

in watershed soils<sup>7,8</sup> and microbial  $\text{SO}_4^{2-}$  reduction<sup>11</sup> in these primarily drainage systems. Thus, if dry deposition may be slightly in excess of wet deposition<sup>12</sup> and the evapoconcentration factor is near two<sup>13</sup>, we expect lake  $\text{SO}_4^{2-}$ :precipitation  $\text{SO}_4^{2-}$  ratios to have an upper bound of ~4:1 to 5:1, although a definitive bound cannot be established. For northeastern lakes included in this study having  $[\text{Ca}^* + \text{Mg}^*] \leq 200 \mu\text{equiv. l}^{-1}$ , this ratio was generally within the expected range (mean  $\pm 2$  s.d. =  $2.92 \pm 1.60$ ). Many lakes with high base cation concentrations ( $[\text{Ca}^* + \text{Mg}^*] > 200 \mu\text{equiv. l}^{-1}$ ) exhibited lake  $\text{SO}_4^{2-}$  enrichment considerably higher than expected ( $4.29 \pm 4.98$ ). For lakes with low base cation concentrations ( $[\text{Ca}^* + \text{Mg}^*] \leq 200 \mu\text{equiv. l}^{-1}$ ), 2.1% of the population had a ratio exceeding 5.0, and 0.2% exceeding 6.0. For lakes with higher base cation concentrations, however, many more lakes exceeded these criteria, 23.1% and 13.7%, respectively. It appears that internal sources of  $\text{SO}_4^{2-}$  are significant for many of the lakes with high base cation and ANC concentrations. Although internal sources of  $\text{SO}_4^{2-}$  cannot be ruled out for lakes with low base cation concentrations, we observed no evidence that such sources are substantial.

Table 1 gives recent lake chemistry distributions from areas of North America currently receiving low wet deposition of  $\text{SO}_4^{2-}$  (generally  $< 10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ). Despite widely varying ANC (median 46 to 317  $\mu\text{equiv. l}^{-1}$ ), estimated organic anion concentrations (median 10 to 94  $\mu\text{equiv. l}^{-1}$ ), geology, soils and vegetation, all subregions were remarkably similar in that they had few or no acidic lakes. Although several acidic lakes with high dissolved organic carbon were sampled in the Okefenokee Swamp of Georgia<sup>3</sup>, it appears that, on a regional basis, in temperate glaciated terrain, acidic lakes are generally absent in areas with low  $\text{SO}_4^{2-}$  deposition. We emphasize, however, that small lakes (especially those  $< 4$  ha and to a lesser extent, those from 4 to 10 ha) are under-represented in the data from Canada and Minnesota (Table 1). Note also that the two pristine subregions containing the highest estimated organic anion concentrations (Northwest Ontario and Northeast Minnesota, 94 and 89  $\mu\text{equiv. l}^{-1}$ , respectively) also had low percentages of low-ANC lakes. Only 4% and 2%, respectively, of the lakes in these subregions had  $\text{ANC} \leq 40 \mu\text{equiv. l}^{-1}$ .

Recognizing the inherent limitations of interregional comparisons because of differences in physical characteristics and deposition history, the data in Table 1 suggest that acidic northeastern lakes  $> 4$  ha would likely not be acidic in the absence of  $\text{SO}_4^{2-}$ . This contention can be further examined on the basis of the  $\text{SO}_4^{2-}/\text{C}_B^*$  ion ratio in acidic NLS lakes. From the charge balance definition of ANC (equation (1)), it follows that if  $\text{SO}_4^{2-}$  exceeds  $\text{C}_B^*$ , then lakewater will be acidic. Of the northeastern lakes measured as acidic (population estimate,  $N = 326$ ), 85% also had a ratio of  $\text{SO}_4^{2-}/\text{C}_B^* > 1$ . This suggests that these lakes are now acidic due to  $\text{SO}_4^{2-}$ .

It is evident that most northeastern lakes that now have  $\text{ANC} \leq 0 \mu\text{equiv. l}^{-1}$  are acidic because of  $\text{SO}_4^{2-}$ . It is not clear, however, whether some of these lakes may previously have been acidic from another source, such as organic acids<sup>14,15</sup>. But available data from low-deposition areas in North America (Table 1) suggest that, for the lakes considered (that is, those generally  $> 4$  ha), temperate North American lakes are not acidic in the absence of anthropogenic sulphate. Palaeolimnological investigations of diatom remains in lake sediments have suggested that many northeastern lakes were acidic in pre-industrial times, but these have almost exclusively been small lakes ( $< 10$  ha)<sup>16</sup>.

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## CO<sub>2</sub> record in the Byrd ice core 50,000–5,000 years BP

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The analysis of air in polar ice cores revealed 30% lower CO<sub>2</sub> values during glacial periods than during interglacial periods. At present this is confirmed by results from six different ice cores, two from Greenland and four from Antarctica<sup>1-5</sup>. In all cores the CO<sub>2</sub> change coincides with the change in the isotopic composition of the ice, expressed as either the  $\delta^{18}\text{O}$  or  $\delta\text{D}$  ratio; both are indicators for the mean annual surface temperature<sup>6</sup>. To investigate the relationship between atmospheric CO<sub>2</sub> concentration changes with changes in climate, the atmospheric CO<sub>2</sub> concentration during and at the end of the last glaciation has to be known in detail. To achieve this, we have studied a great number of samples from the deep ice core from Byrd station, Westantarctica, drilled in 1968. These measurements allow us to reconstruct the atmospheric CO<sub>2</sub> concentration in the time period 50,000–15,000 yr BP in great detail.

The samples from Siple Station, Westantarctica, allow us to study in detail the atmospheric CO<sub>2</sub> concentration of the past 200 years<sup>7</sup>. The ice record overlaps the Mauna Loa record for a short period, and so there are direct atmospheric measurements available for comparison. This is strong evidence that air stored in bubbles of polar ice samples reflect the true atmospheric composition. There are however several 'pitfalls' which can lead to deviations from the true atmospheric composition. Higher concentrations can be found, if melting and refreezing processes occur at the surface during the summer season<sup>2</sup>. For the Byrd core no melt features were observed<sup>8</sup>. Carbon dioxide in the bubbles might also interact with impurities in the ice, particularly alkaline dust. We consider this effect to be of minor influence for the Byrd core, because the Byrd ice is slightly acidic along the whole core. The fact that the same CO<sub>2</sub>-level changes at the glacial/interglacial transition are found in six different cores with different alkalinity, means that alkaline dust is not responsible for the drop in the CO<sub>2</sub>-level. Regarding the different CO<sub>2</sub> irregularities measured in the depth interval 1,850–1,900 m below the surface of the Greenland Dye 3 core<sup>9</sup> we cannot rule out the fact that CO<sub>2</sub> originating from dissolved carbonate dust

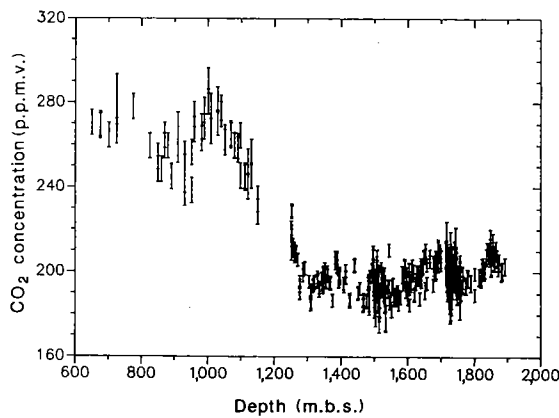


Fig. 1 All measured data points as a function of the depth below surface. The data points are indicated with a bar corresponding to the  $1\sigma$  error.

may be partly or fully responsible for the higher  $\text{CO}_2$  values. Other deviations might result from coring and post-coring effects. Samples which originate from brittle core sections show increased  $\text{CO}_2$  concentrations<sup>2</sup>. Such samples often have internal cracks filled with an organic fluid used to counterbalance the hydrostatic pressure in the drill hole. If the ice samples started to melt during storage or transport, followed by a refreezing, the  $\text{CO}_2$  content in the bubbles could be depleted in some parts of the ice core and enriched in others.

Because the enclosure process acts as a low-pass filter, the  $\text{CO}_2$  record stored in the bubbles of the polar ice archive is a smoothed record of the atmospheric  $\text{CO}_2$  concentration. In the Byrd core the air is enclosed between 60 and 80 m below the surface (m.b.s.) and the duration of the enclosure is  $\sim 50$  yr during the Holocene<sup>10</sup>. The analysis of small adjacent samples allows us to discriminate to a certain extent, variations of  $\text{CO}_2$  in the ice caused by natural atmospheric variations from 'artefacts' (as described above). For non-natural changes, local  $\text{CO}_2$  concentration gradients are expected to be larger and to vary irregularly when compared to natural atmospheric variations, which are smoothed by the enclosure process. Our system has the advantage that we can measure small samples (2–10 g) and therefore we can detect local variations indicating non-atmospheric disturbances.

We report here a new series of measurements of the Byrd core consisting of samples from the depth interval 600–1,900 m below the surface. In the depth interval 600–1,000 m.b.s. the core quality is rather poor. The ability to measure very small samples means that we can avoid samples with visible internal cracks. Unfortunately no more core material was available in the depth interval 1,150–1,250 m.b.s. Figure 1 shows all the measured data as a function of the depth. The results agree generally with earlier published data<sup>2</sup>. Different timescales for the Byrd core are reported in the literature<sup>11–13</sup>. Our interpretation is based on the most recent dating by Hammer *et al.*<sup>13</sup>. It relies on a continuous measurement of the acidity along the whole core. The depth interval 600–1,900 m.b.s. corresponds approximately to the time interval 6,000–50,000 yr BP. The 'missing' depth interval 1,150–1,250 m.b.s. corresponds to an important part of the transition from the last glaciation to the Holocene. During this period fast climatic changes have been reported from different records from the Northern Hemisphere<sup>14,15</sup>. To calculate the atmospheric concentration by deconvolution, with the exception of the depth interval 1,150–1,250 m.b.s. we interpolated the data to obtain an equidistant time series. The mean sampling rate of the measurements corresponds to one sample every 200 years. We used the following expression to describe the enclosure process:

$$c_{\text{ice}}(t) = \int_{-\infty}^{\infty} f(t'-t) c_{\text{atm}}(t') dt' \quad (1)$$

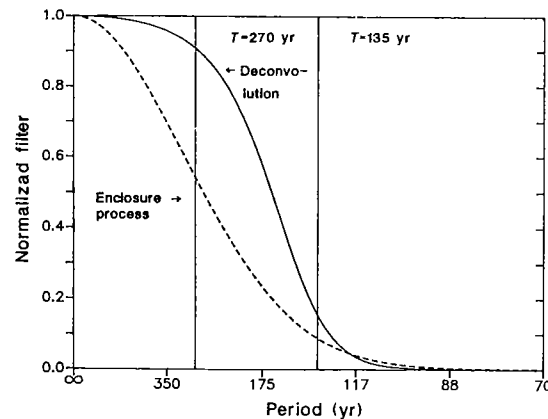


Fig. 2 Filter characteristic of the enclosure process (dotted line) and the deconvolution algorithm (solid line). The vertical lines indicate the periods corresponding to the close-off time and twice the close-off time respectively for ice age conditions.

where  $f(t'-t)$  is a normalized gaussian filter:

$$f(t'-t) = \frac{1}{(\pi\tau^2)^{1/2}} \exp\left[-\frac{(t'-t)^2}{\tau^2}\right] \quad (2)$$

Eighty-four per cent of the gas is enclosed in the time interval  $2\tau$ . For the Holocene (10,000–0 yr BP) we assumed  $\tau$  to be 27 years<sup>10</sup>. There is strong evidence that the yearly accumulation decreased between 15,000 and 10,000 yr BP by a factor of 2.5. We assumed therefore that  $\tau$  increases linearly for this period by the factor of 2.5 up to 67 years<sup>10,16</sup>. The atmospheric concentration has to be calculated from equation (1). The deconvolution is calculated in the frequency domain. Convolution in the time domain corresponds to a multiplication in the frequency domain. The atmospheric concentration is then given by:

$$c_{\text{atm}}(t) = F^{-1}(c_{\text{atm}}(w)) = F^{-1}\left(\frac{c_{\text{ice}}(w)}{f(w)}\right) \quad (3)$$

$F^{-1}$  is the inverse Fourier transform and  $f(w)$  is the Fourier transform of the enclosure function. To achieve meaningful solutions the inverse filter  $f^{-1}(w)$  was slightly modified to suppress the blow-up of high frequencies.

$$f_{\text{mod}}^{-1}(w) = \frac{\exp((-w\tau/2)^2)}{\exp(-2(w\tau/2)^2) + \exp(-2(g/2)^2)} \quad (4)$$

In equation (4)  $g$  was set to a value of 2.5. The filter characteristic of the deconvolution procedure is equal to the ratio of the modified enclosure function and the original enclosure function in the frequency domain. Figure 2 shows the filter characteristic of the deconvolution procedure. The solid line represents the overall characteristic of the deconvolution, the dotted line the characteristic of the enclosure process of the ice. Oscillations of the atmospheric  $\text{CO}_2$  concentration with a period corresponding to twice the enclosure time,  $2\tau$  would be attenuated to 40% in the ice and would be reinstated to 82% of the original value after the deconvolution procedure. For oscillations with a period corresponding to the duration of the enclosure time, the percentages would be 8.5% for the  $\text{CO}_2$  record in ice and 18% for the reconstructed record by the deconvolution procedure. Faster changes are suppressed and cannot be seen either in the ice or reconstructed by deconvolution. The limited accuracy of the measured data points causes a certain uncertainty in the reconstructed atmospheric  $\text{CO}_2$  concentration. We determined a band empirically by superposing 50 different records. For each record the deconvolution was calculated allowing the single measurements to take a random value within the estimated error limit. As a weight function a gaussian distribution was chosen. The band was then calculated as the  $2\sigma$  interval of the mean curve

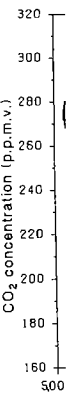


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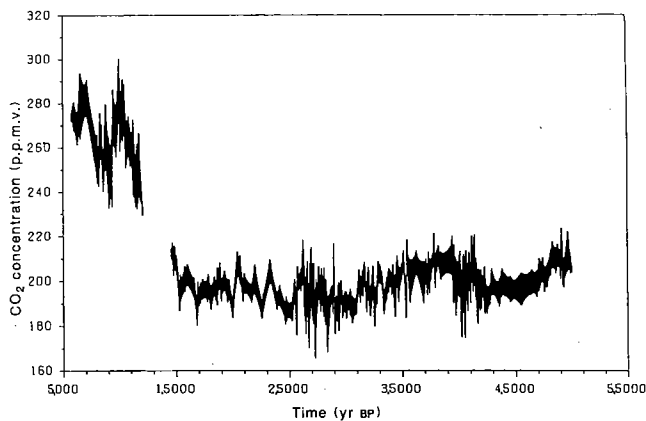


Fig. 3 Calculated band of the atmospheric CO<sub>2</sub> concentration.

where  $\sigma$  is the standard deviation. This band is plotted in Fig. 3.

We discuss the Byrd CO<sub>2</sub> record in two parts. The first part 15,000–5,000 yr BP includes the transition from glacial to post-glacial time. By bridging the missing part with a linear interpolation the CO<sub>2</sub> increase from 200 p.p.m.v. in the glacial period to 280 p.p.m.v. in the Holocene occurred in ~5,000 yr. The value of 280 p.p.m.v. which is reached at 10,000 yr BP corresponds to the pre-industrial value. We consider the observed minimum of 245–255 p.p.m.v. ~8,000 yr BP to be real and not due to artefacts related to the poor core quality. Our data indicate that at least at the beginning of the Holocene changes up to 40 p.p.m.v. of the atmospheric CO<sub>2</sub> concentration occurred. At present we have no explanation for such atmospheric CO<sub>2</sub> variation at the beginning of the Holocene. Figure 4 shows a comparison of the CO<sub>2</sub> record with the  $\delta^{18}\text{O}$  record<sup>17</sup> in the depth interval 1,000–1,600 m.b.s. covering the beginning of the transition from the last glacial age into the Holocene. The  $\delta^{18}\text{O}$  record is shifted by 12 m towards greater depth to compare the same age for both records. This assumes an age difference of 600 years between the ice and the mean age in the bubbles. The  $\delta^{18}\text{O}$  ratio starts to increase between 200 and 1,200 years before the CO<sub>2</sub> starts to rise, the  $\delta^{18}\text{O}$  ratio increase is already 20–30% of the total shift at the glacial/interglacial transition. According to these results the atmospheric CO<sub>2</sub> therefore cannot have triggered the climatic shift observed in the Byrd core, but it could be an important forcing factor establishing the mild climate of the present interglacial.

The second part 50,000–15,000 yr BP shows variations in a band between 180 and 220 p.p.m.v. These variations found in the Byrd core are much smaller than those observed in the Dye 3 core, which are characterized by 50 p.p.m.-elevated CO<sub>2</sub> concentrations for several relatively short periods between 40,000 and 30,000 yr BP.

CO<sub>2</sub> is globally well mixed. The interhemispheric gradient cannot exceed a few p.p.m. Therefore for corresponding gas ages the same concentration must be measured in cores from both hemispheres, if they represent the atmospheric concentration. It is straightforward to check whether a given pattern believed to be atmospheric can be found in different cores. If not, the specific pattern cannot be atmospheric.

There is a contradiction between the CO<sub>2</sub> record from the Byrd deep ice core and from the Dye 3 deep ice core. We see three possible explanations: (1) The elevated CO<sub>2</sub> concentrations in the Dye 3 core are caused by melt features. (2) The duration of the warm periods with higher CO<sub>2</sub> levels is shorter than the gas enclosure process at Byrd station. (3) The dating of at least one core is completely wrong, so that entirely different time sequences are compared in both cores.

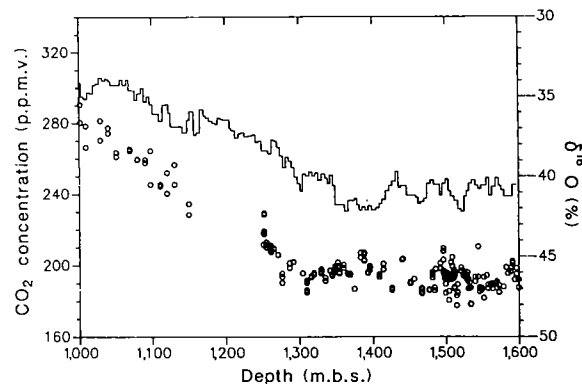


Fig. 4  $\delta^{18}\text{O}$  and CO<sub>2</sub> record 1,000–1,600 m.b.s. The solid line corresponds to the age-adjusted  $\delta^{18}\text{O}$  curve.

The comparison with the Vostok record recently published by Barnola *et al.*<sup>4</sup> shows a good agreement for the long-term variation and support the used dating of the two Antarctic cores.

Two possible mechanisms for the change in atmospheric CO<sub>2</sub> concentration which occurred during the transition from glacial time to interglacial time have been suggested. Broecker<sup>19</sup> first pointed to a redistribution of carbon species in the ocean due to deposition of nutrient-rich sediments on continental shelves during the deglaciation period. With such a mechanism only slow changes as suggested, for example, by a smooth interpolation of the CO<sub>2</sub> data from the Byrd core can be explained. Faster changes, as suggested by CO<sub>2</sub> data from the ice age part of the Dye 3 core<sup>9</sup> could be explained by another hypothesis including changes of circulation or biological productivity in the high-latitude ocean<sup>19,20</sup>.

Variations during the glaciation period, similar to those found in polar ice core data have been reported from sea-sediment records<sup>21</sup>, indicating changes in the ocean biota system. Because of difficulties in dating both the ice sea-sediment cores we cannot yet correlate these variations quantitatively. More polar ice cores from cold locations with good core quality are needed to establish the exact phase relation between  $\delta^{18}\text{O}$  and CO<sub>2</sub> during the glacial/interglacial transition and to characterize quantitatively the small CO<sub>2</sub> variations in the glaciation period.

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