ESTIMATING THE AMOUNT OF $^{14}CO_2$ IN THE ATMOSPHERE DURING THE HOLOCENE AND GLACIAL PERIODS

I Svetlik[1,2] • P P Povinec[3] • K Pachnerova Brabcova[1] • M Fejgl[2] • L Tomaskova[1] • K Turek[1]

ABSTRACT. Radiocarbon has been used to define parameters for modeling past, recent, and future CO_2/carbon amounts in the atmosphere and in other environmental compartments. In the present paper, we estimate the amount of ^{14}C in the atmosphere by calculating the molar activity of $^{14}CO_2$ (quantity of $^{14}CO_2$ molecules per mol of air). Data on the reconstruction of the past concentration of atmospheric CO_2 from Antarctic ice cores and $\Delta^{14}C$ activities from the IntCal09 calibration curve were applied. The results obtained indicate that cosmogenic production had a dominant influence on the ^{14}C amount in the atmosphere between 50 and 20 ka BP, when the CO_2 concentrations were relatively stable, with a slowly decreasing trend. The decreasing ^{14}C activity ($\Delta^{14}C$) between 20 and 2 ka BP seems to be caused predominantly by a dilution of atmospheric $^{14}CO_2$ by input of CO_2 with a depleted amount of ^{14}C (probably from deeper oceanic layers), which is evident from a comparison with the $\Delta^{14}C$ and molar activity time series. A strong linear relation was found between the ^{14}C activity and CO_2 concentration in the air for the period 20–2 ka BP, which confirms a dominant influence of atmospheric dilution of $^{14}CO_2$. The observed linear relation between the CO_2 and $\Delta^{14}C$ levels persists even in the prevailing part of the Holocene. Likewise, the quantity of $^{14}CO_2$ in the atmosphere (calculated as molar activity) during the prevailing part of the deglacial period (20–11 ka BP) was surprisingly increasing, although a decreasing trend in the ^{14}C cosmogenic production rate could be expected.

INTRODUCTION

The radioactive carbon isotope ^{14}C originates naturally as a result of cosmic-ray interactions in the atmosphere. The ^{14}C produced is subsequently oxidized to $^{14}CO_2$ and transferred from the atmosphere to other carbon sinks, especially to oceanic waters and terrestrial biota. The ^{14}C or $^{14}CO_2$ can be released from both of these sinks back into the atmosphere. ^{14}C can also be transferred to long-term sinks, e.g. peat bogs, swamps, organic compounds in soils or deep oceanic waters, and sediments. It is assumed that significant changes in temperature, ocean circulation patterns, or surface ventilation can increase the $^{14}CO_2$ (and CO_2) reflux back into the atmosphere.

Activity of atmospheric $^{14}CO_2$ increased significantly during the 1950s and 1960s due to nuclear weapons tests carried out in the atmosphere. The maximum was observed in the Northern Hemisphere in 1963, when it reached double the natural level caused by cosmogenic production. Over the subsequent years, the $^{14}CO_2$ activity has decreased quickly compared to the ^{14}C half-life, and so by 1970 the "bomb effect" had been reduced by half (Meijer et al. 1995). The rate of the decrease proves that the ^{14}C radioactive decay in the atmosphere affects the $^{14}CO_2$ levels only partially.

Due to the similar chemical and physical properties of CO_2 and $^{14}CO_2$, ^{14}C can be used to define some parameters of models for simulation and prediction of CO_2/carbon transport to the atmosphere and to other carbon reservoirs. Up to now, many of the input parameters have been questioned, as well as their considerable uncertainties (Levin et al. 2008, 2010). Therefore, it would be beneficial to specify the long-term natural behavior of atmospheric $^{14}CO_2$ (in a horizon of thousands or tens of thousands of years). The main chemical form of ^{14}C in the atmosphere is $^{14}CO_2$. Other chemical forms containing ^{14}C (CO, CH_4, and other organic compounds) occur in concentrations at least 10^3 times smaller. During photosynthesis, $^{14}CO_2$ is captured by plants and thus becomes part of the

[1]Nuclear Physics Institute AS CR, Na Truhlarce 39/64, CZ-180 86 Prague, Czech Republic. Corresponding author. Email: svetlik@ujf.cas.cz.
[2]National Radiation Protection Institute, Bartoskova 28, CZ-140 00 Prague, Czech Republic.
[3]Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, SK-842 48 Bratislava, Slovakia.

Proceedings of the 21st International Radiocarbon Conference edited by A J T Jull & C Hatté
RADIOCARBON, Vol 55, Nr 2–3, 2013, p 1546–1555

food chain. It can be therefore assumed that ^{14}C activity data used for ^{14}C dating corrections of terrestrial samples corresponds to the atmospheric $^{14}CO_2$ activity during the same time periods.

CALCULATION OF ATMOSPHERIC $^{14}CO_2$ MOLAR ACTIVITY

The molar activity of $^{14}CO_2$ (quantity of $^{14}CO_2$ in 1 mole of the air) was calculated to estimate a total ^{14}C amount in the atmosphere. Values of $\Delta^{14}C$ (^{14}C activity[4]) were adopted from the ^{14}C calibration curve IntCal09 (Figure 1) (Reimer et al. 2009). The values of $\Delta^{14}C$ correspond to the abundance of ^{14}C in the carbon isotope mixture (Stuiver and Polach 1977). IntCal09 is applied world-wide for correction of natural ^{14}C activity fluctuations in dating of terrestrial samples, and reaches up to 50,000 yr BP. IntCal09 data with time steps of 5 yr are available up to 11.2 ka BP, then the steps expand gradually up to 200 yr for the oldest values. Concentration of atmospheric CO_2 in available databases is reported in ppm_V as a partial volume of CO_2. Several available reconstructions of CO_2 data extend to 50 ka BP (NOAA, http://www.ncdc.noaa.gov/paleo/icecore/icecore-varlist.html).

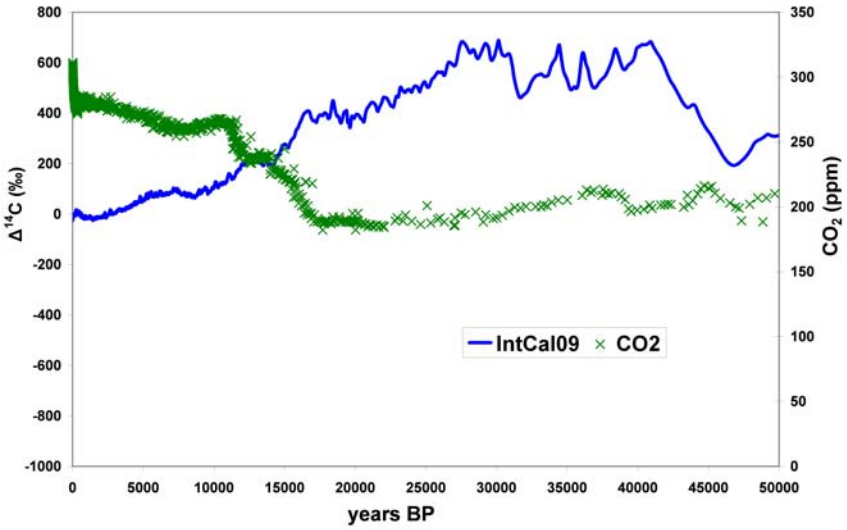

Figure 1 To illustrate the proportionality of the "mirroring effect" since 20 ka BP, both vertical scales begin with "zero" values. The ^{14}C activity (line) during the last 50,000 yr according to the ^{14}C calibration curve IntCal09, from "zero" i.e. from –1000‰ (Reimer et al. 2009), and the CO_2 concentration (×), reported in ppm from 0 ppm, is shown (Indermühle et al. 1999a,b; Petit et al. 1999a; Smith et al. 1999; Monnin et al. 2001, 2004; Flückiger et al. 2002; Siegenthaler et al. 2005; MacFarling et al. 2006; Lourantou et al. 2010).

These time series were assembled on the basis of CO_2 analyses of several Antarctic ice cores (see Figure 1). Table 1 lists the ice cores used. The time intervals at which CO_2 concentration values are available are irregular. The $\Delta^{14}C$ values were calculated for years with known CO_2 concentrations using linear interpolation of the nearest IntCal09 timescale values; these calculations were made using MATLAB® software.

To estimate a past amount of $^{14}CO_2$ in the atmosphere, we calculated a parameter that depends only on the number of $^{14}CO_2$ molecules per unit of air. For such a purpose, weight, molar, or volume (vol-

[4]The symbol $\Delta^{14}C$ instead of the term "^{14}C ($^{14}CO_2$) activity" is reported to prevent confusion with $^{14}CO_2$ molar activity.

Table 1 Antarctic ice cores used in this study.

Name	Time period/data	Reference
EPICA Dome C Ice Core	High-resolution Holocene and transition CO_2 data	Monnin et al. 2004
Dome C	0–22 kyr BP	Monnin et al. 2001
Vostok	0–440 kyr BP	Petit et al. 1999a
Taylor Dome	19–63 kyr BP	Indermühle et al. 1999a
EPICA Dome C Ice Core Termination I	$\delta^{13}CO_2$ data	Lourantou et al. 2010
EPICA Dome C	Nitrous oxide, CO_2, and CH_4 data	Flückiger et al. 2002
EPICA Dronning Maud Land	CO_2 data for the last millennium	Siegenthaler et al. 2005
Law Dome Ice Core 2000-Year	CO_2, CH_4, and N_2O data	MacFarling et al. 2006

ume normalized to standard conditions: 0 °C, 101.325 kPa) units of air can be connected with $^{14}CO_2$ quantity (Svetlik et al. 2010). The molar activity of atmospheric $^{14}CO_2$ is not affected by the fossil CO_2 amount in the atmosphere (i.e. it is not dependent on the quantity of CO_2 molecules with stable carbon isotopes). The $^{14}CO_2$ "concentration" is calculated as a molar activity according to the following formula:

$$a_m = a_{std}(1+0.001\cdot\Delta^{14}C)\, M_C\, k\, c_{CO2}$$

where a_m is the atmospheric $^{14}CO_2$ molar activity (in Bq mol^{-1}), a_{std} is the activity of the ^{14}C standard (Bq g^{-1} of the carbon isotope mixture, which is ~0.226 Bq g^{-1}), $\Delta^{14}C$ represents the ^{14}C activity according to the IntCal09 calibration curve (‰), M_C is a carbon mass (12.01 g mol^{-1}), c_{CO2} is CO_2 concentration, (ppm_V), and k (1.0092) is the ratio of molar volumes of air and CO_2, which are 22.47 and 22.26 10^{-3} m^3 mol^{-1}, respectively (for 0 °C, 101.325 kPa). If the global air content in the atmosphere (number of air moles) is assumed to be stable, the total amount of $^{14}CO_2$ molecules in the atmosphere is proportional to the calculated molar activity. The $^{14}CO_2$ content in the atmosphere is given by the input rate (cosmogenic production of ^{14}C and a $^{14}CO_2$ reflux from the other carbon reservoirs to the atmosphere) and the output rate (transfer of $^{14}CO_2$ from the atmosphere to other carbon sinks). The $^{14}CO_2$ activity decrease due to radioactive decay in the atmosphere is negligible because of the long half-life of ^{14}C, and a relatively short residence time.[5] If the clear fossil (^{14}C-free) CO_2 is released into the atmosphere, it leads to a decrease of $\Delta^{14}C$ values due to a dilution (i.e. the ^{14}C abundance in the carbon isotopic mixture of atmospheric CO_2 is decreased), but without changes in $^{14}CO_2$ molar activity (i.e. the number of $^{14}CO_2$ molecules per mole of air remains the same). If the CO_2 (and $^{14}CO_2$) residence time in the atmosphere increases (e.g. as a result of a shift in atmospheric/oceanic carbon distribution), then both the CO_2 concentration and $^{14}CO_2$ amount (molar activity) will also increase in the atmosphere.

RESULTS AND DISCUSSION

It is apparent from Figure 2 that the $\Delta^{14}C$ ($^{14}CO_2$ activity) and the $^{14}CO_2$ molar activity time series between 50 and 20 ka BP follow similar trends. The CO_2 concentration was relatively stable at that time, without abrupt changes, and with only a slightly decreasing trend (Figure 1). For this reason, the $^{14}CO_2$ activities seem to be influenced mainly by changes in the cosmogenic production rates during this period.

If we compare the calculated $^{14}CO_2$ molar activities with the ^{10}Be production during the period 50–20 ka BP, both time series show similar trends (Figure 3). The parameter "^{10}Be cosmogenic produc-

[5]This is also evident from a sharp decrease in atmospheric $^{14}CO_2$ activity during the 1960s (Meijer et al. 1995).

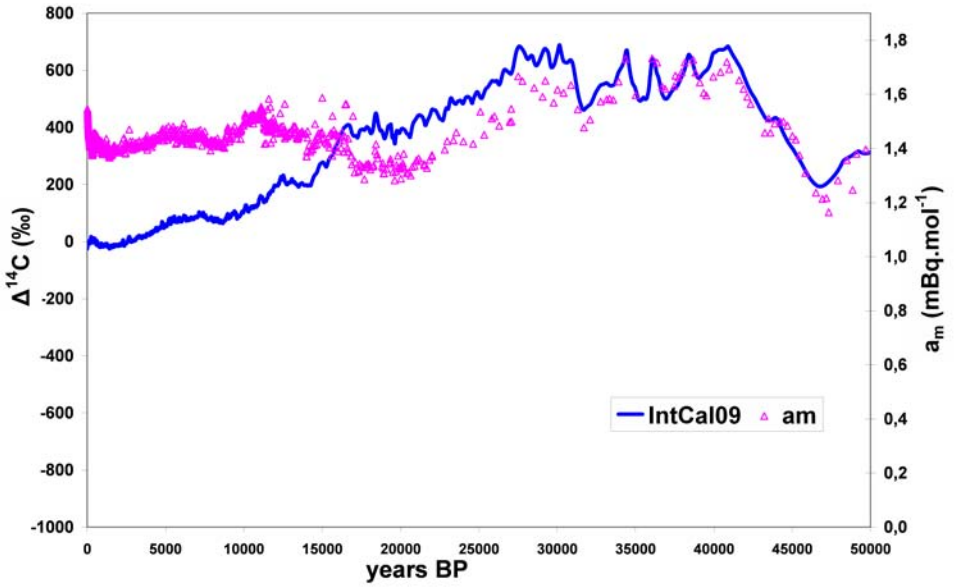

Figure 2 Comparison of ^{14}C activity represented by IntCal09 data (solid line) (Reimer et al. 2009) with calculated molar activity (triangles).

tion" was corrected for ^{10}Be redeposition; it also contains data from a few deep oceanic sediments sampled at geographically distant areas (Frank et al. 2007). The time series called "global ^{10}Be production rate" contains data obtained entirely from the Atlantic sedimentary sequences with an average sedimentation rate larger than 10 cm per 1000 yr, to minimize influence of postdepositional processes and to obtain a better time resolution. The $^{230}Th_{ex}$ normalization has been included with the aim to reduce a (climate-induced) oceanic transport signal, as discussed by Christl et al. (2010).

A different situation can be observed for the younger period up to 20 ka BP. The $\Delta^{14}C$ and atmospheric $^{14}CO_2$ molar activity time-series trends are considerably different. If we compare CO_2 concentrations and $\Delta^{14}C$, apparent "mirroring" of both time series can be observed for the prevailing part of this period (see Figure 1). In the period 20–2 ka BP, a surprisingly high anti-correlation (i.e. relation where $\Delta^{14}C$ is decreasing with increasing concentration of CO_2) of 93.1% between $\Delta^{14}C$ values and CO_2 concentration was found (Figure 4). High anti-correlations were also found for the periods 20–10 ka BP (93.3%) and 10–2 ka BP (76.6%). Therefore, in the period ~20–2 ka BP, the $\Delta^{14}C$ time component seems to be influenced mainly by intake of the CO_2 with a depleted amount of $^{14}CO_2$. A decreased abundance of $^{14}CO_2$ in the CO_2 input to the atmosphere can be probably explained by an extended residence time (comparable to the ^{14}C half-life) in long-term carbon sinks, e.g. CO_2 from deep oceanic waters (Schmittner 2003).

The molar activities of $^{14}CO_2$ increased slowly in the period approximately 20–11 ka BP, which corresponds to the ingrowth in the amount of $^{14}CO_2$ in the atmosphere, although the activities of atmospheric $^{14}CO_2$ ($\Delta^{14}C$) decreased (see Figures 2 and 3). Timescales of ^{10}Be ("^{10}Be cosmogenic production" and "global ^{10}Be production rate") show a systematic decrease during this period, which probably also implies decreasing cosmogenic production of ^{14}C. Hence, growth in the atmospheric $^{14}CO_2$ content during this period could be explained by (1) increased CO_2 residence time in the atmosphere and (2) partial (although depleted) $^{14}CO_2$ content in CO_2 released from long-term carbon sinks.

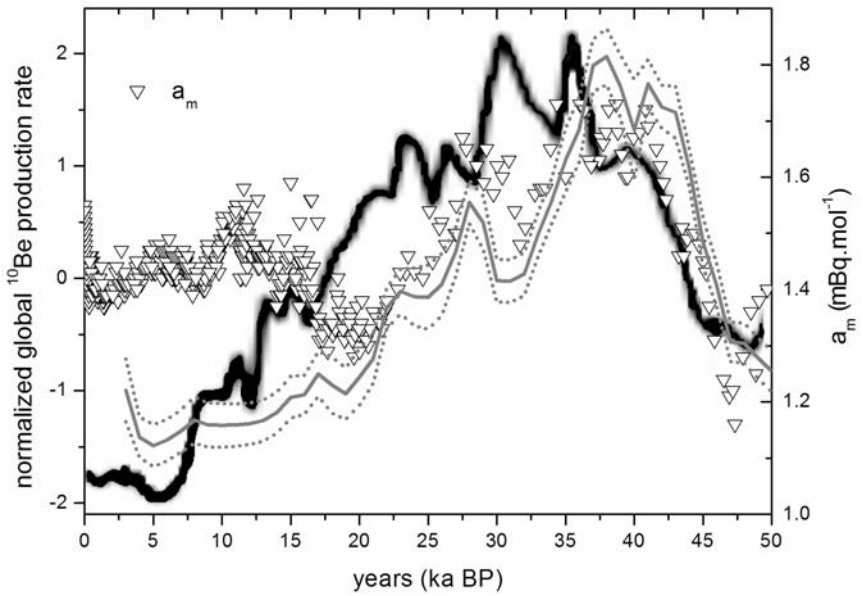

Figure 3 Comparison of calculated $^{14}CO_2$ molar activities (triangles) and ^{10}Be time series: (a) ^{10}Be cosmogenic production (black line) (Frank et al. 1997); (b) global ^{10}Be production rate (gray line) with broken lines representing uncertainties (Christl et al. 2010), where 0 and 1 values correspond to production of 1.5 10^9 and 1.9 10^9 atoms cm^{-2} ka^{-1}, respectively (M Christl, personal communication, 2013).

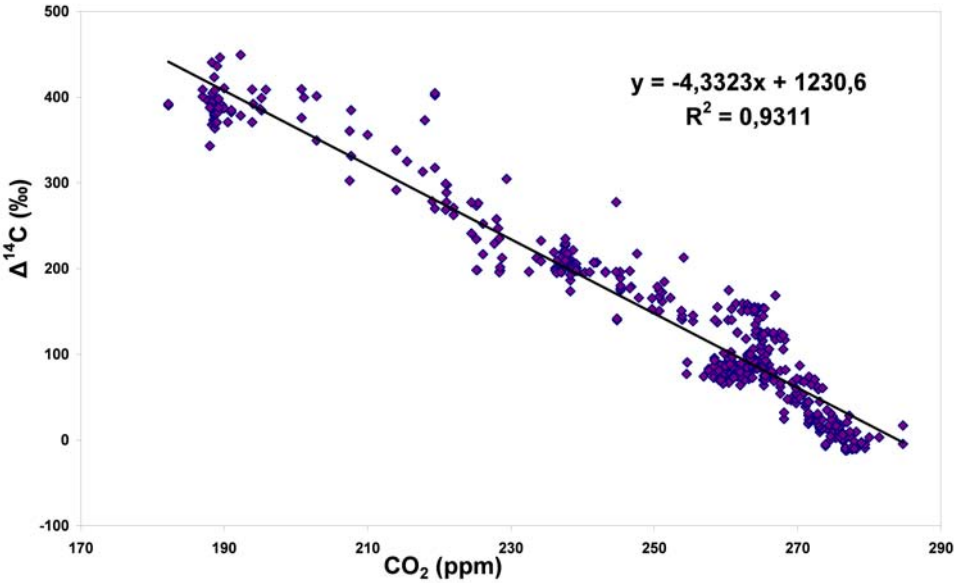

Figure 4 Anti-correlation of ^{14}C activity (Reimer et al. 2009) and CO_2 concentration from 20 to 2 ka BP (CO_2 data: Indermühle et al. 1999a,b; Petit et al. 1999a; Smith et al. 1999; Monnin et al. 2001, 2004; Flückiger et al. 2002; Siegenthaler et al. 2005; MacFarling et al. 2006; Lourantou et al. 2010).

The observed interval of the strong relation between $\Delta^{14}C$ and CO_2 includes the time intervals connected with a distinct rise in CO_2 and $\Delta^{14}C$ drops in the Heinrich Stadial 1 "Mystery Interval," about 17.5–14.5 ka BP, and the Younger Dryas, about 13–11 ka BP (Broecker and Barker 2007; Broecker 2009; Cléroux et al. 2011). Nevertheless, according to our data, this relation seems to continue until ~2 ka BP in the Holocene. The Southern Ocean, where carbon was detained in the reservoir of abyssal water, is usually proposed as a dominant source of CO_2 with a depleted amount of ^{14}C, but other possibilities have also been proposed (Butzin et al. 2005, 2012; Broecker and Barker 2007; Marchitto et al. 2007; Anderson et al. 2009; Broecker 2009; Stott et al. 2009; Basak et al. 2010; Bryan et al. 2010; Skinner et al. 2010; Cléroux et al. 2011; Lund et al. 2011; Sortor and Lund 2011; Menviel et al. 2012; Roth and Joos 2012; Schmitt et al. 2012).

A gradual warming arises during the period of the Late Glacial, and associated changes due to oceanic relations can be estimated in the range between 20.8 and 17 ka BP (Stott et al. 2007; Tachikawa et al. 2009), which also can be seen from reconstructed temperature curves (Figure 5). Two time series of proxy data were used for this purpose: (1) temperature reconstruction based on the Antarctica Vostok ice core, corresponding to the area of disposable CO_2 reconstructions; (2) temperature reconstruction based on the Greenland GISP2 ice core, with available analogous polar data from the Northern Hemisphere (Jouzel et al. 1987, 1993, 1996; Petit et al. 1999b; Alley 2000). Warming continued until approximately 10 ka BP and was accompanied by a gradual decrease in $^{14}CO_2$ activity and by an ingrowth of CO_2 concentration. As previously mentioned, the observed decrease in atmospheric $^{14}CO_2$ activity was probably caused by inputs of CO_2 with depleted amounts of ^{14}C in the carbon isotopic mixture, which is also indicated by the "mirrored" relation between CO_2 and $\Delta^{14}C$ during this period (Figure 1).

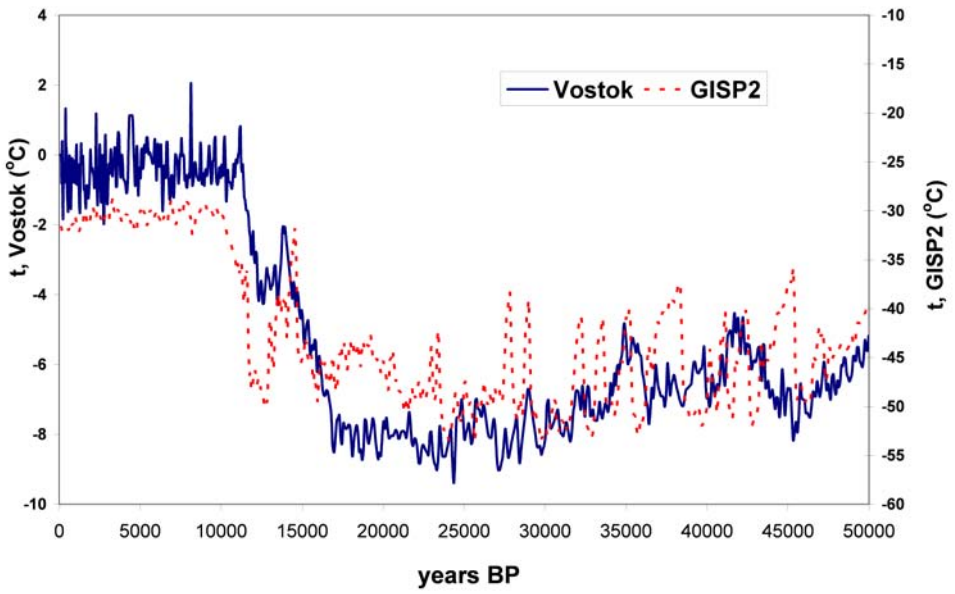

Figure 5 Temperature reconstructions of up to 50 ka BP based on the Antarctic Vostok ice-core data (solid line), and the GISP2 data, Greenland (dashed line) (Data: Jouzel et al. 1987, 1993, 1996; Petit et al. 1999b; Alley 2000).

The period 17–10 ka BP includes a large gradual increase in temperatures and CO_2 concentrations. Nevertheless, 1 exception can be observed during the Younger Dryas and Allerød. The CO_2 concentration increased sharply at ~14.0 ka BP and remained relatively stable until 12.2 ka BP. It must be

pointed out that only CO_2 time series from Antarctic ice cores were available. Hence, the Vostok ice core records were preferred to compare temperature headway. The uniform temperature increase terminates at ~14.0 ka BP, and a sharp cooling period followed for the next 500 yr. In the subsequent period, only fine temperature fluctuations can be observed until 12.3 ka BP, when gradually both the temperature and CO_2 increases resumed. According to the Greenland GISP2 ice-core data, the temperature time series shows a disruption in the increase of the earlier period at ~14.5 ka BP, and gradual warming was recovered starting at ~11.9 ka BP (see Figure 5). Activity of ^{14}C ($\Delta^{14}C$ values) decreases until 14.2 ka BP, followed by moderate, irregular growth from 13.9 ka BP. Retrieval of systematic decreasing $^{14}CO_2$ activity can be observed from 12.4 ka BP. However, the $^{14}CO_2$ quantity in the atmosphere (molar activity of $^{14}CO_2$) was rising since 17 ka BP until 11.1 ka BP, when maximal values are observed. From the perspective of $^{14}CO_2$ molar activity, the period 14.4–14.0 ka BP is connected only with several slightly decreased values, although other parameters show significant changes at this time (see Figures 1, 5). The increasing amount of $^{14}CO_2$ in the atmosphere reached its maximum value (~11.1 ka BP) when the increase in CO_2 concentration decelerated.

A remarkable change in trends also can be observed for the temperature time series at 11.1 ka BP (Figures 1, 5). Both time series of ^{10}Be are connected generally with a uniform decrease during the 17–11 ka BP interval. Only the time series "cosmogenic production of ^{10}Be" reflects a sharp decrease since 14 ka BP of several hundred of years' duration (Figure 3). The period of the maximal amount of $^{14}CO_2$ in the atmosphere can be connected mainly with CO_2 inflow, as is evident from the series of trends and local extremes presented above. From this point of view, it seems again that limitation of CO_2 input also caused a decrease in $^{14}CO_2$ input. Hence, the CO_2 input from long-term carbon sinks seems to contain a significant amount of $^{14}CO_2$, although depleted. The direct influence of cosmogenic ^{14}C production on the culminating amount of $^{14}CO_2$ in the atmosphere during this period was not confirmed by the ^{10}Be time series. A connection between the amount of $^{14}CO_2$ in the atmosphere and other parameters was not observed, which could be due in part to uncertainties in the age calibration of other parameters, particularly applied temperature curves. The sharp temperature decrease at the end of the Allerød and the stagnation of relatively low temperatures in the Younger Dryas are exceptions during the Late Glacial, which can be characterized by a gradual warming in general. A strong temperature decrease in the late Allerød, lasting several hundred years, is the youngest "cooling" period. Various records of ^{14}C activity are available for that time.

Better knowledge of CO_2 and $^{14}CO_2$ transport during this anomalous period could improve the possibility of carbon transport modeling under conditions different from gradual temperature increase, which could also enhance the tools for validation of prediction models. A verification of the course of the atmospheric CO_2 time series for Northern Hemisphere localities, and its comparison with northern and southern polar temperature curves, would be an important asset to this purpose (Bianchi and Gersonde 2002; Schulz and Paul 2004). Likewise, the improvement of time resolution and reduction of uncertainties in the time positions of the extremes during this relatively short period (14–11 ka BP at minimum) would be a benefit. A comparison with cosmogenic production of other radionuclides (namely, ^{10}Be, and ^{36}Cl or ^{26}Al when available) could also facilitate more precise studies of this interesting, unique period.

Long-term trends are not observed in both temperature time series since the beginning of the Holocene (10 ka BP; see Figure 5). In the period 10–7 ka BP, both concentrations of CO_2 and activities of ^{14}C ($\Delta^{14}C$ values) were relatively stable. During 7–2 ka BP, CO_2 concentration increased gradually, in addition to implying ^{14}C activities, as indicated by a continuation of the "mirroring effect" of both parameters with a high correlation for this period (76.6%; see Figure 1). Hence, it can be assumed that releases of CO_2 with partly depleted amounts of $^{14}CO_2$ (from long-term carbon

sinks) also continued at that time. The "mirroring effect" of CO_2 concentrations and ^{14}C activity history is restricted approximately to 2 ka BP. Hereafter, the obtained (anti) correlation of both time series is not statistically significant (2.4%). This implies that the changes in ^{14}C activity ($\Delta^{14}C$) younger than 2 ka BP are not significantly influenced by effect of $^{14}CO_2$ atmospheric dilution caused by releases of CO_2 with depleted amounts of ^{14}C into the atmosphere, as discussed above.

CONCLUSIONS

In the time interval from 50 to 20 ka BP, the cosmogenic production of ^{14}C seems to have a dominant influence on the $^{14}CO_2$ amount in the atmosphere, when the concentrations of atmospheric CO_2 were relatively stable with a slowly decreasing trend. Likewise, the curves of ^{10}Be production seem to have a similar shape as well as calculated molar activity (estimated $^{14}CO_2$ amount in the atmosphere) for this period. High anti-correlation (93.1%) was found for the CO_2 concentration and $\Delta^{14}C$ values from 20 to 2 ka BP. The decrease in $\Delta^{14}C$ levels seems to be caused by atmospheric dilution of $^{14}CO_2$ by inputs of CO_2 with depleted amounts of ^{14}C from deeper oceanic layers, as a result of gradually increasing temperature. The interval of strong relation between CO_2 and $\Delta^{14}C$ covers periods of the Heinrich Stadial 1 "Mystery Interval" (~17.5–14.5 ka BP) and Younger Dryas (~13–11 ka BP) where rapid rises in CO_2 concentrations and drops in $\Delta^{14}C$ activity were observed. Likewise, this relation continues until the prevailing part of the Holocene. The observed quantity of $^{14}CO_2$ in the atmosphere (calculated as molar activity) appears to show an increasing trend during the deglacial period, in the interval 20–11 ka BP, with only fine variations, although the opposite trend is evident for the ^{10}Be time series. During the last 2000 yr, the anticorrelation between the CO_2 and $\Delta^{14}C$ was not significant (2.4%).

It would be interesting to compare a time component of $^{14}CO_2$ molar activity with a calibrated time series for other cosmogenic radionuclides, e.g. ^{26}Al and ^{36}Cl, when such data become available. Extending the CO_2 concentration time series with gas-age calibrated data from Greenland ice cores, if available, could also verify our conclusions.

ACKNOWLEDGMENTS

This study was supported by institutional funding from the Nuclear Physics Institute AS CR (RVO61389005) and by the Ministry of the Interior of the Czech Republic (MV-25972-17/OBVV-2010) for the year 2012. PPP acknowledges a partial support provided by the EU Research and Development Operational Program funded by the ERDF (project No. 26240220004).

REFERENCES

Alley RB. 2000. The Younger Dryas cold interval as viewed from central Greenland. *Quaternary Science Reviews* 19(1–5):213–26.

Anderson RF, Ali S, Bradtmiller LI, Nielsen SHH, Fleisher MQ, Anderson BE, Burckle LH. 2009. Wind-driven upwelling in the southern ocean and the deglacial rise in atmospheric CO_2. *Science* 323(5920): 1443–8.

Basak C, Martin EE, Horikawa K, Marchitto TM. 2010. Southern Ocean source of ^{14}C-depleted carbon in the North Pacific Ocean during the last deglaciation. *Nature Geoscience* 3:770–3.

Bianchi C, Gersonde R. 2002. The Southern Ocean surface between Marine Isotope stages 6 and 5d: shape and timing of climate changes. *Palaeogeography, Palaeoclimatology, Palaeoecology* 187:151–77.

Broecker W. 2009. The mysterious ^{14}C decline. *Radiocarbon* 51(1):109–19.

Broecker W, Barker S. 2007. A 190‰ drop in atmosphere's $\Delta^{14}C$ during the "Mystery Interval" (17.5 to 14.5 kyr). *Earth and Planetary Science Letters* 256: 90–9.

Bryan SP, Marchitto TM, Lehman SJ. 2010. The release of ^{14}C-depleted carbon from the deep ocean during the last deglaciation: evidence from the Arabian Sea. *Earth and Planetary Science Letters* 298:244–54.

Butzin M, Prangeb M, Lohmannc G. 2005. Radiocarbon simulations for the glacial ocean: the effects of wind stress, Southern Ocean sea ice and Heinrich events. *Earth and Planetary Science Letters* 235:45–61.

Butzin M, Prange M, Lohmann G. 2012. Readjustment of glacial radiocarbon chronologies by self-consistent three-dimensional ocean circulation modeling. *Earth and Planetary Science Letters* 317–318:177–84.

Christl M, Lippold J, Steinhilber F, Bernsdorff F, Mangini A. 2010. Reconstruction of global ^{10}Be production over the past 250 ka from highly accumulating Atlantic drift sediments. *Quaternary Science Reviews* 29:2663–72.

Cléroux C, deMenocal P, Guilderson T. 2011. Deglacial radiocarbon history of tropical Atlantic thermocline waters: absence of CO_2 reservoir purging signal. *Quaternary Science Reviews* 30:1875–82.

Flückiger JE, Monnin B, Stauffer J, Schwander TF, Stocker J, Chappellaz D, Raynaud D, Barnola JM. 2002. High resolution Holocene N_2O ice core record and its relationship with CH_4 and CO_2. *Global Biogeochemical Cycles* 16(1): doi:10.1029/2001GB001417.

Frank M, Schwarz B, Baumann S, Kubik PW, Suter M, Mangini A. 1997. A 200 kyr record of cosmogenic radionuclide production rate and geomagnetic field intensity from Be-10 in globally stacked deep-sea sediments. *Earth and Planetary Science Letters* 149:121–9.

Indermühle A, Monnin E, Stauffer B, Stocker TF, Wahln M. 1999a. Atmospheric CO_2 concentration from 60 to 20 kyr BP from the Taylor Dome ice core, Antarctica. *Geophysical Research Letters* 27:735–8.

Indermühle A, Stocker TF, Joos F, Fischer H, Smith HJ, Wahlen M, Deck B, Mastroianni D, Tschumi J, Blunier T, Meyer R, Stauffer B. 1999b. Holocene carbon-cycle dynamics based on CO_2 trapped in ice at Taylor Dome, Antarctica. *Nature* 398(6723):121–6.

Jouzel J, Lorius C, Petit JR, Genthon C, Barkov NI, Kotlyakov VM, Petrov VM. 1987. Vostok ice core: a continuous isotope temperature record over the last climatic cycle (160,000 years). *Nature* 329(6138):403–8.

Jouzel J, Barkov NI, Barnola JM, Bender M, Chappellaz J, Genthon C, Kotlyakov VM, Lipenkov V, Lorius C, Petit JR, Raynaud D, Raisbeck G, Ritz C, Sowers T, Stievenard M, Yiou F, Yiou P. 1993. Extending the Vostok ice-core record of paleoclimate to the penultimate glacial period. *Nature* 364(6436):407–12.

Jouzel JC, Waelbroeck B, Malaize M, Bender JR, Petit M, Stievenard NI, Barkov JM, Barnola T, King VM, Kotlyakov V, Lipenkov C, Lorius D, Raynaud C, Sowers T. 1996. Climatic interpretation of the recently extended Vostok ice records. *Climate Dynamics* 12:513–21.

Levin I, Hammer S, Kromer B, Meinhardt F. 2008. Radiocarbon observations in atmospheric CO_2: determining fossil fuel CO_2 over Europe using Jungfraujoch observations as background. *Science of the Total Environment* 391(2–3):211–6.

Levin I, Naegler T, Kromer B, Diehl M, Francey RJ, Gomez-Pelaez AJ, Steele LP, Wagenbach D, Weller R, Worthy DE. 2010. Observations and modelling of the global distribution and long-term trend of atmospheric $^{14}CO_2$. *Tellus B* 62(1):26–46.

Lourantou A, Lavric JV, Köhler P, Barnola JM, Paillard D, Michel E, Raynaud D, Chappellaz J. 2010. Constraint of the CO_2 rise by new atmospheric carbon isotopic measurements during the last deglaciation. *Global Biogeochemical Cycles* 24: GB2015, doi:10.1029/2009GB003545.

Lund DC, Mix AC, Southon J. 2011. Increased ventilation age of the deep northeast Pacific Ocean during the last deglaciation. *Nature Geoscience* 4:771–4.

MacFarling MC, Etheridge D, Trudinger C, Steele P, Langenfelds R, van Ommen T, Smith A, Elkins J. 2006. The Law Dome CO_2, CH_4 and N_2O ice core records extended to 2000 years BP. *Geophysical Research Letters* 33: L14810, 10.1029/2006GL026152.

Marchitto TM, Lehman SJ, Ortiz JD, Fluckiger J, van Geen A. 2007. Marine radiocarbon evidence for the mechanism of deglacial atmospheric CO_2 rise. *Science* 316(5830):1456–9.

Meijer HAJ, van der Plicht J, Gislefoss JS, Nydal R. 1995. Comparing long-term atmospheric ^{14}C and ^{3}H records near Groningen, the Netherlands with Fruholmen, Norway and Izaña, Canary Islands ^{14}C stations. *Radiocarbon* 37(1):39–50.

Menviel L, Joos F, Ritza SP. 2012. Simulating atmospheric CO_2, ^{13}C and the marine carbon cycle during the Last Glacial–Interglacial cycle: possible role for a deepening of the mean remineralization depth and an increase in the oceanic nutrient inventory. *Quaternary Science Reviews* 56:46–68.

Monnin E, Indermühle A, Dällenbach A, Flückiger J, Stauffer B, Stocker TF, Raynaud D, Barnola JM. 2001. Atmospheric CO_2 Concentrations over the Last Glacial Termination. *Science* 291(5501):112–4.

Monnin E, Steig EJ, Siegenthaler U, Kawamura K, Schwander J, Stauffer B, Stocker TF, Morse DL, Barnola JM, Bellier B, Raynaud D, Fischer H. 2004. Evidence for substantial accumulation rate variability in Antarctica during the Holocene, through synchronization of CO_2 in the Taylor Dome, Dome C and DML ice cores. *Earth and Planetary Science Letters* 224:45–54.

Petit JR, Jouzel J, Raynaud D, Barkov NI, Barnola JM, Basile I, Bender M, Chappellaz J, Davis J, Delaygue G, Delmotte M, Kotlyakov VM, Legrand M, Lipenkov V, Lorius C, Pépin L, Ritz C, Saltzman E, Stievenard M. 1999a. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* 399(6735):429–36.

Petit JR, Jouzel J, Raynaud D, Barkov NI, Barnola JM, Basile I, Bender M, Chappellaz J, Davis M, Delayque G, Delmotte M, Kotlyakov VM, Legrand M, Lipenkov VY, Lorius C, Pepin L, Ritz C, Saltzman E, Stievenard M. 1999b. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica.

Nature 399(6735):429–36.

Reimer PJ, Baillie MGL, Bard E, Bayliss A, Beck JW, Blackwell PG, Bronk Ramsey C, Buck CE, Burr GS, Edwards RL, Friedrich M, Grootes PM, Guilderson TP, Hajdas I, Heaton T, Hogg AG, Hughen KA, Kaiser KF, Kromer B, McCormac FG, Manning SW, Reimer RW, Richards DA, Southon JR, Talamo S, Turney CSM, van der Plicht J, Weyhenmeyer CE. 2009. IntCal09 and Marine09 radiocarbon age calibration curves, 0–50,000 years cal BP. *Radiocarbon* 51(4): 1111–50.

Roth R, Joos F. 2012. Model limits on the role of volcanic carbon emissions in regulating glacial–interglacial CO_2 variations. *Earth and Planetary Science Letters* 329–330:141–9.

Schmitt J, Schneider R, Elsig J, Leuenberger D, Lourantou A, Chappellaz J, Köhler P, Joos F, Stocker TF, Leuenberger M, Fischer H. 2012. Carbon isotope constraints on the deglacial CO_2 rise from ice cores. *Science* 336(6082):711–4.

Schmittner A. 2003. Southern Ocean sea ice and radiocarbon ages of glacial bottom waters. *Earth and Planetary Science Letters* 213:53–62.

Schulz M, Paul A. 2004. Sensitivity of the ocean-atmosphere carbon cycle to ice-covered and ice-free conditions in the Nordic Seas during the Last Glacial Maximum. *Palaeogeography, Palaeoclimatology, Palaeoecology* 207:127–41.

Siegenthaler U, Monnin E, Kawamura K, Spahni R, Schwander J, Stauffer B, Stocker TF, Barnola JM, Fischer H. 2005. Supporting evidence from the EPICA Dronning Maud Land ice core for atmospheric CO_2 changes during the past millennium. *Tellus B* 57(7): 51–7.

Skinner LC, Fallon S, Waelbroeck C, Michel E, Barker S. 2010. Ventilation of the deep southern ocean and deglacial CO_2 rise. *Science* 328(5982):1147–51.

Smith HJ, Fischer H, Mastroianni D, Deck B, Wahlen M. 1999. Dual modes of the carbon cycle since the Last Glacial Maximum. *Nature* 400(6741):248–50.

Sortor RN, Lund DC. 2011. No evidence for a deglacial intermediate water $\Delta^{14}C$ anomaly in the SW Atlantic. *Earth and Planetary Science Letters* 310:65–72.

Stott L, Timmermann A, Thunell R. 2007. Southern Hemisphere and deep-sea warming led deglacial atmospheric CO_2 rise and tropical warming. *Science* 318(5849):435–8.

Stott L, Southon J, Timmermann A, Koutavas A. 2009. Radiocarbon age anomaly at intermediate water depth in the Pacific Ocean during the last deglaciation. *Paleoceanography* 24: PA2223, doi:10.1029/2008PA001690.

Stuiver M, Polach HA. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.

Svetlik I, Povinec PP, Molnár M, Meinhardt F, Michálek V, Simon J, Svingor E. 2010. Estimation of long-term trends in the tropospheric $^{14}CO_2$ activity concentration. *Radiocarbon* 52(2–3):815–22.

Tachikawa K, Vidal L, Sonzogni C, Bard E. 2009. Glacial/interglacial sea surface temperature changes in the Southwest Pacific Ocean over the past 360 ka. *Quaternary Science Reviews* 28:1160–70.