow from the surface to the bubble close-off depth. At the end of the glaciations, that is during the coldest periods, Δt is equal to about 5500 years. This time period is of the order of a deglaciation period and thus this model is not well suited to study the climatic transitions.

2.2.2. Pimienta model. In order to solve this problem, we derived a semi-empirical model for the firn densification from $\rho = 0.05$ to 0.83 g cm^{-3} from a detailed study of the ice densification below the close-off (Pimienta, 1987). In this study, the ice densification is considered to be mainly due to plastic deformation of the ice around the air channels and bubbles. The densification rate $\dot{\rho}/\rho$ and the effective pressure ΔP (i.e., the pressure due to the overburden load, minus the bubble pressure) are then related by the equation:

$$\dot{\rho}/\rho = A f \Delta P^n = A_0 \exp(-Q/RT) f \Delta P^n, \quad (2)$$

where A_0 is a constant, Q the activation energy for mechanical creep, R the gas constant and T the temperature. The function f is given by the spherical pore model of Wilkinson and Ashby (1975) and depends mainly on the density. Below the close-off, a good fit to the experimental data is obtained by taking successively $n=3$ and $n=1$ (Pimienta, 1987). The exponent n is 1 when the effective stress is lower than 0.1 MPa , in good agreement with the Doake and Wolff (1985) field data analyses and the Pimienta and Duval (1987) mechanical tests at low stresses.

In order to determine the function f for the firn, several Antarctic and Greenland density profiles

with temperatures ranging from -14°C to -57°C and accumulation rates from 2.2 to $65 \text{ g cm}^{-2} \text{ year}^{-1}$ were analyzed using eq. (2). ΔP and $\dot{\rho}/\rho$ were directly deduced from these density profiles, n taken to be equal to 3, as the effective stress in the firn is rapidly higher than 0.1 MPa , Q is equal to 60 KJ mole^{-1} (the ice lattice diffusion activation energy) and A_0 equal to $2.54 \cdot 10^4 \text{ MPa}^{-3} \text{ s}^{-1}$. From these profiles, the function, $f_s(\rho)$, of the spherical pore model from Wilkinson and Ashby (1975) appears to be already valid below $\rho = 0.8 \text{ g cm}^{-3}$ and a mean analytical function, $f_e(\rho)$, was empirically deduced for the 0.55 – 0.8 g cm^{-3} density range. This function was calculated in order to make the two functions, $f_e(\rho)$ and $f_s(\rho)$, and their first derivatives equal for $\rho = 0.8 \text{ g cm}^{-3}$:

$$f_e(\rho) = 10^{(\alpha\rho^3 + \beta\rho^2 + \delta\rho + \gamma)}, \quad (3)$$

with $\alpha = -37.455$, $\beta = 99.743$, $\delta = -95.027$, $\gamma = 30.673$,

$$f_s(\rho) = (\frac{3}{16})(1 - \rho/\rho_i)/(1 - (1 - \rho/\rho_i)^{1/3})^3 \quad (4)$$

ρ_i being the pure ice density.

From the surface to $\rho = 0.55 \text{ g cm}^{-3}$ the Herron and Langway (1980) model was used. These two functions and relation (2) allow us to calculate the densification rate and to follow a firn particle from the surface to the density of 0.83 g cm^{-3} in order to evaluate Δt .

2.2.3. Comparison of these two approaches. In Table 1, we compare the results of these two models and the measured data at different Antarctic drilling sites. Both models are in good agreement with the measured profiles, but when the accumulation rate is high relative to the surface temperature, as for the South Pole, Siple or DE08, the Herron and Langway model becomes less suitable. The model of Pimienta is not strictly physical. However, it considers the temperature and accumulation rate via the effective pressure, ΔP , in a more realistic way and seems to be valid over a wider range of climatic conditions than the Herron and Langway (1980) model. Moreover modifications of the climate during the densification can be taken into account.

Applied to the past Vostok climatic conditions, the results of these two approaches are very similar (Fig. 1, curve 1B for the Herron and Langway

Table 1. Comparison of the firn densification models with present day data from different Antarctic sites

Site	T (°C)	λ (g cm ⁻² yr ⁻¹)	measured			Herron-Langway			Pimienta		
			$h_{0.8}$ (m)	$h_{0.83}$ (m)	Age (yr)	$h_{0.8}$ (m)	$h_{0.83}$ (m)	Age (yr)	$h_{0.8}$ (m)	$h_{0.83}$ (m)	Age (yr)
Vostok ⁽¹⁾	-55.5	2.2	86	96	2600	82	94	2610	89	98	2670
Dôme C ⁽²⁾	-53	3.4	81	95	1700	83	97	1700	89	99	1780
S. Pole ⁽³⁾	-51	8	102	115	850	107	125	950	102	114	850
D 57 ⁽⁴⁾	-32	16	68	76	275	63	73	278	64	72	274
Byrd ⁽⁵⁾	-28	16	57	64	250	54	63	240	57	63	240
Siple ⁽⁶⁾	-24	50	68	76	95	73	86	106	66	74	92
DE08 ⁽⁷⁾	-19	120	71	81	40	89	106	55	71	80	41

Measured and calculated depths corresponding to 0.8 and 0.83 g cm⁻³ ($h_{0.8}$ and $h_{0.83}$) are given for the different site temperatures (T) and accumulation rates (λ). Ages of the ice at the mean depth level between $h_{0.8}$ and $h_{0.83}$ are also indicated. Data are from Barnola et al. (1987),⁽¹⁾ Benoist et al. (1982),⁽²⁾ Kuivinen et al. (1984),⁽³⁾ Raynaud and Barnola (1985b),⁽⁴⁾ Gow (1968),⁽⁵⁾ Schwander and Stauffer (1984)⁽⁶⁾ and Etheridge and Woakey (1989).⁽⁷⁾

model and curve 2B for the Pimienta model). The difference is always less than 500 years, and Δt varies from about 2500 years during warm periods to 6000 years during the coldest periods. The width of the age distribution of the air increases from about 300 years up to about 900 years when going from the warmest to the coldest conditions.

2.3. Discussion

The fact that under present-day conditions density profiles depend on the temperature and accumulation rate implies that the age of the air trapped in the Vostok ice core has to be evaluated using variable close-off depth models and that the results published by Barnola et al. (1987) have to be corrected. From Fig. 1, the main correction is due to the incorporation of densification changes with temperature and accumulation rate variations. The air is now younger than previously and the correction is small during the warm periods and is about 2000 years during the coldest stages. The uncertainty due to the choice of the model is small (about 500 years) compared to Δt (up to 6000 years). As the model derived from Pimienta (1987) seems to be better suited to study the climatic transitions, we have applied it to the CO₂ data presented here. From Table 1, the uncertainty in the determination of Δt is about 5%.

Note that we assume that the air is in equilibrium with the atmosphere until the pores close which implies that the CO₂ mixes rapidly within the entire firn. Schwander (1989), from laboratory measurements of diffusivity, concludes that, at

least in high accumulation areas, the air in the firn is effectively isolated from the atmosphere at a density of about 0.8 g cm⁻³. This effect would decrease Δt by about 10%, that is about 600 years during the cold periods, but as the accumulation rates and thus the sinking rate of a layer are very low at Vostok (less than 2.2 g cm⁻² year⁻¹), the CO₂ could have time to diffuse to densities higher than 0.8 g cm⁻³. The results are discussed below with and without this effect. Furthermore, Craig et al. (1988) and Schwander (1989) pointed out that separation of the different gases can occur in the firn, due to gravitation. Since CO₂ is heavier than the air (O₂ and N₂), this effect would increase its concentration in the lower part of the firn. But calculation made with the Vostok climatic conditions shows that this effect would increase the absolute CO₂ concentration by less than 2 ppmv and that the relative variations would be insignificantly changed.

3. CO₂ results

New CO₂ measurements have been performed all along the Vostok profile because some of the previous results were doubtful due to analytical problems (Barnola et al., 1987), with a detailed sampling around 145 Kyr BP corresponding to the beginning of the penultimate deglaciation. The analytical accuracy of these new results is about 5 ppmv.

3.1. Comparison of the two sets of results

In Fig. 2, we present, as a function of age, the new results compared to the profile already published. The agreement between the two sets is good even if the new results seem to be slightly lower than the previous ones between 10 and 50 Kyr BP. This could be due to the poor quality of the ice in this part of the core (above 850 m). We confirm in particular the low CO₂ concentrations (about 180 ppmv) around 40 Kyr BP and the high level (close to 290 ppmv) at the beginning of the last interglacial period around 135 Kyr BP. However, the decrease of the CO₂ concentrations near the onset of the last glaciation (around 115 Kyr BP) is less rapid than suggested by the previous measurements. We have also checked that the spectral analysis of the CO₂ profile was not essentially modified, neither by the new results, nor by the new air dating.

3.2. Climatic transitions

The new CO₂ measurements and the Vostok isotopic temperature profile from Jouzel et al. (1987) are shown in Fig. 3 for the period between 100 and 160 Kyr BP. This time interval includes the penultimate deglaciation, the last interglacial and the beginning of the last glaciation.

Around the beginning of the previous glacial to interglacial transition (from 150 to 140 Kyr BP), the sampling step is about 800 years, which is close

to the width of the age distribution of the air in the firn. The CO₂ starts to increase at around 144,300 years BP while the temperature increase begins at 145,000 years BP. This difference of 700 years is reduced to only about 100 years if we consider that the air is effectively sealed from the atmosphere at a density of 0.8 g cm⁻³. In any case, these differences are not significant compared to the uncertainties associated with the densification models. We conclude that the CO₂ increase is in phase or slightly lags (by less than 1000 years) the Vostok temperature. The main uncertainty in this evaluation arises from the dating of the air with respect to the ice. At the beginning of the last deglaciation (around 15 Kyr BP), our sampling is too sparse to deduce the precise timing between CO₂ and the temperature changes, but data were obtained from other Antarctic ice cores such as those from Byrd or Dome C. From detailed results obtained on the Byrd core, Neftel et al. (1988) conclude that CO₂ lags the temperature by less than 1200 years. Note that in the Byrd case, with the data of Neftel et al. (1988), the uncertainty in air dating introduced by the choice of the firn densification model is low (about 100 years), compared to the lag deduced. From measurements performed on the Dome C core, Raynaud and Barnola (1985a) conclude that CO₂ and temperature increases are in phase. So it seems that the phase relationship between the atmospheric CO₂ and the Antarctic temperature is

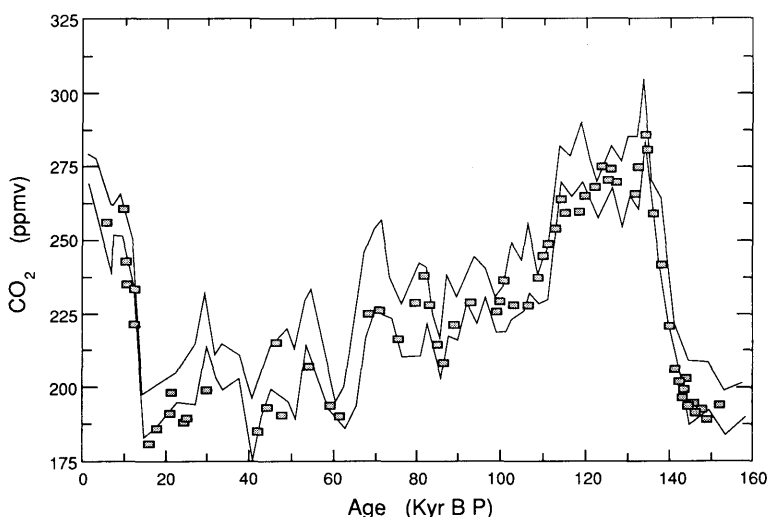


Fig. 2. Comparison of the CO₂ profile (envelope) from Barnola et al. (1987) and the measurements performed for this study (squares). The age of the gas has been evaluated from curve 2B of the Fig. 1.

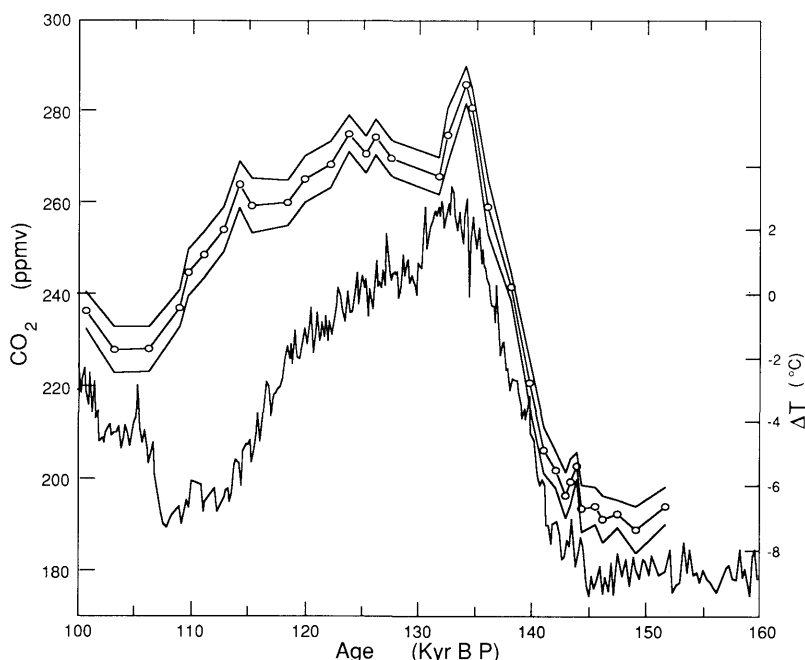


Fig. 3. CO_2 and surface temperature variations (adapted from Jouzel et al. (1987)) recorded in the Vostok ice core between 100 Kyr BP and 160 Kyr BP. The envelope of the CO_2 curve corresponds to the measurement uncertainties.

similar at the beginning of the two last deglaciations, i.e., CO_2 increases in phase or slightly lags the Antarctic temperature by less than about 1000 years.

The mechanisms suggested to explain the atmospheric CO_2 variations recorded in polar ice involve mainly oceanic modifications (see e.g., Broecker and Peng, 1986). They differ, in particular, in the response time of the atmospheric CO_2 content to the oceanic perturbation. It is thus important to know the phase relationship between the CO_2 increase and the sea level change at the beginning of the deglaciations. Bender et al. (1985) have proposed to use the $\delta^{18}\text{O}$ ratio of the oxygen trapped in the ice as a tool to reconstruct the $\delta^{18}\text{O}$ of the ocean and thus the sea level changes. Since the two signals are recorded in the same medium, this procedure avoids dating problems. Comparison of CO_2 and $\delta^{18}\text{O}$ measurements of air trapped in the Dome C core (Raynaud and Barnola, 1985a and Bender et al., 1985) suggests that, at the beginning of the last deglaciation, the CO_2 increases about 2000 years before the $\delta^{18}\text{O}$ and

thus before the sea level. But further measurements are needed to confirm this phase relationship.

When entering the last glaciation, changes in temperature and CO_2 signals are more complex to analyse than in the case of the deglaciation. Nevertheless, the marked CO_2 decrease (from about 260 ppmv to about 230 ppmv) begins around 114,000 years BP, when the Vostok surface temperature is already 6°C lower than the present day temperature. Considering the beginning of the glaciation as the significant slope change of the temperature curve occurring 118,500 years BP, the CO_2 lags the temperature by about 4500 years. This time lag cannot be explained by air dating problems and is most likely real. The published Vostok CO_2 profile seems to exhibit the same behaviour around 80 Kyr BP, where CO_2 decreases well after a temperature drop. The comparison of these lags with the phase relationship determined for the deglaciations suggests that the interactions between CO_2 ocean and Antarctic climate may depend on the type of climatic transition.

4. Conclusion

We have stressed how important it is to investigate thoroughly the problem of air dating when interpreting the past CO₂ in parallel with climate changes. Semi-empirical models of densification allow us to account for the effect of climatic conditions on firn densification rates. Applied to the past Vostok climate, these models show that the age difference between air and ice is about 6000 years during the coldest periods instead of about 4000 years, as previously assumed. Detailed CO₂ measurements for the period extending from the penultimate deglaciation to the beginning of the last glaciation and comparison with other ice cores indicate that at the beginning of the deglaciations, the CO₂ increase is in phase or lags by less than 1000 years

the Antarctic temperature change, whereas CO₂ clearly lags the temperature at the onset of the last glaciation.

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