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TELLUS

Atmospheric CO_2 during the 13th century AD: reconciliation of data from ice core measurements and stomatal frequency analysis

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ABSTRACT

Atmospheric CO_2 reconstructions are currently available from direct measurements of air enclosures in Antarctic ice and, alternatively, from stomatal frequency analysis performed on fossil leaves. A period where both methods consistently provide evidence for natural CO_2 changes is during the 13th century AD. The results of the two independent methods differ significantly in the amplitude of the estimated CO_2 changes (10 ppmv ice versus 34 ppmv stomatal frequency). Here, we compare the stomatal frequency and ice core results by using a firn diffusion model in order to assess the potential influence of smoothing during enclosure on the temporal resolution as well as the amplitude of the CO_2 changes. The seemingly large discrepancies between the amplitudes estimated by the contrasting methods diminish when the raw stomatal data are smoothed in an analogous way to the natural smoothing which occurs in the firn.

1. Introduction

Analysis of gas enclosures in polar ice is the most established and widely accepted source of information on atmospheric CO_2 dynamics during the Late Quaternary. While glacial–interglacial cycles are generally characterized by large shifts in atmospheric CO_2 levels, Antarctic ice core records document only small natural variations of at most 15 ppmv during the warm stages (Indermühle et al., 1999; Monnin et al., 2001; Barnola et al., 1995; Etheridge et al., 1996).

Alternatively, atmospheric CO_2 proxy records can be generated by studying the genetically controlled leaf morphological adaptation of selected C3 plants, in which the number of stomata (gas exchange pores) on the leaf is directly determined by the ambient CO_2 mixing ratio during the growth period (Wagner et al., 1996; Lake et al., 2001). The high abundance of leaf fossils in Quaternary lake and peat deposits increasingly focuses interest on this time interval. Numerous stomatal frequency-based CO_2 records, especially for the Holocene, are already available (Beerling et al., 1995; Wagner et al., 1999; Rundgren and Beerling, 1999; Wagner et al., 2002; McElwain et al., 2002; Rundgren and Björck, 2003; Kouwenberg et al., 2005).

All available records indicate a significant variability of atmospheric CO_2 levels throughout the Holocene, showing repeated short-lived CO_2 shifts of 20–40 ppmv, independently reproduced in the different studies (Wagner et al., 2004). Moreover, available CO_2 reconstructions covering the past millennium reveal a CO_2 shift of approximately 30 ppmv (Rundgren and Beerling, 1999; Wagner et al., 2004; van Hoof, 2004). The most recent reconstruction of a shift as high as 60 ppmv, shows a highly comparable temporal pattern; however, the provided CO_2 range may be an overestimate resulting from remaining uncertainties in the newly developed inference model for conifers (Kouwenberg et al., 2003, 2005). A common pattern to all these records is that the estimated CO_2 shifts clearly exceed the fluctuations documented in polar ice.

The major differences between the results of the two techniques are: (1) the different CO_2 average base levels for the Holocene, (2) the pacing of CO_2 variations and (3) the amplitude of the detected shifts. These factors need attention if we are to understand natural, short-term climate dynamics. Whether the apparent discrepancies are real, however, or just a result of accumulated inaccuracies introduced by the uncertainties inherent in the technique is difficult to assess.

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It is well known that diffusion processes within the firn layer and the gradual enclosure of the air in the lock-in-zone of the ice lead to a reduced signal of the original atmospheric variability and may obscure high-frequency variations (e.g. Trudinger et al., 2003). In stomatal frequency analysis, the intrinsic variability of plants, resulting from environmental factors other than CO_2, often affects the precision of CO_2 inference models and commonly leads to relatively high standard deviations of the mean CO_2 values predicted (Wagner et al., 2005). To explore the accuracy of the atmospheric CO_2 reconstructions based on the different methods, the results need to be directly compared. Here, we make a contribution to the comparison of stomatal frequencies and ice core results by using a firn diffusion model. A period where both methods consistently provide evidence for natural CO_2 changes is the 13th century AD. A significant increase in CO_2 with a range of 12 ppmv at this time is measured in at least two Antarctic ice cores, namely South Pole and D47 (Siegenthaler et al., 1988; Barnola et al., 1995) while stomatal frequency reconstructions from The Netherlands and the USA show a CO_2 increase of at least 34 ppmv during the same period (van Hoof, 2004; Wagner et al., 2004; Kouwenberg et al., 2005).

In the present study we try to answer the question of whether the amplitude differences of fast shifts in CO_2, detected by the two methods for the early part of the last millennium, are caused by overestimation of the amplitude of CO_2 mixing ratios in stomatal frequency records or result from alteration of CO_2 content by diagenetic processes involved during trapping of the air in the firn and ice.

In order to assess the influence of smoothing during enclosure on the temporal resolution, as well as on the amplitude of the CO_2 changes, we apply a 1-D numerical firn air diffusion model (Kaspers et al., 2004a) on the high-resolution stomatal frequency based the CO_2 record from The Netherlands (van Hoof, 2004; Wagner et al., 2004). In this way the stomatal frequency record can be directly compared with the ice core results. It simulates how the stomatal frequency record would be observed in a synthetic ice core. The firn air diffusion model is forced with the meteorological conditions characterizing the ice core drilling site at D47 (based on a meteorological model). The smoothed output is subsequently compared with the actual CO_2 measurements from core D47 (Barnola et al., 1995). This procedure makes the two independent data sets compatible and allows us to comment on the likelihood of the higher-amplitude CO_2 changes observed in the stomatal frequency record during this particular time interval.

2. Material and methods

The stomatal frequency CO_2 reconstruction (Fig. 1A; hereafter CO_2 [SI]) is based on stomatal index measurements of buried oak leaves (*Quercus robur*) derived from channel deposits of the River Roer (Sint Odiliënberg, The Netherlands, 51.08°N, 6.00°E van Hoof, 2004; Wagner et al., 2004). A detailed chronology for the CO_2 [SI] reconstruction is provided by 11 accelerator mass spectrometry (AMS) ^{14}C dates wiggle-matched

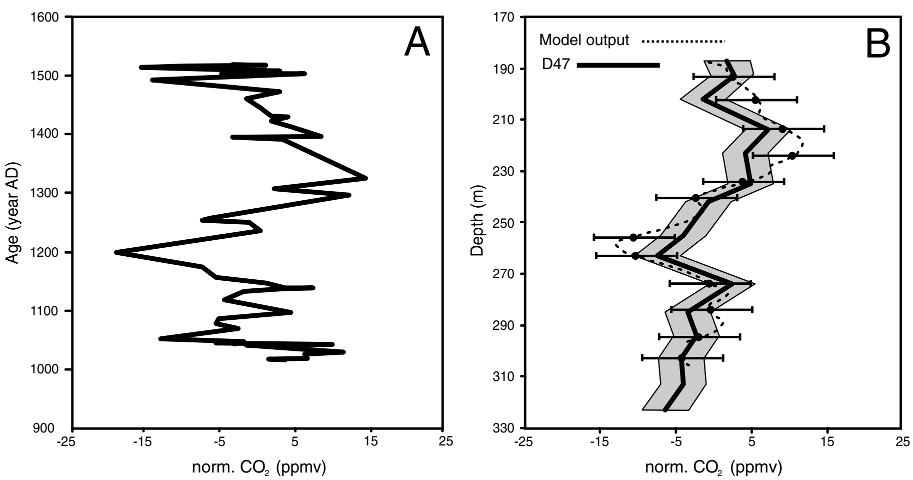

Fig. 1. (A) Raw data: normalized stomatal frequency based CO_2 mixing ratios as calculated from stomatal index: stomatal index (SI) (%) = [stomatal density (SD) (number/mm^2)]/[stomatal density (SD) (number/mm^2) + epidermal cell density (ED) (number/mm^2)] × 100 of fossil *Q. robur* (oak) leaves derived from channel deposits of the River Roer (The Netherlands) (van Hoof, 2004; Wagner et al., 2004). The chronology of the stomatal frequency record is based on wiggle-match dating of eleven AMS ^{14}C measurements (van Hoof, 2004). (B) The dotted black line represents the CO_2 [SI] output after application of the firn densification model (Kaspers et al., 2004a). Of selected data points that resemble the actual sample depth of the CO_2 [ice] measurements of the D47 core, averaged errors of the CO_2 [SI] are shown. The black line represents normalized CO_2 mixing ratios (CO_2 [ice]) of the D47 ice core and the grey area resembles the methodological error (Barnola et al., 1995).

to the INTCAL98 calibration curve (Stuiver et al., 1998) and supplemented with a high-resolution palynologically based biostratigraphy of the channel deposits (van Hoof, 2004). The leaf-bearing part of the deposits is restricted to the time period from AD 1000 to 1500, of which 60 horizons were sampled for stomatal frequency analysis, thereby obtaining a decadal resolution of the record. CO_2 [SI] estimates were obtained by using the inverse relationship between SI and CO_2 of this species, as was monitored and modelled during the post-industrial atmospheric CO_2 increase of the last two centuries (van Hoof, 2004). Reconstructed subdecadal CO_2 shifts occurring within the range of the methodological error (6 ppmv) are not regarded as representing actual atmospheric CO_2 perturbations.

A suitable CO_2 profile based on gas enclosure analysis (hereafter CO_2 [ice]) that covers the same time slice is available from the D47 ice core (67°23′S,154°03′E) (Barnola et al., 1995). The Antarctic D47 record provides the highest data density of the available ice cores covering the last millennium and shows a distinct 13th century AD CO_2 shift (Barnola et al., 1995). We have considered using South Pole data as well (Siegenthaler et al., 1988) but the resolution of the ice core for this time period is too low to allow for a thorough comparison between the two methods.

The first step towards comparison of stomatal frequency and ice core data was to transform the atmospheric CO_2 [SI] record into a yearly resolved CO_2 record by means of linear interpolation. The interpolated CO_2 [SI] record was subsequently used as input data for a firn air diffusion model (Schwander et al., 1993; Spahni et al., 2003; Kaspers et al., 2004a) which was forced with the present-day characteristic site conditions of the D47 core drilling site. The meteorological quantities used in the diffusion model, e.g. annual mean temperature (at 10 m depth; 247.2 K) and the accumulation rate for site D47 (26.8 cm w.e.a-1, centimeters water equivalence per year), are derived from the initial study of the D47 ice core (Barnola et al., 1995). While the values for annual mean surface pressure (780 hPa) and wind speed at the lowest altitude of the atmosphere model (10 m; 7 m s^{-1}) are derived from a regional atmospheric climate model for Antarctica (RACMO-ANT, van Lipzig et al., 2002). From the meteorological quantities site-specific parameters were obtained: surface snow density (407 kg m^{-3}), the density at pore close-off (818 kg m^{-3}), pore close-off depth (56 m) and the tortuosity (4.1). The site-specific parameters were derived from the parametrizations described in Kaspers et al. (2004b). This parametrization is based on a compilation of all existing firn air measurements to date. The firn air diffusion model is applied over the entire period with a resolution of approximately 1 m between 350 m depth and 56 m depth, the pore close off depth for D47. Sensitivity tests have been performed for changes in temperature and accumulation, but have been shown to have a negligible effect on the results. Additional diffusion near pore close-off is neglected.

For the direct comparison of the modelled CO_2 [SI] with the D47 CO_2 [ice] measurements, only the interval between 190 and 310 m depth of the model output is used, as this represents the stomatal frequency-based part of the input data.

3. Results

The model output of CO_2 [SI] versus CO_2 [ice] D47 is presented in Fig. 1B. Model output data are shown as a function of depth, and accordingly plotted on a CO_2 [ice] depth scale. The CO_2 [SI] model output has a maximum amplitude of 25 ppmv, with a CO_2 minimum at 260 m and a maximum at 215 m. Of selected data points that resemble the actual sample depths of the CO_2 [ice] measurements of the D47 core, averaged errors of the CO_2 [SI] are shown. CO_2 [ice] measurements show a maximum amplitude of 12 ppmv with a CO_2 minimum at 265 m and a maximum at 210 m (Fig. 1B; Barnola et al., 1995). The grey band represents the 3 ppmv methodological error of the D47 record (Barnola et al., 1995).

4. Discussion

The effect of the synthetic smoothing of CO_2 [SI] leads to a 25% reduction of the amplitude from 34 ppmv in the raw data to a maximum of 25 ppmv according to the model output. Furthermore, the numerous single high-resolution data point shifts that characterize the CO_2 [SI] record are eliminated due to the diffusion. The output sequence follows the CO_2 [ice] mixing ratio data measured in D47 in great detail. The resulting profiles are not significantly different. By applying the firn air densification model to the raw stomatal frequency CO_2 data, a hypothetical profile is generated, where the main processes acting on atmospheric CO_2 in air bubbles trapped in ice are simulated. During enclosure, the trapped air is subjected to processes that alter the CO_2 mixing ratio ultimately preserved in the ice (Anklin et al., 1995; Schwander, 1996; Trudinger et al., 2003). Diffusion through the firn layer and gradual enclosure in the bubbles leads to smoothing of the record and, thus, underestimation of the amplitude of the CO_2 changes (Trudinger et al., 2003). In the present study, we assume that the high-amplitude fluctuation of the CO_2 [SI] record during the 13th century AD reflects actual change in atmospheric CO_2. The applied smoothing during firn densification should then reduce the information to a level on which it would be preserved in the air measured from the specific ice core, in this case D47. If the trends in stomatal frequency data do correctly reflect past CO_2 changes, the match between CO_2 [SI] and CO_2 [ice] should be perfect. The observed firm correspondence between the CO_2 [SI] and CO_2 [ice] data indeed confirm that the observed amplitude differences between the raw stomatal frequency record and the D47 ice core data can be explained by the smoothing of CO_2 during ice formation.

The remaining discrepancies between CO_2 [SI] and CO_2 [ice] may very well be an artefact of the uncertainties in the CO_2 inference model used for CO_2 estimates from SI values of oak leaves.

For atmospheric CO_2 reconstructions, the adaptation of oak to the industrial CO_2 increase from 280 ppmv to 370 ppmv serves as modern training set from which response rates are determined. The response of oaks to changing CO_2 mixing ratios, however, is a sigmoidal function, since the number of stomata on the leaf surface can neither become zero, nor infinite (Kürschner, 1997). For calibration purposes only the linear phase of the resulting sigmoidal response curve is interpreted in the CO_2 inference model, since secure quantification of the asymptotes is hampered by the lack of response data under pre-industrial CO_2 mixing ratios below 280 ppmv. The model is thus conservative in reconstructing past CO_2 mixing ratios outside the monitored response range, which introduces inaccuracies in the CO_2 range where the linear model diverges from the sigmoidal response (van Hoof, 2004).

The most prominent feature in both profiles is the distinct CO_2 oscillation between AD 1150 and 1350. Both data sets show an initial decrease of 10 ppmv, reaching minimum levels at AD 1200 followed by a CO_2 increase of 12 ppmv in CO_2 [ice] and 15 ppmv in CO_2 [SI] during the 14th century. The timing as well as the rates of change are in excellent agreement in the CO_2 [SI] model output and the CO_2 [ice] record. A CO_2 increase associated with the 13th century AD was originally measured in the South Pole ice core, where a maximum increase of 10 ppmv was calculated by deconvolving the raw data (Siegenthaler et al., 1988). The exact temporal pattern of this fluctuation, however, is difficult to assess, due to the weakly confined age width of the ice samples (Barnola et al., 1995). More recent cores like Law Dome (Etheridge et al., 1996) or Taylor Dome (Indermühle et al., 1999) that cover the last millennium also indicate fluctuating CO_2 levels, but the interpretation of these records is severely hampered due to low sample resolution and/or age uncertainties (Etheridge et al., 1996; Indermühle et al., 1999). So far, no conclusive temporal delineation of the CO_2 variation during the early part of the last millennium has been achieved.

Although an indirect proxy measure, stomatal frequency analysis has the major advantage of providing real-time data. The leaf morphological CO_2 signal is permanently fixed at the moment of growth, and remains resistant to diagenetic processes acting on the leaf material during fossilization. For actual reconstructions this implies that the potential temporal resolution is high, often on the (sub-)decadal scale (Wagner et al., 2004).

The detailed ^{14}C wiggle-match dating (WMD) age assessment of the stomatal frequency record allows us to give an accurate age range with a maximum uncertainty of 30 yr. The reconstructed CO_2 oscillation started at AD 1150, with a CO_2 minimum at AD 1200 and maximum levels at AD 1320.

5. Conclusions

A significant CO_2 change during the 13th century AD is evident from direct measurements of CO_2 in gas enclosures in the Antarctic ice core D47 as well as from stomatal frequency analysis of fossil oak leaves. The independent detection of this CO_2 shift, and the good agreement between the different records, provides persuasive evidence for the reality of this event.

The seemingly large discrepancies between the amplitude of the CO_2 oscillation estimated by the contrasting methods diminish when effects of natural smoothing of the ice-core record is simulated for the raw data of the stomatal frequency record. The results show that the differences derived by the two methods may be less significant than previously thought. Consequently, cross-testing of the additional CO_2 fluctuations observed in stomatal frequency records with the CO_2 records of ice may help to improve our knowledge of Holocene CO_2 dynamics.

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