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Rapid changes in ice core gas records – Part 1: On the accuracy of methane synchronisation of ice cores

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Abstract

Methane synchronisation is a concept to align ice core records during rapid climate changes of the Dansgaard/Oeschger (D/O) events onto a common age scale. However, atmospheric gases are recorded in ice cores with a log-normal-shaped age distribution probability density function, whose exact shape depends mainly on the accumulation rate on the drilling site. This age distribution effectively shifts the mid-transition points of rapid changes in CH_4 measured in situ in ice by about 58% of the width of the age distribution with respect to the atmospheric signal. A minimum dating uncertainty, or artefact, in the CH_4 synchronisation is therefore embedded in the concept itself, which was not accounted for in previous error estimates. This synchronisation artefact between Greenland and Antarctic ice cores is for GRIP and Byrd less than 40 years, well within the dating uncertainty of CH_4 , and therefore does not calls the overall concept of the bipolar seesaw into question. However, if the EPICA Dome C ice core is aligned via CH_4 to NGRIP this synchronisation artefact is in the most recent unified ice core age scale (Lemieux-Dudon et al., 2010) for LGM climate conditions of the order of three centuries and might need consideration in future gas chronologies.

1 Introduction

One important approach to align climate records derived from different ice cores along a common time scale is the synchronisation of prominent and rapid changes in methane (CH_4) (Blunier et al., 1998, 2007; Blunier and Brook, 2001). During the last glacial period the rapid stadial/interstadial changes of Dansgaard/Oeschger (D/O) events recorded in Greenland ice cores (Johnsen et al., 1992) were connected with fast (decades to centuries) and large changes in the CH_4 concentration (Chappellaz et al., 1993), which is measured in situ in the gases entrapped in the ice. These rapid temperature changes during D/O events in the north are within the concept of the bipolar seesaw (Stocker and Johnsen, 2003) connected with similar rapid changes of opposite sign in the South Atlantic (Barker et al., 2009). All D/O events of marine isotope stage

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(MIS) 3 have been identified to be connected with more gradual Antarctic warm events, called Antarctic Isotope Maxima (AIM), in Antarctic ice cores. The gradual temperature rise in the Antarctic ice cores during a stadial cold phase in the north was exactly switching to a gradual cooling in the south at the onset of rapid warming in Greenland

5 (EPICA-community-members, 2006). The more gradual changes in Antarctic temperature proxies were attributed to the large heat reservoir of the Southern Ocean (Stocker and Johnsen, 2003). The D/O events during MIS 5 are connected to AIM in a more complicated pattern than suggested by the bipolar seesaw (Capron et al., 2010).

Recently, a consistent synchronisation of various ice cores (NGRIP, EPICA Dome 10 C (EDC), EPICA DML (EDML), Vostok) was proposed (Lemieux-Dudon et al., 2010) which 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 rapid changes in CH_4 was 15 a prominent target to align ice core climate records over the last glacial cycle, especially over Termination I (Fig. 1). In addition to the age markers to synchronise ice cores, models are used to calculate the thinning of ice sheets (Huybrechts et al., 2007) and the firn densification during gas enclosure (Schwander et al., 1993; Goujon et al., 2003). Furthermore, in the case of Greenland ice cores annual layers are counted over 20 the last 60 kyr (Svensson et al., 2008).

Ice cores gas records are significantly younger than the ice matrix, this age difference is called Δ age. To synchronise ice cores via CH_4 one has to perform various subsequent steps. (1) Develop a chronology for the ice matrix of one ice core which agrees best with absolute age (here: annual layer counted ice core age scale of Greenland ice cores GICC05 (Svensson et al., 2008)). (2) Calculate a gas age chronology (or Δ age) based on rapid changes in both the isotopic temperature measured in the ice matrix and CH_4 during D/O events. (3) Synchronise the gas chronology of other ice cores via CH_4 to this first ice core. (4) Refine (or calculate) the ice chronology for the other cores.

However, gases entrapped in ice and measured *in situ* in ice cores have a typical age distribution probability density function (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

5 (Fig. 2). These PDF are very similar for CO_2 and CH_4 (Spahni et al., 2003). The age distribution PDF effectively leads to gas records in the ice cores that differ during rapid changes from the true atmospheric signal. The *in situ* measured CH_4 signal is attenuated in comparison to the true atmospheric one. The back calculation from the *in situ* ice core measurements to the atmospheric signal is not unique. This leads to chronology artefacts in two of the four mentioned steps necessary for ice core synchronisation 10 mentioned above (Fig. 3): (i) The alignment of rapid changes in the isotopic temperature proxy and *in situ* measured CH_4 to constrain Δage (step 2), or to connect the ice and gas chronologies of individual cores is biased. (ii) The synchronisation of ice cores along rapid changes in CH_4 measured *in situ* (step 3) has an embedded dating artefact 15 which depends on the gas age distribution PDF. Both potential sources of dating errors were not mentioned explicitly in descriptions of gas chronologies and synchronisation attempts (Blunier et al., 2007; Loulergue et al., 2007; Lemieux-Dudon et al., 2010). We will focus here on the synchronisation effect (artefact ii). In detail, we will estimate the size of this synchronisation artefact for the two EPICA ice cores and NGRIP as contained in the most recent age scale (Lemieux-Dudon et al., 2010). Finally, we discuss 20 its consequences and that of the age distribution for Δage (artefact i) for our current understanding of the bipolar seesaw. In a companion paper (Rapid changes in ice core gas records – Part 2) the effect of the age distribution PDF on the rapid rise in CO_2 at the onset of the Bølling/Allerød is discussed (Köhler et al., 2010b). There, the final 25 interpretation which needs to set the CO_2 rise into the correct temporal context to other climate events was only possible after the correction of the age model which followed the understanding of the CH_4 synchronisation artefact.

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2 Methods

The age distributions PDF of gases entrapped in ice cores calculated with firn densification models (Joos and Spahni, 2008) can be approximated (Köhler et al., 2010a) by the following log-normal function (Fig. 2).

$$y = \frac{1}{x \cdot \sigma \cdot \sqrt{2\pi}} \cdot e^{-0.5 \left(\frac{\ln(x) - \mu}{\sigma} \right)^2} \quad (1)$$

with x (yr) as the time elapsed since the last exchange with the atmosphere. We chose for simplicity $\sigma = 1$, which leads to an *expected value (mean)* E of the PDF of $E = e^{\mu - 0.5}$. Equation (1) is thus fully described once E is known and yields for the LGM and current conditions for EDC (Fig. 2) a reasonable agreement ($r^2 \approx 0.9$) with the results of a firn densification model (Joos and Spahni, 2008). The age distribution PDF for CH_4 and CO_2 are very similar and differ only in detail (Fig. 2). The *expected value* E is in the terminology of gas physics described as *width* of the PDF, a terminology which we will also use in the following. E is different, and should not be confused with the *most likely value* defined by the location of the maximum of the PDF.

Although, these age distribution PDF are calculated with firn densification models for all ice cores, for which a gas chronology needs to be applied, they are seldomly shown in details in publications (e.g. Spahni et al., 2003; Joos and Spahni, 2008). The usage of Eq. (1) as a substitute for the age distribution PDF therefore allows us without the usage of a firn densification model to mimic the effect of the gas enclosure process on an ice core gas record. Furthermore, besides published values for the width of the age distribution PDF for EDC and GRIP we estimate E based on the inverse relationship between E and the accumulation rate (Table 1). This is certainly a simplification, but should still be a reasonable approach to show the order of magnitude of the synchronisation artefact.

The age distribution PDF acts like a filter function on peaks in the true atmospheric CH_4 . Its application shifts the onset of a CH_4 peak by E years towards older ages (Fig. 4a). This age offset is corrected during the preparation of gas chronologies of ice cores

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with the effect, that the onset in a rapid change in CH_4 in the true atmospheric signal and that measured in situ in ice cores occur simultaneously (Fig. 4b).

3 Results

During wiggle matching of different paleo records the mid-transition point of rapid changes is often taken as reference tie-point, on which the respective transition is 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 artefact 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 mean gas age of the relevant ice core in the respective climate period of interest (Fig. 5). The alignments of various ice cores performed so far synchronised the in situ measured CH_4 data. A more precise approach would try to use the underlying true atmospheric CH_4 for synchronisation. 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.

We show for the cases of EDC, EDML and NGRIP typical mean gases ages as calculated from firn densification models or as approximated from recent accumulation rates for pre-industrial and LGM climates (Table 1). This should illustrate the orders of magnitude. The width E of the age distribution PDF in NGRIP is always below 100 yr, while it rises to 600 yr in EDC for LGM climate, with EDML values in-between.

We now apply how an artificial CH_4 peak with a true atmospheric amplitude of 400 ppbv, which changes in 50 years, would be recorded in different ice cores. If the age correction by the width E of the age distribution 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 356, 143 and 55 (120, 50 and 25) years later than

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in the atmosphere under LGM (pre-industrial) conditions for EDC, EDML and NGRIP, respectively (Fig. 4b, c). A wiggle matching alignment of ice core CH₄ is therefore at maximum as accurate as the difference of the dating of these mid-transition points from the true atmospheric signal:

- 5 1. For EDC and NGRIP at LGM: 356–55 = 301 years.
2. For EDC and EDML at LGM: 356–143 = 213 years.
3. For EDML and NGRIP at LGM: 143–55 = 88 years.

The embedded synchronisation error between EDML and NGRIP falls within the given uncertainty of 100 to 160 years assumed so far (Lemieux-Dudon et al., 2010).

10 The synchronisation artefact between EDC and both other ice cores of 200 to 300 years for LGM conditions is however to my knowledge larger than uncertainties given so far, e.g. the uncertainty in the CH₄ synchronisation between EDC and EDML is in general (with a few exceptions) smaller than 200 years (Loulergue et al., 2007). Furthermore, Loulergue et al. (2007) and Lemieux-Dudon et al. (2010) do not mention the effect of 15 the gas age distribution PDF on the accuracy of the synchronisation as discussed here. It is presumably not included in their estimated uncertainties.

4 Discussions and conclusions

The Byrd and GRIP ice cores are those on which the asynchrony of fast climate change of Antarctic and Greenland was first discovered (Blunier et al., 1998). If our understanding 20 of the effect of the age distribution PDF on the dating accuracy as proposed here is applied to these ice cores a CH₄ synchronisation artefact of less than 40 years during LGM climate conditions is achieved (Table 1). Furthermore, for the one-to-one coupling of all Greenland D/O events to Antarctic Isotopic Maxima a synchronisation error of 400–800 yr in MIS 3 was given (EPICA-community-members, 2006). Both conclusions imply that our current understanding of the bipolar seesaw does not need to 25

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be revised. However, the acknowledgment of the CH_4 synchronisation artefact as discussed here enables us to either correct for it, or to state a more realistic, e.g. larger uncertainty connected to it.

The consequence of this dating artefact embedded in CH_4 synchronisation is especially important for the interpretation of other gas records (e.g. CO_2 or N_2O), while for the synchronisation of records from the ice matrix the still large uncertainty of several centuries in Δ age has also to be taken into account (e.g. Blunier et al., 2007). The still existing most precise and temporally highest resolved record of CO_2 over Termination I was measured on the EDC ice core (Monnin et al., 2001; Lourantou et al., 2010) (Fig. 10 1a). Because CH_4 measured on the same ice core was used for synchronisation it seemed so far possible to set rapid changes in CO_2 precisely in temporal relation to changes in northern hemispheric temperature (e.g. NGRIP $\delta^{18}\text{O}$). However, this assumption is now weakened by the additional synchronisation error between EDC and NGRIP of ~ 200 years at the onset of the Bølling/Allerød. Furthermore, the whole concept of gas age distribution has also to be applied for CO_2 to account for the effect, that the in situ CO_2 data of EDC are not the true atmospheric signal, but only its attenuation after the application of the age distribution PDF to account for the gas enclosure process in the firn column (Köhler et al., 2010b).

What are now the consequences of the embedded dating error for Termination I, for 20 which the newest age model of Lemieux-Dudon et al. (2010) provided a very accurate synchronisation of ice core CH_4 (Fig. 1b)? A firm densification model with heat diffusion (Goujon et al., 2003) calculates for the onset of the Bølling/Allerød warming a width E of the age distribution PDF in EDC, which lies with 400 years in-between those of the LGM and the pre-industrial climate (Köhler et al., 2010b). If similar in-between values 25 of E are assumed for the other ice cores we then calculate for an artificial CH_4 peak as substitute for the Bølling/Allerød warm interval an error in the CH_4 synchronisation of 244, 110 and 50 between the true atmosphere and EDC, EDML and NGRIP, respectively (Fig. 4d).

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In summary, we provided details how the age distribution of atmospheric gases entrapped in ice cores is responsible for a difference of the in situ measured values from the true atmospheric signal. The gas age distribution therefore blurs the accuracy of CH₄ synchronisation of fast D/O events. This embedded synchronisation error was so far unaccounted for and introduces a dating artefact of up to several centuries between individual ice cores and between ice cores and the true atmospheric signal. Mid-transition points are shifted by about 58% of the width E of the age distribution PDF towards younger ages.

Acknowledgements. Renato Spahni kindly provided electronic output from the firn densification model published in Joos and Spahni (2008).

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Ice core	recent accumulation rate a_{PRE} mm (water eq.) yr^{-1}	E_{PRE} yr	E_{LGM} yr
EPICA Dome C (EDC)	25 ^a	200^b	600^b
EPICA Dome DML (EDML)	65 ^a	80 ^c	240 ^c
NGRIP	174 ^d	30 ^c	90 ^c
GRIP	211 ^e	25^f	75 ^c
Byrd	110 ^e	45 ^c	136 ^c

References:

^a: Blunier et al. (2007)

^b: Joos and Spahni (2008)

^c: E estimated based on $E \times a \approx \text{constant}$ for either present or LGM climates.

^d: Andersen et al. (2006)

^e: Chappellaz et al. (1997)

^f: Spahni et al. (2003)

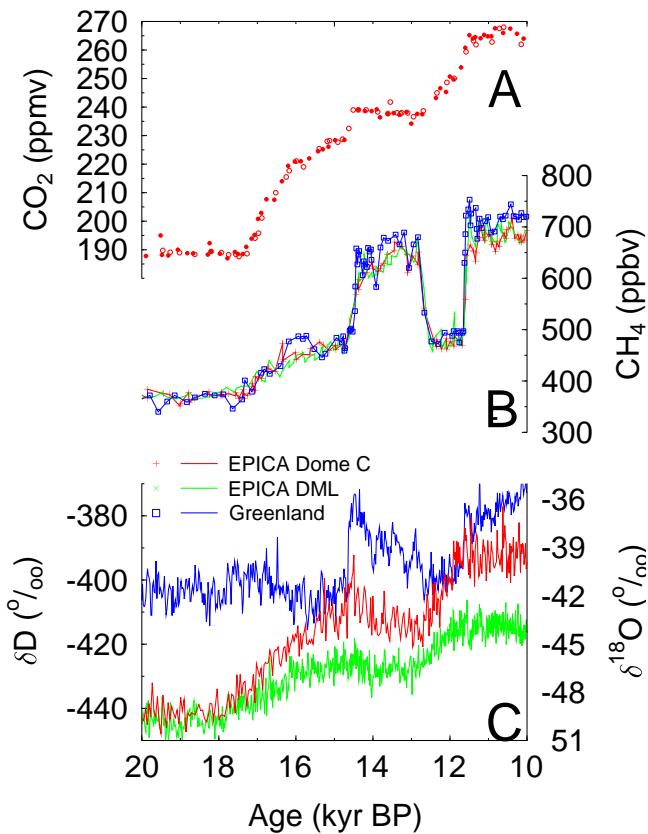


Fig. 1. Ice core records over Termination I. **(A)** EDC CO₂, closed circles: (Monnin et al., 2001), open circles: (Lourantou et al., 2010). **(B)** CH₄ (Spahni et al., 2005; EPICA-community-members, 2006). **(C)** isotopic temperature proxies δD (EDC) and $\delta^{18}\text{O}$ (EDML, NGRIP) (Stenni et al., 2001; NorthGRIP-members, 2004; EPICA-community-members, 2006). All records on the new synchronised age scale (Lemieux-Dudon et al., 2010).

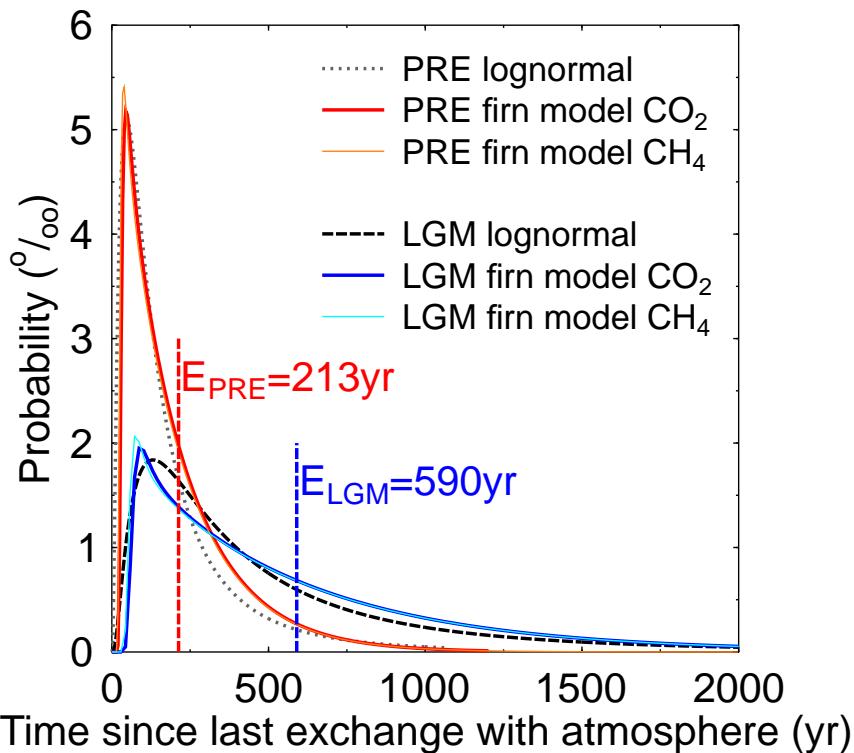


Fig. 2. Age distribution probability density function for CO_2 and CH_4 calculated with a firn densification model (Joos and Spahni, 2008) and approximated with the log-normal function (Eq. 1). Calculations of the firn densification model differ only very slightly for CO_2 and CH_4 .

Fig. 3. Conceptual sketch of ice core synchronisation of NGRIP and EDC via CH_4 for 14.6 kyr BP, the onset of the Bølling/Allerød warm period. **(A)**: Following the dating of Lemieux-Dudon et al. (2010). **(B)**: Proposed revised dating, if not CH_4 measured in situ in ice cores, but potentially atmospheric CH_4 are taken for synchronisation. From top to bottom: NGRIP $\delta^{18}\text{O}$, NGRIP CH_4 , EDC CH_4 , EDC CO_2 , EDC δD . Black lines are in situ ice core measurements, red lines are potentially underlying atmospheric records. Red numbers indicate the dating offset at mid-transition points between ice core and atmospheric gas records.

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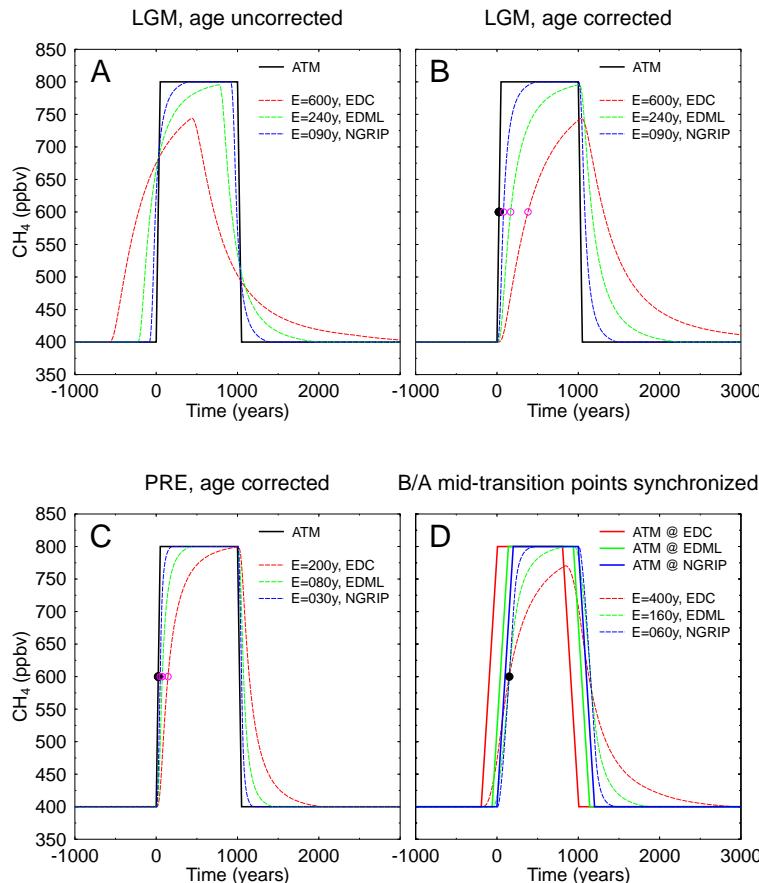


Fig. 4.

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Fig. 4. Effect of the gas age distribution on a synthetic CH_4 peak of 400 ppbv. **(A)** Peak attenuation for three different mean gas ages E , which represent LGM conditions of the NGRIP, EDML and EDC 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 600 ppbv. **(C)** Same as in (B) for pre-industrial climate conditions. **(D)** Potential synchronisation error during Termination I for the transition into the Bølling/Allerød, here the width E of the age distribution PDF lie in-between those of LGM and PRE. Mid-transition points are synchronised and bold lines show what the atmospheric signal would look like depending on the potential ice core CH_4 from which it is deconvolved. Atmospheric CH_4 rises and declines in 50 years in A, B, C and in 200 years in D.

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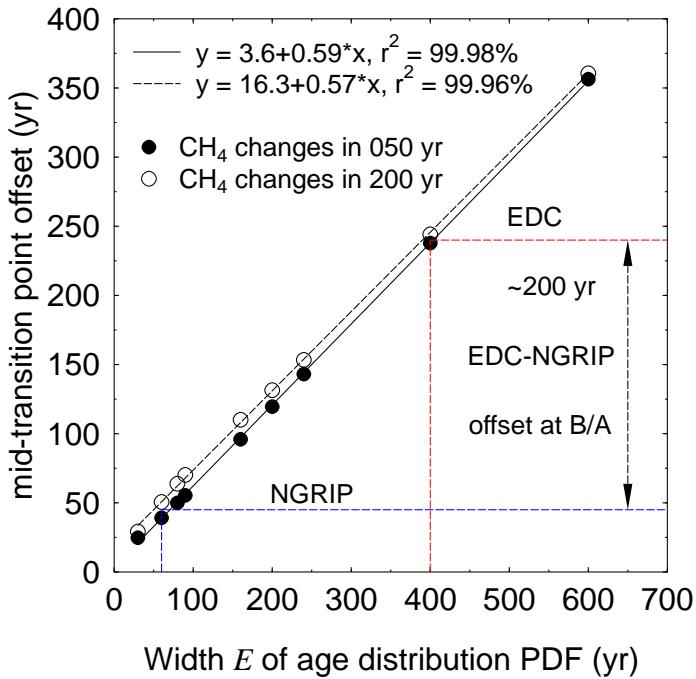


Fig. 5. Difference of the mid-transition points of rapid changes in atmospheric CH_4 and potential in situ measurements of CH_4 in ice cores depending on the width E of the age distribution PDF in the ice core and the rate of change in atmospheric CH_4 (here rapid changes in atmospheric CH_4 occurred in either 50 or 200 years). The example of the mid-transition points offset of the CH_4 rise at the Bølling/Allerød (B/A) recorded potentially in NGRIP and EDC is illustrated in detail.