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Supplemental Material for: Abrupt rise in atmospheric $\mathrm{CO_2}$ at the onset of the Bølling/Allerød: in-situ ice core data versus true atmospheric signals

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Appendix A Investigating the principle behaviour of the log-normal function describing the age distribution PDF during gas enclosure in ice cores

The log-normal function which was applied here as the age distribution PDF of $\mathrm{CO_2}$ was fitted as described in the methods section of the main text to the output of a firn densification model (Joos and Spahni, 2008). Furthermore, the chosen width $E = 400$ yr of this function for the onset of the B/A warm period was determined by another firn densification model, which includes heat diffusion (Goujon et al., 2003). When this function (Eq. 1 in the main text) is applied onto atmospheric $\mathrm{CO_2}$ time series derived from our carbon cycle model simulations it then acts as a filter whose resulting output has the characteristics of a $\mathrm{CO_2}$ time series potentially recorded in the EDC ice core.

A data-based investigation of the principle behaviour of this filter function would provide an independent support for this approach. We therefore test the behaviour of the filter with ice core $\mathrm{CH_4}$ data, which exist for our time window of interest not only from EDC (our ice core of interest with low accumulation rates), but also from Greenland sites. These Greenland sites have high accumulation rates and therefore the process of gas enclosure has a smaller impact on the $\mathrm{CH_4}$ time series than in EDC.

A1 Target

The behaviour of the filter can be tested on the abrupt rise in atmospheric $\mathrm{CH_4}$ which occurs in parallel to the abrupt rise of atmospheric $\mathrm{CO_2}$ around 14.6 kyr BP. For this test the $\mathrm{CH_4}$ record in an ice core with highest accumulation rate (namely a composite record from Greenland (EPICA-community-members, 2006)) might serve as a substitute for atmospheric $\mathrm{CH_4}$. Applying the chosen filter function for the EDC ice core gas enclosure to the Greenland ice core $\mathrm{CH_4}$ record should provide a temporal behaviour (in terms of slope or gradient m) similar to that recorded in $\mathrm{CH_4}$ in EDC (Monnin et al., 2001). Performing the same test not only for the Greenland composite $\mathrm{CH_4}$ record but also for other ice cores might in principle extend the robustness of the filter, but the lower accumulation rates in Antarctic ice cores (implying also a lower temporal resolution) have already large effects on the recorded $\mathrm{CH_4}$, which implies further difficulties in the interpretation.

A2 Requirements

It is essential that the gas enclosure characteristics in terms of age distribution PDF are similar for $\mathrm{CH_4}$ and $\mathrm{CO_2}$. This seems to be the case based on the output of a firn densification model (Joos and Spahni, 2008).

A3 Limitations

There are certain limitations to this investigation:

1. Because the gas enclosure of $\mathrm{CH_4}$ in Greenland already changed the true original atmospheric signal, a principle understanding of the filter is necessary. This can be obtained by using an artificial $\mathrm{CH_4}$ time series as input data to the filter. Thus, by filtering this artificial $\mathrm{CH_4}$ record for conditions typical for EDC (*step a*: width $E = 400$ yr), for Greenland (*step b*: $E = 60$ yr) and then finally by filtering the output for Greenland of *step b*: a second time with conditions typical for EDC (*step c*: $E = 400$ yr) we can generate two artificial time series whose behaviour in terms of the slope m can be compared with that of the ice core data of Greenland and EDC (see Appendix B of the Supplemental Material for details on E for Greenland).

   The difficulty of this comparison of the behaviour of the filter for artificial and real input data is, that the comparison works best, if the artificial $\mathrm{CH_4}$ is as similar as

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Table A1. Slope m of CH_4 rise at onset of B/A warm event in ppbv per century

ice core	ice core data	artificial atmospheric CH_4 with different m		
		$m = 2000$	$m = 400$	$m = 250$
Greenland	171 ± 15	234 ± 50	181 ± 24	146 ± 15
Greenland filtered to EDC ($E = 400$ yr)	28 ± 5	32 ± 7	32 ± 6	33 ± 7
EDC target	39 ± 4	36 ± 8	36 ± 5	35 ± 7
Δm difference (Greenland – EDC)	132 ± 16	198 ± 51	145 ± 25	111 ± 17

possible to the original atmospheric CH_4 peak. However, the atmospheric CH_4 peak is not precisely known, and thus the slope m in the artificial data can only be estimated to lie somewhere between infinity (instantaneous rise of CH_4) and the slope calculated in the ice core CH_4 data with highest accumulation rate (Greenland, $m = 171$ ppbv per century).

2. This comparison is further complicated by a potential interhemispheric gradient in CH_4. Although data analysis suggests a stronger interhemispheric gradient in warm interstadials than in cold stadials (Dällenbach et al., 2000), the change in the interhemispheric gradient in CH_4 in the very narrow time window of the transition into the B/A warm period is not precisely known (Brook et al., 1999).
3. Checking if the filtered Greenland CH_4 time series fits onto single CH_4 points measured in EDC is not meaningful, because the filtering affects the age model of the time series, which needs to be corrected accordingly.
4. For our problem at hand, which focuses on the transition into the B/A warm period, the dynamics of CH_4 and the usability of the applied filter function at other times with different climate background conditions, as well as different accumulation rates and densification characteristics (e.g. at the beginning and the end of the Younger Dryas), is not relevant.

A4 Results

Within the given limitations and estimated uncertainties (CH_4: $1\sigma = 10$ ppbv measurement uncertainty (Monnin et al., 2001); 20% uncertainty in the suggested widths E of the age distribution PDF; ignoring errors and uncertainties in the gas age models) the filter produces slopes in the artificial CH_4 peaks which are similar to those of the ice core data (see Tab. A1 and Fig. A1 of the Appendix). The artificial CH_4 did not include an interhemispheric gradient in CH_4 and therefore the difference in the slope Δm between Greenland and EDC should be larger or similar in the analysis of the ice core data than in the artificial data. This difference in the slope depends on the original slope of the assumed artificial atmospheric CH_4 and this knowledge can be used to suggest, that the slope m of the true atmospheric CH_4 was likely smaller than 400 ppbv/century, probably m was between 200 and 350 ppbv/century.

We therefore conclude that the investigations on the principle behaviour of the age distribution PDF used here to mimic the gas enclosure process does not introduce any systematic bias to the gas records. The age distribution PDF operates as a filter on atmospheric CH_4 or CO_2 records and produces convoluted time series of the respective gas records which are comparable in their slope or gradient with in-situ measurements in ice cores. The application of the filter on the abrupt rise in CO_2 during the onset of the B/A warm period seems therefore to be justified. These investigations based on ice core CH_4 data are a very reliable support for the gas enclosure characteristic assumed for the abrupt rise of CO_2 into the B/A.

Appendix B Uncertainty in methane synchronisation of ice cores

Recently, a consistent synchronisation of the ice cores NGRIP, EPICA Dome C (EDC), EPICA DML (EDML) and Vostok was published (Lemieux-Dudon et al., 2010) (named here: QSR2010 age scale). This effort combined the use of various different age markers from the ice matrix (e.g. volcanic horizons, magnetic reversals, ^{10}Be peaks) and the gas phase to overcome shortcomings of previous age scales (Ruth et al., 2007; Loulergue et al., 2007; Parrenin et al., 2007). Here, especially the synchronous matching of abrupt changes in CH_4 was a prominent target to align ice core climate records over the last glacial cycle, especially over Termination I. This new ice age scale was used within our study.

As described in the methods section of the main text gases entrapped in ice cores have a typical age distribution PDF which they derive during mixing in the firn before bubble close-off. This age distribution PDF mainly depends on local accumulation rate and temperature, and can be calculated with firn densification models (main text Fig. 2). These PDFs are very similar for CO_2 and CH_4 for the EDC ice core (Joos and Spahni, 2008). The effect of the age distribution PDF is, that the ice cores do not record the true atmospheric signal, but one that is attenuated. The back calculation from the

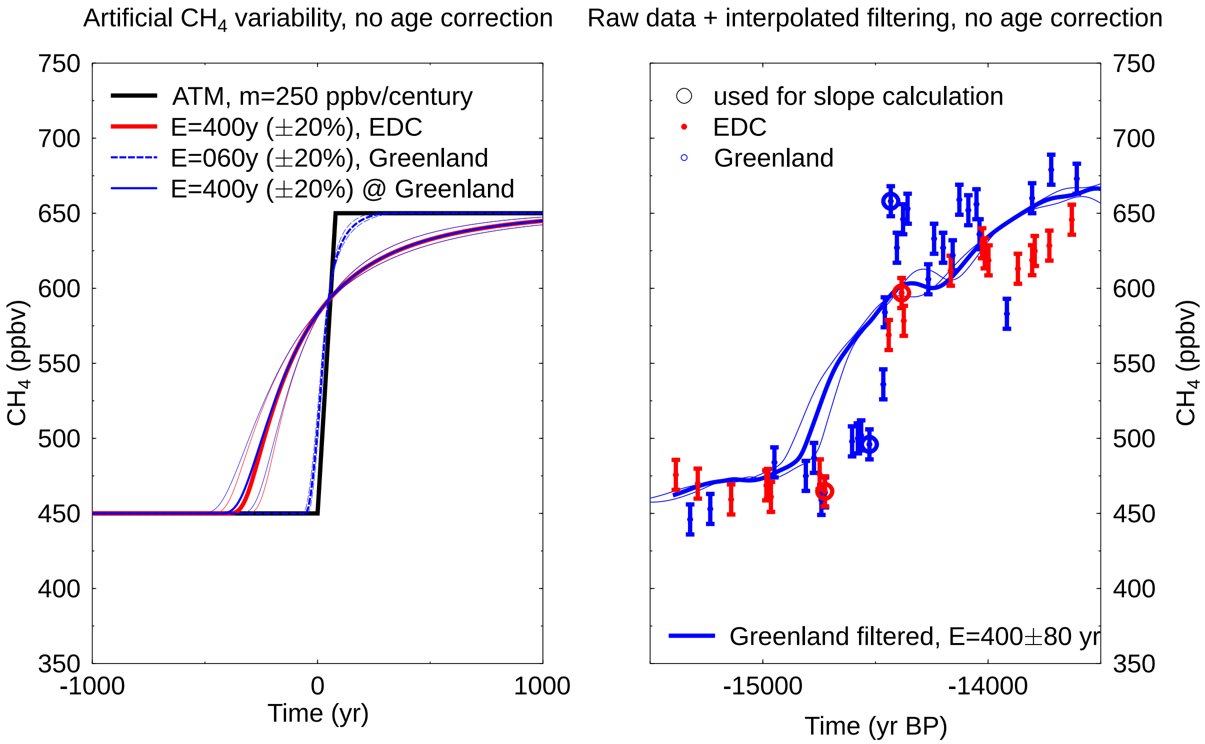

Fig. A1. Left: Artificial methane peak, filtered with the log-normal function with various widths E including a relative uncertainty of 20%. An interhemispheric gradient in methane is not considered. Right: Ice core raw data from EDC (Monnin et al., 2001) and Greenland composite (EPICA-community-members, 2006) and Greenland filtered data. The circled data points were taken to calculate the slope m in the CH_4 data as given in Table 1.

in-situ ice core measurements to the atmospheric signal is not unique. Nevertheless, certain details of the atmospheric signal can be prescribed based on the knowledge of gas enclosure in ice cores: (1) Fast changes in atmospheric records are always more abrupt and larger than their in-situ measurements in ice cores. Due to typically higher accumulation rates in Greenland this partly explains the interhemispheric gradient in CH_4 during D/O events. (2) Synchronisation of ice cores along abrupt changes in in-situ measured CH_4 have an embedded dating artefact which depends on the gas age distribution PDF. The second point, the embedded dating artefact, was not mentioned explicitly as a source of dating errors in descriptions of gas chronologies and synchronisation attempts (Blunier et al., 2007; Loulergue et al., 2007; Lemieux-Dudon et al., 2010) and is presumably not included in their uncertainty estimates.

The pure application of the age distribution PDF of CH_4 as a filter function on a true atmospheric CH_4 peak shifts the onset of a CH_4 peak by the width E of the gas age distribution PDF towards older ages (Fig. B1A of Appendix). This age offset is corrected for during the preparation of gas age scales of ice cores (Spahni, personal communication) with the effect, that the onset in the true atmospheric signal and those recorded in ice cores occur simultaneously (Fig. B1B of Appendix). However, this correction comes on the cost of uncertainty in the timing of the peak and the transition.

During wiggle matching of different paleo records the mid-transition points of abrupt changes are often taken as reference tie-points, on which the respective transitions are aligned to. The approach of mid-transition points is taken here for the sake of argument, but we are aware, that more sophisticated models might be used, which would nevertheless still have to cope with the synchronisation uncertainty discussed here. In the case of CH_4 synchronisation from ice cores the in-situ measured mid-transition points differ from the true atmospheric CH_4 by about 58% of the width E of the gas age distribution PDF of the relevant ice core in the respective climate period of interest (Fig. B1D of Appendix). The alignments of various ice cores performed so far (Lemieux-Dudon et al., 2010) synchronised the in-situ measured CH_4 data. A more precise approach would try to use the underlying true atmospheric CH_4 for synchronisa-

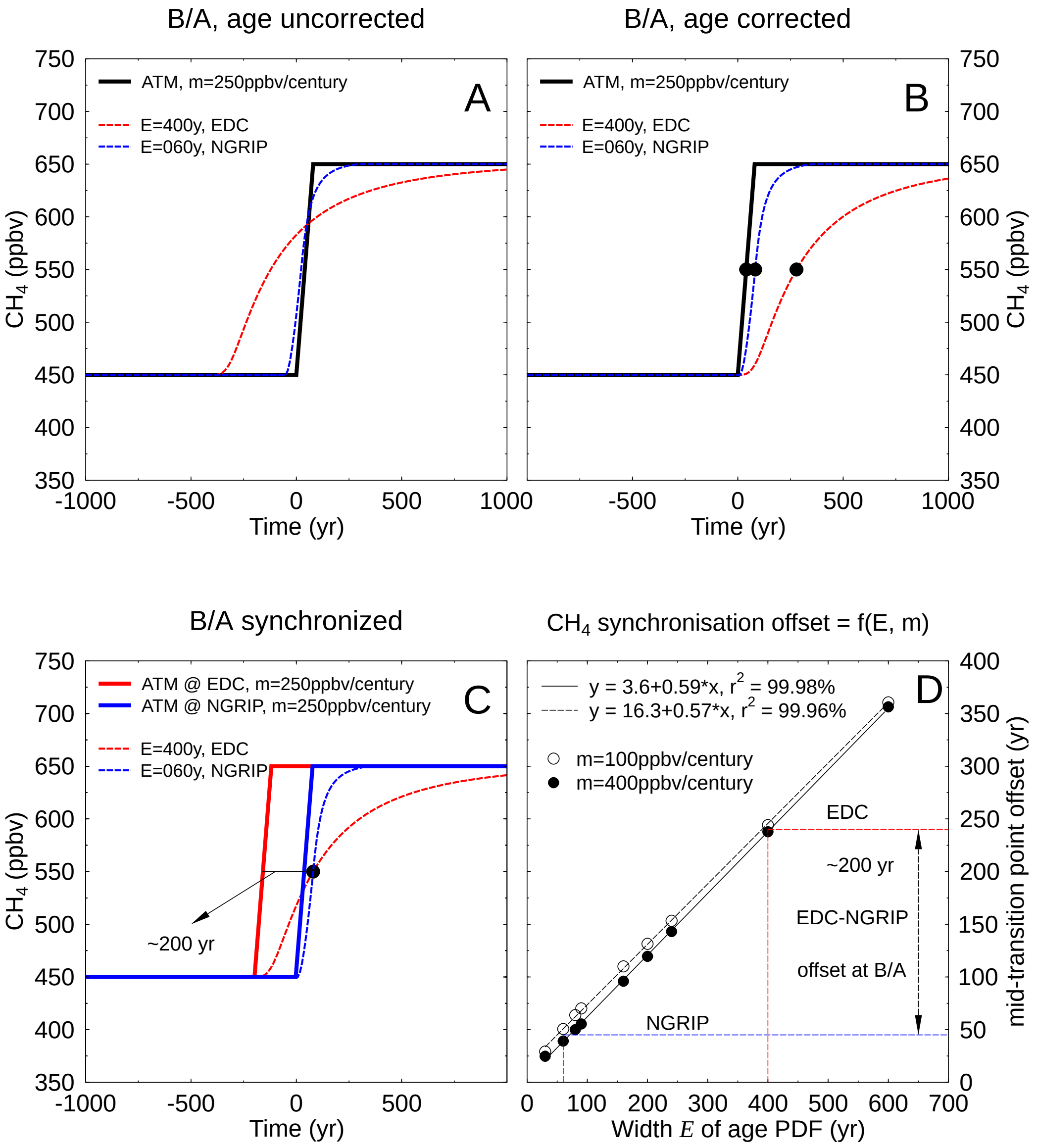

Fig. B1. Effect of the age distribution PDF on an artificial time series of atmospheric CH_4, which includes a abrupt rise in CH_4 by 200 ppbv. (A) Peak attenuation for two different widths E of the age distribution PDF, which represent B/A conditions of the NGRIP ($E = 60$ yr) and EDC ($E = 400$ yr) ice cores without age correction. (B) Same as in (A), but potential ice cores records are now aged corrected (shifted by E to younger ages). Circles mark the mid-transition points defined as a CH_4 concentration of 550 ppbv. (C) Potential synchronisation error for the transition into the B/A. Here, the mid-transition points of the smoothed time series (potential recorded in ice cores) are synchronised. The bold lines show the temporal settings of the atmospheric signals connected to the synchronised potential ice core CH_4. (D) Summary on the synchronisation effect for different width E of the age distribution PDF and different slopes m, by which atmospheric CH_4 changed during its abrupt rise. Results are based in the difference of the mid-transition points in atmospheric CH_4 and potential ice core records.

tion. Unfortunately, the true atmospheric signal is not precisely known and can only be approximated using assumptions on the rates of change and amplitudes which might have been occurred in the atmosphere. However, if CH_4 synchronisations rely on the ice core CH_4 data they then have a dating artefact which depends on the embedded age offset between true atmospheric values and in-situ measurements.

For EDC a width E of the gas age distribution PDF of 400 yr was calculated here with a firn densification model for the climate around 14.6 kyr BP. An estimate of the width

E at NGRIP based on firn densification models was not available. For the GRIP ice core (recent accumulation rate of 211 mm water equivalent per year (Chappellaz et al., 1997)) E is estimated by a firn densification model to 25 yr for present day climate (Spahni et al., 2003). NGRIP has a recent accumulation rate of 174 mm water equivalent per year (Andersen et al., 2006), which is about a factor seven larger than at EDC (Blunier et al., 2007). Using the inverse of the ratio of the accumulation rates as an estimate for the ratio of the width E of the gas age distribution PDF leads to a $E = 60$ yr at NGRIP during the onset of the B/A. Our estimate for E therefore seems to be in a right order of magnitude and this approach should illustrate the orders of magnitude for our problem at hand.

We now apply how a abrupt rise in artificial CH_4 with a true atmospheric amplitude of 200 ppbv, which rises with a slope m between 100 and 400 ppbv per century, would be recorded in these two ice cores with the given gas enclosure characteristics. If the age correction by the width E of the gas age PDF is applied, the onset in CH_4 in the atmosphere and in all ice cores is dated to be simultaneously, but the mid-transition points in the ice cores are recorded 240 and 45 years later than in the atmosphere under conditions typical for the B/A for EDC and NGRIP, respectively (Fig. B1B,D of Appendix). The wiggle matching alignment of CH_4 of the two ice cores is therefore at maximum as accurate as the difference of the dating of these mid-transition points from the true atmospheric signal. The QSR2010 gas age scale used here (Lemieux-Dudon et al., 2010) is at the onset of the B/A due to the embedded CH_4 synchronisation artefact about 200 years too old (Fig. B1C,D of Appendix). We need to correct for this temporal offset to set our proposed atmospheric CO_2 signal into context with the dating of MWP-1A. The correction for this temporal offset aligns our proposed true atmospheric CO_2 shift to the occurance of MWP-1A (Fig. 7 of main text).

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