



The local insolation signature of air content in Antarctic ice. A new step toward an absolute dating of ice records

Dominique Raynaud^{a,*}, Vladimir Lipenkov^b, Bénédicte Lemieux-Dudon^a, Paul Duval^a,
Marie-France Loutre^c, Nicolas Lhomme^{a,d}

^a *Laboratoire de Glaciologie et Géophysique de l'Environnement, CNRS/UJF, BP 96, 38402 Saint-Martin-d'Hères, France*

^b *Arctic and Antarctic Research Institute, 38 Bering street, St. Petersburg 199397, Russia*

^c *Université catholique de Louvain, Chemin du Cyclotron, 2, B-1348 Louvain-la-Neuve, Belgium*

^d *The University of British Columbia, Department of Earth and Ocean Sciences, 6339 Stores Road, Vancouver, Canada BCV6T 1Z4*

Received 24 January 2007; received in revised form 18 June 2007; accepted 18 June 2007

Available online 5 July 2007

Editor: M.L. Delaney

Abstract

An accurate chronology of ice cores is still needed for interpreting the paleoclimatic record and to understand the relation between insolation and climate. A new domain of research in this area has been stimulated by the work of M. Bender linking the record of N_2/O_2 ratio in the air trapped in the ice with the local insolation. Here we investigate the potential of the air content of polar ice, V , as another and complementary ice proxy of local insolation. We propose that the long-term changes in air content recorded in ice from the high Antarctic plateau is dominantly imprinted by the local summer insolation. The V measurements covering the last 440,000 yr and obtained along the EPICA DC (EDC) ice core are presented. 86% of the variance observed in the V record can be explained neither by air pressure nor by temperature changes, and then should reflect properties influencing the porosity at close-off other than temperature. A wavelet analysis indicates a dominant obliquity period (around 41 ka) over the last 440 ka. We propose a mechanism, which can account for the observed anti-correlation between local insolation and V and explain how the local insolation, via the integrated summer insolation, can affect the near-surface snow structure and consequently the porosity at close-off. The V and the integrated summer insolation changes show high coherency over all the record and a variable phase relationship with a maximum phase difference of about 4000 yr around 200 ka ago. The phase difference may reflect the difference between the EDC2 chronology based on an inverse dating method and an accurately dated insolation curve. Our work, by proposing a new and complementary ice proxy for local insolation should eventually contribute to the establishment of an absolute dating of the ice paleo-record.

© 2007 Elsevier B.V. All rights reserved.

Keywords: ice air content; Antarctic insolation; absolute dating of ice; snow metamorphism; ice porosity at close-off

1. Introduction

Paleoclimatic data provide information about the climatic system and a target to test climate models and their ability to reproduce past climate changes. Understanding the interplay between forcing and feedbacks, as

* Corresponding author. Fax: +33 4 76 82 42 01.

E-mail address: raynaud@lgge.obs.ujf-grenoble.fr (D. Raynaud).

well as model testing, require assessment of the phase relationship (leads and lags) between the different properties recorded, especially in ice cores and deep marine sediments. Recent progresses have been made in this area, and for instance the time sequence between greenhouse gas, ice volume and temperature changes during glacial–interglacial cycles is now documented with much better confidence (e.g.: [Petit et al., 1999](#); [Shackleton, 2000](#); [Pépin et al., 2001](#)). In contrast, the phasing between responses of the climate system and the orbital and rotational parameters, which modulate the insolation distribution at the surface of the Earth and act as pacemaker of the glacial–interglacial climate variability ([Hays et al., 1976](#)), is generally unknown.

Changes in the solar radiation received at the top of the atmosphere (often called insolation) induced by the journey of the Earth around the Sun can be accurately calculated for each position on Earth's surface. They show the frequencies of the three astronomical parameters governing the position of Earth's surface versus the Sun: 100, 41, 23 and 19 ka respectively for the eccentricity of the Earth's orbit, the obliquity and the precession of the Earth axis of rotation. So, if one of the properties measured in the ice core record contains a clear signature of the local insolation at the surface, we should, in principle, be able to tune the local climatic signals recorded in ice on the local insolation, and this in a fairly absolute way because the phase difference between insolation and climate will be at a minimum since occurring at the same place. Following the pioneering work of [Bender \(2002\)](#), which proposed to use O_2/N_2 ratio measured in the air trapped in ice as marker of local insolation, we investigate here the extent to which the air content record in ice reflects the local insolation, and what is the potential of this new method to constrain the dating of the EPICA DC (EDC) record.

In the first section we summarize what we know, from previous works, concerning the properties influencing the air content of polar ice. Then, we present the air content, V , measurements obtained on the first 2797.8 m of the EPICA DC (EDC) Antarctic ice core ([EPICA community members, 2004](#)), which cover approximately the last 440,000 yr. We show that the record remarkably displays the signature of the Milankovitch cycles. We suggest that the eccentricity (100 ka) signature reflects glacial–interglacial changes of elevation of the ice formation site and show that the dominant obliquity band found in the V record should be related with long-term changes of the porosity at close-off, which is the porosity at the firn–ice transition when the air bubbles close-off from the atmosphere. In the following step we discuss different processes that could link the porosity at close-off with local insolation and we propose a mechanism able to

explain how the long-term insolation changes at the surface can affect the snow structure and consequently the porosity at close-off. Finally, we show the potential of using the V signature of local insolation for testing the EDC chronology, which is based on an inverse dating method ([EPICA community members, 2004](#); [Parrenin et al., 2001](#)), and for approaching an absolute dating of long ice core records.

2. Primary parameters influencing V : a summary of previous works

The largest natural experiment of sintering takes place at the surface of the ice sheets, when the snow transforms progressively into ice. During the last stage of the transformation the pores, initially connected with the free atmosphere at the surface, close-off. The amount of air trapped in the newly formed bubbles is given by the ideal gas law ([Martinerie et al., 1992](#)):

$$V = V_c \cdot P_c / T_c \cdot T_o / P_o \quad (1)$$

With:

- V the air content of ice
- V_c the pore volume at close-off,
- P_c and T_c the pressure and temperature of the air contained in V_c at the enclosure time,
- P_o and T_o the standard atmospheric pressure and temperature (1013 mb, 273 °K).

Pioneering works on air content developed the concept that V , because of its pressure dependence, could be used as a barometric measure of the past surface elevations of the ice sheet ([Raynaud and Lorius, 1973](#); [Raynaud, 1976](#)). The air content–pressure dependence is clearly illustrated by V measurements performed on ice recently formed in different sites ([Fig. 1a](#)), for which we assume that P_c as well as T_c have been, at the time of ice formation, similar to that measured at present.

These pioneering works assumed that V_c was a constant. Later it was empirically shown by [Raynaud and Lebel \(1979\)](#), that V_c calculated from V using Eq. (1) was decreasing with the mean annual temperature of the ice formation site.

[Arnaud \(1997\)](#) has first proposed a physical basis of this empirical relationship ([Arnaud et al., 2000, 1998](#)). According to this model, V_c increases with the proportion of the ice-grain edges occupied by pores at close-off. The latter structural parameter appears to depend on the critical relative density D_0 , which corresponds to a change from ice grain sliding to power law creep as the

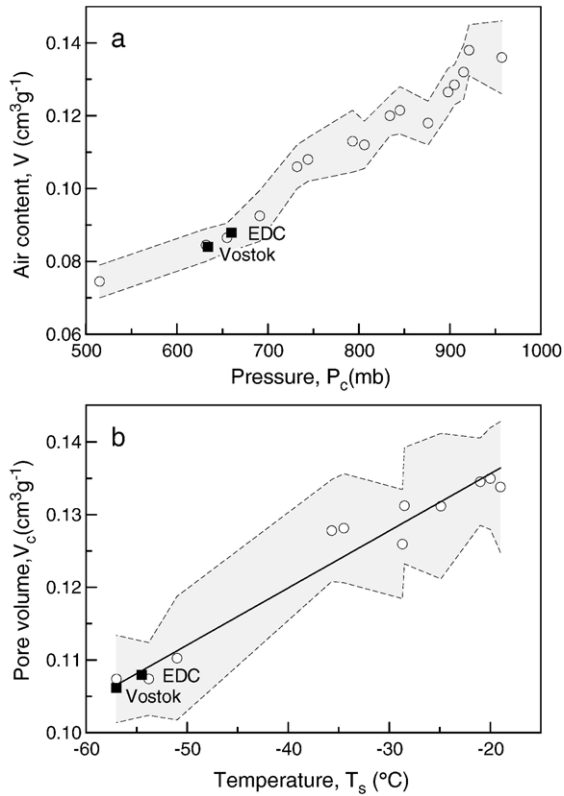


Fig. 1. a. Present-day relationship between air content of recent ice and atmospheric pressure at the level of pore closure. The data for sixteen sites shown by open circles and the uncertainty envelope are from Martinerie et al. (1992). The solid squares indicate the mean V values obtained for Holocene ice at Vostok (Lipenkov et al., 1997) and EDC (this work) drilling sites. b. Pore volume at close-off versus temperature. The data sources as in Fig. 1a (the five sites with summer snow melting are not considered). The solid line corresponds to the relationship V_c (cm³ g) = $7.6 \cdot 10^{-4} T_s$ (K) – 0.057 (Martinerie et al., 1992) used in this work. Note that the scattering around the regression is minimum for the coldest sites.

dominant mechanism of densification and marks the transition between snow and firn in an ice sheet. The higher critical density of snow implies greater number of pores per grain and lower firn density at close-off. Both the experimental (Benson, 1962) and modeling (Arnaud, 1997) results show that D_0 , in turn, increases with snow temperature T_s , thus making V_c larger at warmer sites as illustrated in Fig. 1b.

However, present-day spatial variations of V_c and the long-term air content records obtained from deep ice cores suggest that a large fraction of the V_c variability is not correlated with temperature (Martinerie et al., 1992, 1994; Raynaud et al., 1997; Delmotte et al., 1999). The seasonal stratification of firn and possible changes in the seasonality of temperature and/or precipitation have been invoked to explain the V_c non-thermal variability in the

regions with high snow accumulation (Raynaud et al., 1997; Delmotte et al., 1999). According to Arnaud et al. (2000), D_0 and therefore V_c can be affected by structural properties of the near-surface snow, which are controlled by meteorological conditions such as wind speed, surface temperature, temperature gradients and insolation (Bender, 2002; Alley, 1988; Lipenkov et al., 1998). Thus the long-term changes in the mean characteristics of snow structure can cause corresponding V_c non-thermal variations even in the case of less heterogeneous firns typical for low-accumulation sites (Martinerie et al., 1994).

To study the non-thermal variations of V_c we introduce the residual term as

$$V_{cr} = V^* T_c/P_c^* P_o/T_o - V_c(T_s). \quad (2)$$

The aim of the paper is to investigate the potential influence of local insolation on the millennial scale variability of V and V_{cr} by accurate measurements performed on the Antarctic EDC ice core.

3. The EPICA DC air content record

A description of the experimental technique (Lipenkov et al., 1995) and procedure as well as the evaluation of the overall error used for our V measurements can be found in the on-line supplementary material in the Appendix. The overall error of the obtained V values is 1%, except in the uppermost 30 m of the V profile where it can reach 1.5%.

Two cores have been drilled at the EPICA Dome C drilling site (75°06' S, 123°21' E; 3233 m a.s.l.) within a distance of 10 m: the first one, EDC96, down to 780 m and the second one, EDC99, close to the bedrock. The 10-m temperature at the site is -54.5 °C (hereafter we assume $T_s = T_c = -54.5$ °C at present time), the snow accumulation rate is $25 \text{ kg m}^{-2} \text{ yr}^{-1}$, and the atmospheric pressure at the close-off level (P_c) is estimated to be 660 mb. The EDC site conditions are slightly different from those reported for the old Dome C site (Martinerie et al., 1992), which is located 56 km apart.

We present here the air content profile measured in the depth range 115–2800 m of the EDC ice cores. The measurements were performed on the EDC96 ice core to 360 m depth and mostly on the EDC99 ice core at greater depths. The total number of measurements exceeded 200, which allowed us to obtain an air content record covering the last 440 ka with the mean time-resolution of about 2 ka.

Each sample (about 3 cm along the core axis) corresponds to 1–20 yr of accumulation depending on

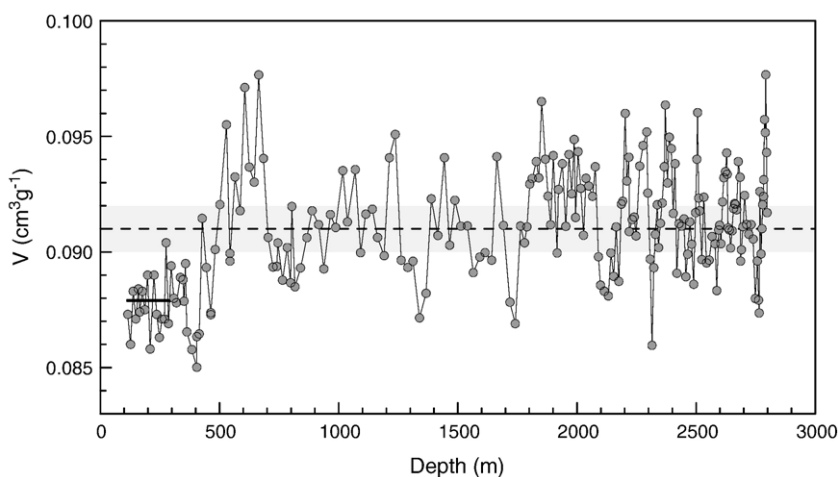


Fig. 2. Air content profile of the EDC ice core versus depth. The dashed line is the mean value ($0.091 \text{ cm}^3 \text{ g}^{-1}$) for the whole profile whereas the shadowed strip surrounding the line designates the uncertainty of a single measurement. The solid line shows the mean V value ($0.088 \text{ cm}^3 \text{ g}^{-1}$) obtained for the Holocene section of the core.

depth. We have not attempted to evaluate the short-term (stratigraphic) variability of air content in the EDC core by conducting continuous measurements on adjacent samples along selected core increments. Such a study has been performed on the Vostok ice core recovered at a site with similar conditions. The results demonstrate that the short-term V variability expressed by standard deviation of single measurements from the mean V value is about $\pm 1\%$ in the Holocene ice (Lipenkov et al., 1997).

We thus conclude that at low-accumulation sites like Vostok and Dome C, the variations of air content linked with stratigraphic heterogeneity of firm and ice are

relatively small and, as a rule, comparable with uncertainties of the V measurements. For such ice cores, single V measurements appear to be well representative to detect long-term changes in air content of Antarctic ice. In general, results obtained at Vostok reflect low heterogeneity of firm at low-accumulation sites and rule out, for such sites, the significance of the “sealing effect” on the air content earlier reported for high-accumulation sites (Martinerie et al., 1992).

Results of our measurements along the EDC ice cores are plotted versus depth in Fig. 2 (numerical data are given in the supplementary material in the

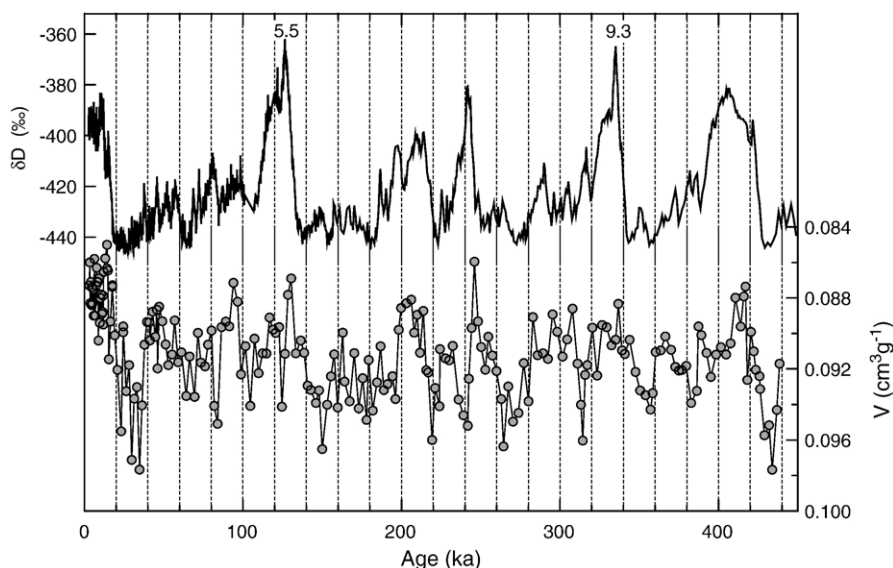


Fig. 3. EDC ice core: Isotopic composition (δD) and air content (V) versus ice age (EDC2 chronology). The well-marked interglacial stages 5.5 and 9.3 are numbered.

Appendix). The mean air content of ice between 115 and 2800 m depth is $0.091 \text{ cm}^3 \text{ g}^{-1}$, the standard deviation is about $\pm 3\%$ and the maximum amplitude of the V variations around the mean reaches $\pm 7\%$. The observed signal generally exceed both the experimental uncertainties (indicated by the shadowed strip in Fig. 2) and expected short-term stratigraphic variations of the air content.

The V measurements performed in the 115–357 m depth range of the EDC core (Fig. 2), actually the Holocene section of the core (Fig. 3), show no significant trend and a mean value of $0.088 \text{ cm}^3 \text{ g}^{-1}$, which we propose as an estimate of the air content of recent ice at the EDC drilling site (compared with $0.0865 \text{ cm}^3 \text{ g}^{-1}$ obtained for the old Dome C core (Martinerie et al., 1992)). We note that our estimate based on 24 measurements is not very sensitive to changes in the depth range of averaging. Using Eq. (1) and the site conditions we calculate a corresponding present-day V_c value of $0.108 \text{ cm}^3 \text{ g}^{-1}$ (compared with $0.1075 \text{ cm}^3 \text{ g}^{-1}$ from the old core).

The new data on the present-day V_c obtained for the EDC core (this work), Vostok (Lipenkov et al., 1997), and GRIP and Law Dome (Raynaud et al., 1997; Delmotte et al., 1999) do not significantly change the V_c –temperature empirical relationship shown in Fig. 1b

after Martinerie et al. (1992), which we use for the purpose of the present work:

$$V_c(\text{cm}^3 \text{ g}^{-1}) = 7.6 \cdot 10^{-4} T_s(\text{K}) - 0.057. \quad (3)$$

Both the temperature at the close-off depth, T_c , and the snow temperature, T_s (measured at 10 m depth), have been used to obtain the above empirical relationship (Martinerie et al., 1992). Consistent with Arnaud's theory and in contrast with earlier works, we define the temperature in empirical Eq. (3) as snow temperature T_s . For the present-day conditions, $T_s = T_c$ within uncertainties rarely exceeding 1.3°C (Martinerie et al., 1992). However, due to possible short-term variations of the snow temperature with periodicity of the order of 10 – 10^2 yr (Lipenkov et al., 2004), the present-day temperature at the close-off depth appears to be a more reliable estimate of T_s corresponding to the age of the recent ice than the temperature measured today at 10 m.

The next step for interpreting the record is to establish a depth–age relationship. Dating an ice core record depends on whether we are considering the time of snow deposition at the surface of the ice sheet which determine the age of ice, or of bubble close-off which takes place several thousands years after the snow

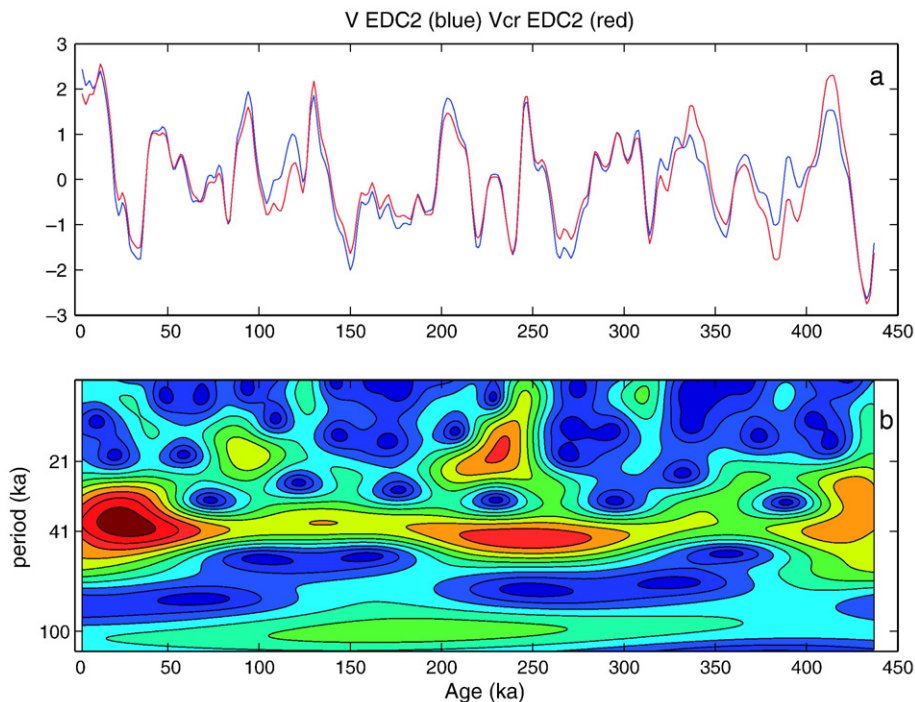


Fig. 4. Normalised and inversed time-series for V (blue) and V_{cr} (red), 2 points running window, versus EDC2 chronology. V_{cr} has been calculated with P_c varying according to the elevation history (see supplementary material in the Appendix). Wavelet analysis of V . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

deposition and corresponds to the gas age. In the context of air content, the age to be considered depends on which parameter influencing V we are dealing with. Studying how the V record is sensitive to P_c or T_c changes (cf. Eq. (1)) is relevant to the gas age chronology. On the other hand, when we investigate the influence of V_c non-thermal changes on air content, which can be imprinted by modifications of the snow structure at the surface (Section 2), it is appropriate to consider the temporal changes of the near-surface snow. Here we investigate the signature of local insolation in the EDC air content record attributed to the insolation imprint on the snow structure. That is why the V results have been plotted versus the age of ice on Fig. 3. The EDC time scale (EDC2) (EPICA community members, 2004) has been established using an inverse dating method (Parrenin et al., 2001) and the major aim of the present work is to develop a new method based on the air content record for checking the validity of EDC2.

4. The Milankovitch signature of the EDC air content record

In this section we discuss how the large variability observed along the EDC air content record is related to changes in surface and close-off temperatures (T_s and T_c), pressure at close-off (P_c) and the non-thermal component of the porosity at close-off (V_{cr}).

T_s time series are obtained from the deuterium record (Fig. 3), which is used as a proxy for mean annual surface temperature (EPICA community members, 2004; Stenni et al., 2001).

T_c changes are calculated taking into account thermal diffusion through the firn (Goujon et al., 2003).

P_c changes (see supplementary material in the Appendix) are obtained from the variations in depositional surface elevation predicted by a coupled ice sheet-tracer model described in Lhomme (2004) and Lhomme et al. (2005).

V_{cr} is calculated from Eq. (2).

V and V_{cr} are highly correlated as shown on Fig. 4a (correlation coefficient: 0.93) and 86% of the variance of V is explained by V_{cr} . In addition, we estimate the maximum contribution of the temporal P_c changes to the air content variability over the last 440 ka to be of the order of 3% (supplementary material in the Appendix). Finally, according to Eqs. (1) and (3) the remaining 10% or so of the observed V variability has to be attributed to temperature changes. Fig. 3, which shows the comparison between the records of V and the deuterium (δD) content of the EDC ice (a proxy for temperature), confirms the weak correlation between air content and temperature

changes. In particular, the major climatic warm periods corresponding to the well-marked interglacial stages 5.5 or 9.3 have no clear counterparts on the air content record, and so only a small part of the V variability can be explained by temperature changes.

In order to understand the reason of the large variability observed in the V_{cr} time series, and hence in the V record, we investigated their spectral domain. The results of a wavelet analysis (Mallat, 1998; Torrence and Compo, 1999) on the smoothed V record (moving average 2 points) is shown on Fig. 4b. Only the obliquity period (41 ka) is dominant all along the record. We note that a dominant obliquity is also found in the Antarctic Dome Fuji (DF) air content record (Kawamura, 2000). A significant precession signal appears, but only around 80–100 and 200–250 ka BP, and the analysis also shows a weak eccentricity signature. The same analysis has been performed on the V_{cr} record (not shown on Fig. 4). The overall dominance of the obliquity is confirmed and the precession signal is weaker and centred on the 80–100 and 200–240 ka intervals. The main difference is the disappearance of the 100 ka. Because V_{cr} is the non-thermal residual of the porosity at close-off and very weakly, if not at all, affected by pressure changes (see supplementary material in the Appendix), the disappearance of the 100 ka band in V_{cr} reflects the fact that the eccentricity signal observed on V is due to the influence of temperature and/or pressure changes on the air content. Since, as mentioned above, the major climatic warm periods corresponding to the well-marked interglacial stages 5.5 or 9.3 have no clear counterparts in the air content record, the 100 ka periodicity in the V record should have been preferentially driven by pressure changes induced by long-term changes in surface elevation of the ice formation site (see supplementary material in the Appendix).

Thus, the air content record of the EDC core remarkably contains the three major Milankovitch frequencies: obliquity and precession of the Earth axis of rotation and orbital eccentricity, but the dominant one is obliquity (41 ka). The 100 ka band mainly results from elevation changes of the surface of the ice sheet, whereas the large similarity between the wavelet analysis of V and V_{cr} at EDC for the other Milankovitch frequencies indicates that most of the variability of V in the obliquity and precession bands is due to V_{cr} , it is to say essentially independent of temperature.

5. How to explain the multi-millennial scale variability of V and V_{cr} in low-accumulation sites?

The 200 ka Vostok (Martinerie et al., 1994) and the 340 ka Dome F (Kawamura, 2000) air content records

show similar large multi-millennial scale variability as the EDC record, which is neither due to changes in pressure or temperature, nor to thermal changes in the close-off porosity. Spectral analysis of V time series are reported for Dome F (Kawamura, 2000) and EDC (this work) and shows, as already mentioned in Section 4, a dominant obliquity power in both cases. Importantly for further consideration, the three drilling sites are located approximately at the same latitude in the low-accumulation area of East Antarctica.

A discussion of different mechanisms, that can affect the bubble close-off process in low accumulation sites for explaining long term V variability, can be found in Martinerie et al. (1994). In the case of Vostok, the composite V profile obtained with three different analytical techniques to 2546 m is characterised by a large scattering of the data. Martinerie et al. (1994) suggested that the snow packing by wind at the surface of the ice sheet may have influenced the porosity at close-off and could thus partly account for the observed variability. We now believe that the wind effect cannot convincingly explain the large V variability observed in sites like Vostok, Dome C or Dome F. Indeed there is a wind speed threshold of about 6 m/s above which wind impact significantly the snow density (Lipenkov et al., 1998), and the mean annual wind speed observed at present over the East Antarctic Plateau do not, as a rule, exceed 6 m/s. We also note that, according to simulations of ice sheet surface climate, wind speed changes between the Last Glacial Maximum (LGM) and today are too weak to have a significant impact on the air content (Lipenkov et al., 1997; Krinner et al., 2000).

5.1. Local insolation imprint in the ice record

As mentioned in the Introduction, Bender (2002) first proposed that local insolation may leave an imprint in the ice record. He found a dominant precession signal (23 ka) in the O_2/N_2 ratio measured in the air trapped in the Vostok ice and concluded that summertime insolation influences the snow metamorphism and that the insolation signature in these properties, being retained throughout the firn column, influences O_2/N_2 fractionation during bubble close-off. Several processes by which summertime insolation can influence surface grain properties and O_2/N_2 fractionation during bubble close-off are discussed. According to Bender, the relation between the grain structure and the O_2/N_2 fractionation has still to be determined.

More recently, Kawamura et al. (2004) proposed that in low accumulation sites wind crusts or other high density layers formed at the surface are homogenized

under high insolation conditions, whereas at times of low insolation this stratigraphic high density features are just retained throughout the firn column and will seal off prematurely layers with a lower bulk density (or higher porosity). Such a mechanism would indeed account for decreasing V_{cr} values with higher local insolation levels. However, this explanation based on a sealing effect of high density thin layers is not supported by observations made under present-day conditions at low-accumulation sites (Martinerie et al., 1992).

Let's assume that both signatures of air content at EDC and O_2/N_2 at Vostok are influenced by the imprint of local summer insolation on surface grain properties. Then, why are their spectral domains different with a dominance of precession for O_2/N_2 -Vostok and of obliquity in the case of V-EDC? The O_2/N_2 fractionation during bubble close-off is generally explained, due to its relatively small molecular diameter, by the selective escape of O_2 molecules from bubbles closing-off, whereas the air content, via the porosity at close-off, depends on pore geometry (number of pores per grain). The observed spectral difference points to different mechanisms leading to an insolation dependence of O_2/N_2 fractionation and to porosity during bubble close-off. We also note that part of the spectral difference could be explained by the shorter length of the O_2/N_2 -Vostok record (200–390 ka BP) compared to the length of the V-EDC record. Indeed, the wavelet analysis of V at EDC shows, in addition to a dominant obliquity all over the record, a strong precession in the 200–250 ka BP interval (Fig. 4b). Thus, we cannot rule out that the same insolation-dependent processes of snow metamorphism might control both O_2/N_2 and air content of ice.

There are also latitudinal gradients of insolation, which spectrum contains enhanced obliquity power over precession (see for instance Loutre et al. (2004)). In principle, changes in the meridional gradient between low and high latitudes could have affected the wind patterns over Antarctica but, as mentioned above, the wind effect cannot satisfactorily explain the observed V variability. Although we cannot completely rule out a contribution of changes in the latitudinal gradients of insolation through a mechanism different from the local wind effect, the local insolation appears to be the most realistic candidate for explaining the dominant obliquity signal found in the V_{cr} and V records.

5.2. Local insolation and porosity at close-off: a proposed mechanism

None of the processes described above can fully satisfactorily explain the observed V_{cr} changes at EDC.

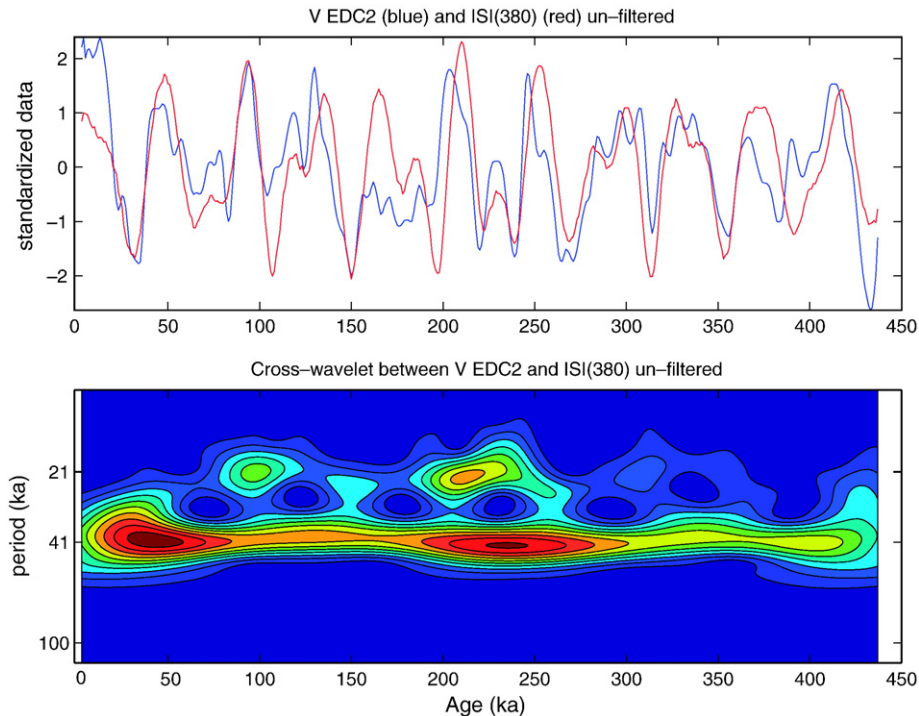


Fig. 5. The top panel shows the normalised time series of ISI (in red, $w_{\text{threshold}}=380 \text{ W m}^{-2}$, orbital chronology) and of inversed V (in blue, 2 points running window, EDC2 chronology); their cross-wavelet analysis is shown in the bottom panel. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

We propose here to investigate the relationship between insolation and the pore volume at close-off, by considering the insolation imprint on the snow structure and the successive mechanisms that lead from the sintering of snow at the surface of ice sheets to the closure of pores. We base our consideration on the model results showing that the porosity at close-off is affected by the *size of snow grains* (single crystals or grain clusters) playing a direct role in the densification process (Arnaud, 1997; Arnaud et al., 2000). The rapid growth of crystals or grains in the top 3–5 m of ice sheets is attributed to the effects of sustained temperature gradient during summer (Gow, 1969; Alley and Koci, 1988). Conduction of heat through the snow due to solar radiation contributes to the evolution with time of the temperature profile in the first meters of snow. But, latent-heat transfer by water vapour migration and convection of air in the pore spaces are other significant processes (Brandt and Warren, 1993, 1997). The absorption of near-infrared radiation close to the surface leads to snow heating whereas the compensatory cooling by emission of the thermal infrared radiation to the outside atmosphere is likely insignificant in the case of Antarctic snow (Brandt and Warren, 1993). We assume that the rapid grain growth in the first meters of snow is related to insolation by way of the *summer*

temperature gradients. From sub-surface temperature measurements at South Pole (Dalrymple et al., 1966), grain growth should essentially occur, under present-day conditions, between November and March when temperature is above the mean annual temperature and above 4 m in depth where large temperature gradients are present.

From our own observations at Vostok Station, the growth of faceted grains associated with depth hoar just beneath the snow surface is not representative of the snow structure. Detailed stratigraphy studies were performed in several 2–12 m pits at Vostok (Ekaykin et al., 2004), showing that coarse grained low-density layers comprise more than 70% of the deposited snow, fine-grained dense layers (wind slabs) about 28%, and depth hoar represents less than 2% of the total snow thickness. Similar observations were obtained at Dome C (East Antarctica) (Palais, 1984). There is a clear indication that these variations in the surface snow structure progressively disappear with depth in cold sites (Alley, 1980). The size of grains below some meters would be therefore directly related to the integrated summer insolation.

Deeper, densification of snow is mainly a structural re-arrangement of grains driven by the snow load

(Anderson and Benson, 1963; Alley, 1987). This densification mechanism ceases to be the dominant densification mechanism at a critical relative density D_0 of about 0.6 (Anderson and Benson, 1963). D_0 (the ratio between snow and pure ice density at the snow–firn transition) is considered to be associated with the transition between grain-boundary sliding and power-law creep as the dominant densification mechanism (Arnaud et al., 1998; Alley, 1987). The observed increase of D_0 with temperature (Arnaud, 1997; Benson, 1962; Nishimura et al., 1983) must be related to the increase of the snow load at the snow–firn transition when temperature decreases (Gow, 1975; Herron and Langway, 1980). Indeed, the increase of the snow load promotes densification by power-law creep at the expense of densification by grain boundary sliding, which is linearly stress dependent. The increase of grain size with insolation should induce a decrease of D_0 since the rate of densification by grain-boundary sliding decreases with the increase of the size of grains (Alley, 1987).

Near the bottom of the firn layer, the closure of cylindrical pores located along the edges of grains is assumed to occur by the growth of small perturbations (fluctuations of diameter) by diffusion mechanisms (Shieh and Evans, 1991). For a given grain size, shape of grains and porosity, the diameter of pores decreases as the number of pores per grain increases. As a consequence, the density at close-off should increase when the number of pores per grain decreases (Arnaud, 1997). By assuming that the distribution of pores does not significantly change after the snow–firn transition, there is therefore a direct link between the density at close-off and the density at the snow–firn transition: the density at close-off increases as D_0 decreases.

As discussed above, more intense insolation leads to lower D_0 . The density at close-off is therefore expected to increase with insolation, which means that the porosity at close-off should decrease with more intense insolation. It is worth noting that the effect of insolation on the porosity at close-off must be viewed as one cause of the departure from the linear law relating the pore volume at close-off at temperature (Fig. 1b).

6. Integrated summer insolation (ISI), porosity at close-off, and ice dating

6.1. Integrated summer insolation

In Section 5.2 we assume that insolation and porosity at close-off (and hence air content of ice) are related through the effect of summer temperature gradients on

grain growth in the near surface snow layer and we conclude that Vcr should decrease when insolation increase. The next question is about the type of insolation that could control the heat conduction through the snow and contribute to the temporal evolution of the temperature gradients in the first meters of snow, and at the same time account for the spectral characteristics of Vcr. For instance, should we consider the time of maximum intensity or the duration of the summer insolation? As an example, when the surface of the Earth is closest to the sun during the summer, the summer duration is shortest. The seasonal irradiation from the sun, which is a measure of the total energy (generally expressed in joules/m²) received at any given latitude at the top of the atmosphere during a specific season, shows a dominant power in the obliquity band. On the other hand the daily or seasonal irradiance, the corresponding irradiation divided by the length of the day or the season and expressed in W/m², is dominated by changes in precession (Berger and Pestiaux, 1984). In the case of regions beyond the polar circle both summer irradiation and summer irradiance are potentially important parameters that can affect the surface and near-surface snow conditions. This is especially true if we assume a direct link between the insolation received at the top of the atmosphere and at the ground, which is a fair assumption in the case of the central Antarctic plateau. Because irradiance changes are primarily controlled by precession, they may be considered for explaining the dominant precession signature of the O₂/N₂ ice record at Vostok (Bender, 2002), whereas irradiation changes may account for the V and Vcr dominant obliquity power found along the EDC record.

As mentioned in Section 5.2 grain growth in surface snow, which controls the porosity at close-off, mainly occurs above a temperature- and hence insolation-threshold. However, we lack information about such thresholds, even under present-day conditions. We thus assume that the spectral signatures of V and Vcr in obliquity and precession essentially reflects local insolation changes and then tune in amplitude both obliquity and precession peaks of the integrated summer irradiation, *that we will equally call integrated summer insolation or ISI*, with the corresponding peaks of V . Following Huybers (2006), ISI is obtained by summing over the year the daily insolation w_i :

$$ISI = \sum \beta_i (w_i * 86,400) \quad (4)$$

where ISI is expressed in joules and w_i in W/m², with $\beta_i = 1$ when $w_i \geq w_{\text{threshold}}$, and $\beta_i = 0$ otherwise.

The $w_{\text{threshold}}$, evaluated by tuning the precession to obliquity amplitude ratio of ISI on the corresponding ratio of air content (Fig. 2 in the Appendix), is equal to about 380 W/m^2 when using the EDC2 timescale.

Under present-day conditions, mid-month daily insolation and mean monthly temperature are well correlated; the mid calendar-month daily insolation is $\geq 380 \text{ W/m}^2$ during the summer period from approximately mid-November to mid-February when the mean monthly temperature is $\geq -40^\circ\text{C}$ (Fig. 3 in the Appendix). Such temperature threshold, above which ISI influences significantly the close-off porosity, is in agreement with our proposed mechanism linking insolation and porosity at close-off (Section 5.2).

Both ISI, as calculated by Eq. (4), and the V record, plotted versus EDC2, are shown on Fig. 5. V and consequently V_{cr} decrease with more intense insolation. This is exactly what our proposed mechanism (Section 5.2) predicts. The cross-wavelet analysis (Fig. 5) highlights the high degree of coherence between the two signals in the obliquity and precession bands.

In conclusion, we built an ISI signal, which accounts for the V and V_{cr} spectral powers in the obliquity and precession bands. This signal is physically coherent with our knowledge of the mechanisms linking insolation and porosity at close-off.

6.2. Constraining the EDC chronology

Our reconstructed ISI is an accurately dated local insolation curve. Since the V signal recorded in the EDC ice appears to be essentially imprinted by ISI within a very short delay (probably not exceeding one summer season), we should be able to date accurately the V EDC-record by identifying common features in the records of both ISI and V .

In order to calculate the difference between the EDC2 ice chronology, the one used to plot our air content record, with the astronomical chronology corresponding to ISI, we filtered the V and ISI records in the high coherency bands of obliquity and precession (between 15 and 46 ka, Fig. 6). The phase analysis between the two filtered records indicates (Fig. 6) that over the last 450 ka EDC2 is generally younger than the astronomical chronology and that the maximum difference is of about 4 ka around 200 ka BP.

Our assumption that all the obliquity and precession power found in the V and V_{cr} records is due to ISI is certainly an important limitation for the accuracy of our method toward an absolute dating of the ice. Indeed, we cannot completely rule out the possibility that some part of the observed obliquity to precession amplitude ratio can be due to different properties or uncertainties that we

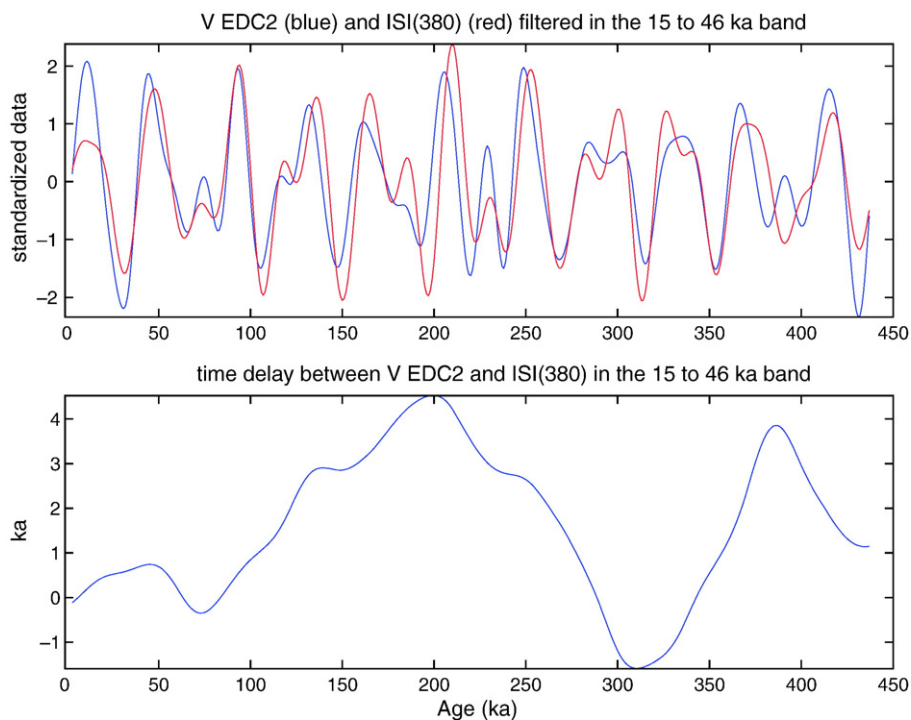


Fig. 6. Time delay (bottom panel) between V (top panel, 2 points running window, EDC2 chronology) and ISI (top panel, $w_{\text{threshold}}=380 \text{ W m}^{-2}$, orbital chronology) filtered in the 15–46 ka band. (For interpretation of the references to colour in the top panel, the reader is referred to the web version of this article.)

have neglected in our approach, such as the non-linearity of the response of V to insolation changes, the surface albedo effect, which can affect the mechanisms linking insolation and porosity at close-off, or the uncertainty in the empirical V –temperature relationship used to deduce the non-thermal variations of the porosity at close-off. To test the sensitivity of our approach to the obliquity to precession amplitude ratio we have changed the $W_{\text{threshold}}$ value by $\pm 10\%$. Although this range of $W_{\text{threshold}}$ corresponds to a large amplitude ratio bracket, the results show that the time difference between the two chronologies is weakly dependent on $W_{\text{threshold}}$. By assuming reasonably that $W_{\text{threshold}}$ cannot vary by more than $\pm 10\%$, the method accuracy for assessing the time difference is always < 1 ka over the last 440 ka. The weak chronology dependence on the amplitude ratio between obliquity and precession reflects the dominance of obliquity in ISI time series. This contrasts with the daily summer insolation, which is dominated by precession and is out of phase by roughly 2 ka for consecutive months (Loutre and Berger, 1995).

7. Conclusions

Air content at EDC has been measured with a very high precision, generally within $\pm 1\%$. It includes all the measurements performed and constitutes a unique and robust time series covering the past 450,000 yr. The time resolution of about 2000 yr has been chosen in order to pick up changes at the precession frequencies.

The record indicates that 86% of the orbital scale variability observed cannot be attributed to climate or paleo-elevation history of the EDC ice found in depth, and then reflect changes in the porosity at close-off due to other forcing. We propose here a mechanism able to explain that more intense insolation induces a decrease in the porosity at close-off, which is exactly what our EDC air content results indicate. Nevertheless more data on snow structure and subsurface summer temperature gradients in different sites of the ice sheet are required before implementing our proposed mechanism in a numerical model taking into account the successive mechanisms involved from the sintering of snow at the surface to the closure of pores.

The clear dominance in the obliquity power all along the V record, together with a weaker and discontinuous precession signature, is best explained when comparing the records with the integrated summer solar irradiation. We propose to use this property to make a new step toward an absolute dating of the long-term ice core records, and in particular to better constrain the EDC chronology. For the last 450,000 yr the EDC2 chronology is generally slightly younger than the age predicted by the astronomical ISI metronome, with a

maximum difference of about 4 ka around 200 ka BP. We estimate the accuracy of our method to be on the order of, or better than, one ka in the case of the last 450,000 yr EDC record. That the EDC2 chronology on the whole is too young for the last 450,000 yr, is consistent with the new EDC3 chronology, which has been recently proposed (Parrenin et al., submitted for publication). Like EDC2, EDC3 is built on a combination of age markers and modelling information but using an improved ice flow models and new age markers, including preliminary air content age markers corresponding to minimal obliquity peaks. Our approach here suggests that the age of the EDC ice around 200 ka can be even younger than the one given by the EDC3 chronology.

Finally, although it remains to clarify the exact reason for – and how large is – their spectral difference, we can arguably conclude that both V and O_2/N_2 are affected by local insolation. Combining air content and O_2/N_2 time series should provide a robust test toward an absolute dating of ice core records.

Acknowledgements

This work is a contribution to the European Project for Ice coring in Antarctica (EPICA), a joint European Science Foundation/European Commission (EC) scientific programme, funded by the EC and by national contributions from Belgium, Denmark, France, Germany, Italy, The Netherlands, Norway, Sweden, Switzerland and the UK. This work has in particular benefited from the support of EPICA-MIS of the European 6th framework. The main logistic support at Dome C was provided by IPEV and PNRA and we thank the drilling team that made the science possible. The laboratory work also got support from the GDRE Vostok (French INSU/CNRS funding, Russian funding through RFBR-CNRS grant 05-05-66801). M-F. Loutre was supported by FRFC-FNRS (Belgium) and by the CGRI/CNRS agreement for her stay at LGGE. We are especially grateful to Jean-Marc Barnola for stimulating and useful discussions, as well as to G. Dreyfus, M. Hutterli, G. Krinner, K. Kawamura, F. Parrenin and C. Ritz. The manuscript has been improved thanks to the comments of three anonymous reviewers and we thank a lot John Mak for reading carefully the final manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.epsl.2007.06.025](https://doi.org/10.1016/j.epsl.2007.06.025).

References

- Alley, R.B., 1980. *Densification and Recrystallization of Firm at Dome C, East Antarctica*. Institute of Polar Studies. The Ohio State University, Columbus, Ohio.
- Alley, R.B., 1987. Firm densification by grain boundary sliding. *J. Phys. (Paris)* 48, 249–256.
- Alley, R.B., 1988. Concerning the deposition and diagenesis of strata in polar firm. *J. Glaciol.* 34, 283–290.
- Alley, R.B., Koci, B.R., 1988. Ice-core analysis at site A, Greenland: preliminary results. *Ann. Glaciol.* 10, 1–4.
- Anderson, D.L., Benson, C.S., 1963. The densification and diagenesis of snow. In: Kingery, W.D. (Ed.), *Ice and Snow*. The MIT Press, pp. 391–411.
- Arnaud, L., 1997. *Modélisation de la Transformation de la Neige en Glace à la Surface des Calottes Polaires; étude du Transport des gaz dans ces Milieux Poreux*, PhD. Université Joseph Fourier.
- Arnaud, L., Barnola, J.-M., Duval, P., 2000. Physical modeling of the densification of snow/firm and ice in the upper part of polar ice sheets. In: Hondoh, T. (Ed.), *Physics of Ice Core Records*. Hokkaido University Press, Sapporo, pp. 285–305.
- Arnaud, L., Lipenkov, V., Barnola, J.-M., Gay, M., Duval, P., 1998. Modeling of the densification of polar firm: characterization of the snow–firm transition. *Ann. Glaciol.* 26, 39–44.
- Bender, M., 2002. Orbital tuning chronology for the Vostok climate record supported by trapped gas composition. *Earth Planet. Sci. Lett.* 204, 275–289.
- Benson, C.S., 1962. Stratigraphic studies in the snow and firm of the Greenland ice sheet. *SIPRI Res. Rep.* 70, 76–83.
- Berger, A., Pestiaux, P., 1984. Accuracy and stability of the Quaternary terrestrial insolation. In: Berger, A., Imbrie, J., Hays, J., Kukla, G., Saltzman, B. (Eds.), *Milankovitch and Climate*, 126. D. Reidel, Dordrecht.
- Brandt, R.E., Warren, S.G., 1993. Solar-heating rates and temperature profiles in Antarctic snow and ice. *J. Glaciol.* 39, 99–110.
- Brandt, R.E., Warren, S.G., 1997. Temperature measurements and heat transfer in near-surface snow at the South Pole. *J. Glaciol.* 43, 339–351.
- Dalrymple, C., Lettau, H.H., Wollaston, S.H., 1966. South Pole micrometeorology program: data analysis. *Studies in Antarctic Meteorology Antarctic Research Series*, vol. 9. AGU, Washington D.C., pp. 13–57.
- Delmotte, M., Raynaud, D., Morgan, V., Jouzel, J., 1999. Climatic and glaciological information inferred from air-content measurements of a Law Dome (East Antarctica) ice core. *J. Glaciol.* 45, 255–263.
- Ekaykin, A.A., Lipenkov, V.Y., Kuzmina, I.N., Petit, J.-R., Masson-Delmotte, V., Johnsen, S.J., 2004. The changes in isotope composition and accumulation of snow at Vostok Station over the past 200 years. *Ann. Glaciol.* 39, 569–575.
- EPICA-COMMUNITY-MEMBERS, 2004. Eight glacial cycles from an Antarctic ice core. *Nature* 429, 623–628.
- Goujon, C., Barnola, J.-M., Ritz, C., 2003. Modeling the densification of polar firm including heat diffusion: application to close-off characteristics and gas isotopic fractionation for Antarctica and Greenland sites. *J. Geophys. Res.* 108. doi:10.1029/2002JD003319.
- Gow, A.J., 1969. On the rates of growth of grains and crystals in south polar snow. *J. Glaciol.* 8, 241–252.
- Gow, A.J., 1975. Time–temperature dependence of sintering in perennial isothermal snowpacks. *IAHS Publ.* 114, 25–41.
- Hays, J.D., Imbrie, J., Shackleton, N.J., 1976. Variations in the Earth's orbit: pacemaker of the Ice Ages. *Science* 194, 1121–1132.
- Herron, M.M., Langway Jr., C.C., 1980. Firm densification: an empirical model. *J. Glaciol.* 25, 373–385.
- Huybers, P., 2006. Early Pleistocene glacial cycles and the integrated summer insolation forcing. *Science* 313, 508–511.
- Kawamura, K., 2000. *Variations of Atmospheric Components Over the Past 340,000 years from Dome Fuji Deep Ice Core, Antarctica*, PhD. Tohoku University.
- Kawamura, K., Nakazawa, T., Aoki, S., Fujii, Y., Watanabe, O., Severinghaus, J.P., 2004. Close resemblance between local summer insolation, O_2/N_2 and total air content from the Dome Fuji Ice Core, Antarctica. *Eos Trans. AGU* 85, Fall Meet. Suppl. (Abstract C33C-0356).
- Krinner, G., Raynaud, D., Doutriaux, C., Dang, H., 2000. Simulations of the Last Glacial Maximum ice sheet surface climate: implications for the interpretation of ice core air content. *J. Geophys. Res.* 105, 2059–2070.
- Lhomme, N., 2004. *Modelling water isotopes in polar ice sheets*, PhD. University of British Columbia, University Joseph Fourier of Grenoble.
- Lhomme, N., Clarke, G.K.C., Ritz, C., 2005. Global budget of water isotopes inferred from polar ice sheets. *Geophys. Res. Lett.* 35. doi:10.1029/2005GL023774.
- Lipenkov, V., Candaudap, F., Ravoire, J., Dulac, E., Raynaud, D., 1995. A new device for air content measurements in polar ice. *J. Glaciol.* 41, 423–429.
- Lipenkov, V.Y., Ekaykin, A.A., Barkov, N.I., Pourchet, M., 1998. O svyazi plotnosti poverkhnostnogo sloya snega v Antarktide so skorost' u vetra (On the relationship between surface snow density in Antarctica and wind speed). *Mater. Glyatsiol. Issled.* 85, 148–158.
- Lipenkov, V.Y., Salamatin, A.N., Duval, P., 1997. Bubbly-ice densification in ice sheets: II. Applications. *J. Glaciol.* 43, 397–407.
- Lipenkov, V.Y., Shibayev, Y.A., Salamatin, A.N., Ekaykin, A.A., Vostretsov, R.N., Preobrazhenskaya, A.A., 2004. Recent climatic variations reflected in the upper 80 m of the Vostok borehole temperature profiles. *Mater. Glyatsiol. Issled.* 97, 44–56.
- Loutre, M.F., Berger, A., 1995. Solar radiation, paleoclimates of the Northern and Southern Hemispheres. The PANASH Project, The Pole-Equator-Pole Transects, *PAGES Series* 95-1, IGBP-PAGES, Bern, pp. 51–58.
- Loutre, M.F., Paillard, D., Vimeux, F., Cortillo, E., 2004. Does mean annual insolation have the potential to change the climate? *Earth Planet. Sci. Lett.* 221, 1–14.
- Mallat, S., 1998. *A Wavelet Tour of Signal Processing*. Academic Press.
- Martinerie, P., Lipenkov, V.Y., Raynaud, D., Chappellaz, J., Barkov, N.I., Lorius, C., 1994. The air content paleo record in the Vostok ice core (Antarctica): a mixed record of climatic and glaciological parameters. *J. Geophys. Res.* 99, 10565–10576.
- Martinerie, P., Raynaud, D., Etheridge, D.M., Barnola, J.-M., Mazaudier, D., 1992. Physical and climatic parameters which influence the air content in polar ice. *Earth Planet. Sci. Lett.* 112, 1–13.
- Nishimura, H., Maeno, N., Satow, K., 1983. Initial stage of densification of snow in Mizuho plateau, Antarctica. *Mem. Natl. Inst. Polar Res., Spec. Issue* 29, 149–158.
- Paillard, D., Labeyrie, L., Yiou, P., 1996. Macintosh program performs time-series analysis. *Eos Trans. AGU* 77, 379.
- Palais, J.M., 1984. *Snow Stratigraphic Investigations at Dome C, East Antarctica*, Institute of Polar Studies. The Ohio state University, Columbus, Ohio.
- Parrenin, F., Jouzel, J., Waelbroeck, C., Ritz, C., Barnola, J.-M., 2001. Dating the Vostok ice core by an inverse method. *J. Geophys. Res.* 106, 31837–31851.
- Parrenin, F., Barnola, J.-M., Beer, J., Blunier, T., Castellano, E., Chappellaz, J., Dreyfus, G., Fischer, H., Fujita, S., Jouzel, J.,

- Kawamura, K., Lemieux-Dudon, B., Loulergue, L., Masson-Delmotte, V., Narcisi, B., Petit, J.-R., Raisbeck, G., Raynaud, D., Ruth, U., Schwander, J., Severi, M., Spahni, R., Steffensen, J.P., Svensson, A., Udisti, R., Waelbroeck, C., Wolff, E., submitted for publication. The EDC3 chronology for the EPICA Dome C ice core.
- Pépin, L., Raynaud, D., Barnola, J.-M., Loutre, M.F., 2001. Hemispheric roles of climate forcings during glacial–interglacial transitions, as deduced from the Vostok record and LLN-2D model experiments. *J. Geophys. Res.* 106, 31,885–31,892.
- Petit, J.-R., Jouzel, J., Raynaud, D., Barkov, N.I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V.M., Legrand, M., Lipenkov, V.Y., Lorius, C., Pépin, L., Ritz, C., Saltzman, E., Stievenard, M., 1999. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* 399, 429–436.
- Raynaud, D., 1976. Les inclusions gazeuses dans la glace de glacier; leur utilisation comme indicateur du site de formation de la glace polaire; applications climatiques et rhéologiques, Doctorat d'État, Université Scientifique et Médicale de Grenoble.
- Raynaud, D., Lorius, C., 1973. Climatic implications of total gas content in ice at Camp Century. *Nature* 243, 283–284.
- Raynaud, D., Lebel, B., 1979. Total gas content and surface elevation of polar ice sheets. *Nature* 281, 289–291.
- Raynaud, D., Chappellaz, J., Ritz, C., Martinerie, P., 1997. Air content along the GRIP core: a record of surface climatic parameters and elevation in central Greenland. *J. Geophys. Res.* 102, 26607–26613.
- Shackleton, N.J., 2000. The 100,000-year ice-age cycle identified and found to lag temperature, carbon dioxide, and orbital eccentricity. *Science* 289, 1897–1902.
- Shieh, S.Y., Evans, J.W., 1991. The stability of cylindrical voids and of cylinders subject to closure by viscous flow or evaporation/condensation. *J. Appl. Phys.* 70, 2968–2972.
- Stenni, B., Masson-Delmotte, V., Johnsen, S., Jouzel, J., Longinelli, A., Monnin, E., Röthlisberger, R., Selmo, E., 2001. An oceanic cold reversal during the last deglaciation. *Science* 293, 2074–2077.
- Torrence, C., Compo, G.P., 1999. A practical guide to wavelet analysis. *Bull. Am. Meteorol. Soc.* 79, 61–78.