

# Climatic and insolation control on the high-resolution total air content in the NGRIP ice core

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## Abstract.

Because the total air content ( $TAC$ ) of polar ice is directly affected by the atmospheric pressure and temperature, its record in polar ice cores was initially considered as a proxy for past ice sheet elevation changes. However, the Antarctic ice core  $TAC$  record is known to also contain an insolation signature, although the underlying physical mechanisms are still a matter of debate. Here we present a high-resolution  $TAC$  record over the whole North Greenland Ice Core Project ice core, covering the last 120,000 years, which independently supports an insolation signature in Greenland. Wavelet analysis reveals a clear precession and obliquity signal similar to previous findings on Antarctic  $TAC$ , with different insolation history. In our high-resolution record we also find a decrease of 4-6% (4-5 mL kg<sup>-1</sup>) in  $TAC$  as a response to Dansgaard-Oeschger-Events (DO events).  $TAC$  starts to decrease in parallel to increasing Greenland surface temperature and slightly before CH<sub>4</sub> reacts to the warming, but also shows a two-step decline that lasts for several centuries into the warm interstadial. The  $TAC$  response is larger than expected considering only changes in air density by local temperature and atmospheric pressure as a driver, pointing to a transient firnification response caused by the accumulation-induced increase in the load on the firn at bubble close-off, while temperature changes deeper in the firn are still small.

## 1 Introduction

The total air content ( $TAC$ ) in ice cores from polar regions is one of the many parameters that inform about past environmental conditions.  $TAC$  was initially developed to provide robust information about the past surface elevation of ice sheets (Lorius et al. (1968), Raynaud and Lorius (1973)), due to its pressure and, thus, altitude dependence. However, consecutive studies showed that the densification and bubble close-off processes have an even larger influence on the pore volume enclosed in polar ice and, thus, on  $TAC$ . We suggest that air enclosure is primarily dependent on two competing processes during densification and bubble close-off. On the one hand increasing ice deformation (creep) with depth leads to expulsion of air and therefore a reduction of the pore

space. On the other hand water vapor transport tries to minimize surface free energy of the pore surfaces enlarging pores and keeping the pore space open against the closure supported by creep. Both processes intensify with increasing temperature. To date no established theory exists that quantitatively describes the temporal evolution of densification and bubble enclosure of polar firn columns to produce the observed  $TAC$  changes in ice cores. However, an empirical relationship with temperature for steady-state firnification conditions exists based on  $TAC$  and firn air observations. Raynaud and Lebel (1979) discovered an empirical relationship of pore volume at bubble close-off and snow temperature in the Camp Century (Greenland) ice core, owing to changes in the densification process at equilibrium conditions. Martinerie et al. (1992) confirmed this positive correlation, mainly in Antarctic, but also alpine and Greenland ice cores in late Holocene snow. Krinner et al. (2000) show that interpreting  $TAC$  as an elevation proxy is also limited by secular variations in surface pressure as well as by porosity and temperature changes.

More recently Raynaud et al. (2007), Parrenin et al. (2007) and Lipenkov et al. (2011) reported an apparent anti-correlated local summer insolation imprint in  $TAC$  and used it to constrain the timescale of Antarctic ice core records. This orbital synchronization is further supported by variations in the  $O_2/N_2$  ratio, which is also correlated with summer insolation (Bender, 2002). The latter relation was shown to hold for the Greenland record GISP2 as well (Suwa and Bender, 2008). Further, Suwa and Bender (2008) showed increasing  $O_2/N_2$  ratios for DO events in the GISP2 ice core. Local summer insolation changes are apparently affecting snow surface properties like structure or grain size that remain preserved through firnification down to the pore close-off depth. Grain size in the uppermost 3 m is influenced (increased) by summer insolation (Measurements from EPICA Dronning Maud Land drill site, Antarctica, *J. Freitag pers. comm.*), but also on daily weather events. Hutterli et al. (2009) state that the total temperature gradient metamorphism (tTGM) influences the physical properties of the snow pack. tTGM is not necessarily synchronous with insolation, leading to a lag between the orbital parameters and the proxies depending on snow structure. Lipenkov et al. (2011) suggest how the summer insolation signal in the firn at Vostok, Antarctica, a low accumulation area, might influence the  $TAC$  at bubble close-off. However, in the light of the observed faster densification of winter layers with higher  $Ca^{2+}$  concentrations in Greenland firn (Hörhold et al., 2012), it is unclear how surface snow structure in Greenland (high accumulation sites) might survive the recrystallization process in the firn. In view of this on-going discussion and of the fact that a clear insolation effect has so far only been documented in Antarctic ice cores, an independent validation based on Greenland ice, which has a different insolation history, is of great importance.

In this paper we present a high-resolution  $TAC$  record from the North Greenland Ice Core Project (NGRIP) ice core with 1688 new data points from 134 to 3082m depth. The aim of this work is twofold: First, to test known influences on  $TAC$ , such as the orbital insolation effect observed in Antarctica, for the first time in Greenland; second, to document transient effects on  $TAC$  due to rapid temperature changes known as Dansgaard-Oeschger-Events (DO events). Note that the insola-

tion effects on pore volume represent a signal imprinted on the firn structure during densification and thus are a signal imprinted in the ice matrix. In contrast, variations in  $TAC$  due to direct temperature changes, as expected during DO events, reflect changes in air density at bubble close-off and thus are imprinted in the gas record itself.

This paper is organized as follows. Section 2 explains the method to determine  $TAC$  and discusses uncertainties. The new NGRIP record of  $TAC$  is presented in section 3. In section 4 we investigate the time characteristics of the  $TAC$  record and its signature during DO events. Conclusions are given in section 5.

## 2 Methods

Following Martinerie et al. (1992), the  $TAC$  (sometimes also denoted  $V$  in the literature) results are expressed in  $\text{mL kg}^{-1}$  STP and are related to temperature, pore volume and pressure via (Martinerie et al., 1992):

$$TAC = V_c \frac{P_c \cdot T_0}{T_c \cdot P_0}, \quad (1)$$

with  $V_c$  the pore volume,  $P_c$  the pressure and  $T_c$  the temperature at bubble close-off,  $P_0$  the standard pressure (1013 hPa) and  $T_0$  the standard temperature (273 K).

### 2.1 Measurement and calibration

The  $TAC$  data presented here stem from two different instruments with different procedures. Neither method delivers absolute values and had to be calibrated. In the method by Schmitt et al. (2011) the samples were melted after evacuation using infrared radiation.  $TAC$  was determined by pressure and temperature measurements of the released air under well controlled conditions. These data are referred to as vacuum-melt data. Schmitt et al. (2014) gauged their instrument in an intercalibration exercise with the Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) in Grenoble on EPICA Dome C (EDC) ice. In short, two time intervals of the EDC ice core, which were previously measured at the LGGE (Raynaud et al., 2007), were re-measured with the vacuum-melt device. Using 54 overlapping samples derived from the LGGE device and 59 samples from the vacuum-melt device constrained the uncertainty of the calibration to  $0.5 \text{ mL kg}^{-1}$ . Using this vacuum-melt technique also 62 NGRIP samples of 160 g were measured and are presented in this study.

The 1626 other data points were measured as a by-product of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  concentration measurements performed in Berne over many years (Flückiger et al. (2004), Schilt et al. (2010), Baumgartner et al. (2012), Schilt et al. (2013), Baumgartner et al. (2014)), with a different instrument. The melt water was refrozen during the gas extraction process, therefore we refer to this data as melt-refreeze data. More detail on the extraction technique of this data is given in the section 2.1.1, more on the offset correction between different melt-refreeze measurement periods in section 2.1.2. To reach

consistent absolute  $TAC$  values, we intercalibrated the melt-refreeze data to the vacuum-melt data. 42 of the 62 vacuum-melt data points lie within 250yrs to our melt-refreeze data, and were used for a nearest-neighbour analysis. For this analysis, each point of the vacuum-melt data was compared  
 100 with at most the two nearest neighbours of the offset-corrected (see section 2.1.2) NGRIP data in each time direction, if they were not more than 70 (250)yrs apart from each other. The mean difference between the two methods was  $-0.7 \pm 2.0 \text{ mL kg}^{-1}$  ( $-0.53 \pm 2.1 \text{ mL kg}^{-1}$ ). Accordingly, the vacuum-melt data and the melt-refreeze data match within error and were therefore not corrected.

### 2.1.1 Extraction technique for the melt-refreeze data

105 The melt-refreeze data of 2010, 2011 and 2012, in total 1339 data points, were measured as a by-product of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  concentration measurements. To extract the air from the ice samples, the samples are melted in an evacuated vessel. We then refreeze the melt water slowly from below to expel dissolved gases (see e.g. Flückiger et al. (2004)). The extracted gas is then expanded into the sampling loop,  $V_2$  (Fig. 1). In the apparatus the mole number of extracted gas  $n$  is split between two  
 110 different volumes  $V_1$  and  $V_2$  and therefore using the ideal gas law and the gas constant  $R$ , we define:

$$TAC = \frac{V_0}{m} = \frac{n \cdot R \cdot T_0}{m \cdot p_0} = \frac{R \cdot T_0}{m \cdot p_0} \cdot (n_1 + n_2). \quad (2)$$

In the sample extraction device we consider three volumes (Fig. 1), the head space over the ice sample  $V_h$ , the tube volume  $V_t$  and the expansion volume  $V_2$ . We combine  $V_h$  and  $V_t$  to  $V_1 = V_h + V_t$ . The mole fractions  $n_1$  and  $n_2$  in Eq. 2 refer to the volumes  $V_1$  and  $V_2$ , respectively.  $V_h$  is dependent  
 115 on the size of each individual vessel and on the volume of refrozen meltwater in the vessel, so  $V_1$  is corrected for the small vessel-specific differences and assuming an ice density of  $\rho_{\text{ice}} = 917 \text{ kg m}^{-3}$ . The temperature in the headspace  $V_h$  and  $V_t$  is not homogeneous, since  $V_h$  is cooled below the freezing point, while the tubing  $V_t$  is exposed to ambient, stabilized lab temperature.  $T_1$  is therefore close to the freezing point, but could not be measured directly. Instead it is determined to be 275.15 K  
 120 on average through a calibration with NEEM ice and LGGE data, as described in the supplementary information of NEEM community members (2013). The temperature  $T_2$  in the sampling loop is held constant at  $-60 \pm 0.5 \text{ }^\circ\text{C}$ . The expanded gas stabilizes in the volume  $V_1 + V_2$  at the expansion pressure  $p_{\text{exp}}$ , measured with the pressure gauge denoted  $P$  in Fig. 1. With

$$p_{\text{exp}} = \frac{n_1 \cdot R \cdot T_1}{V_1} = \frac{n_2 \cdot R \cdot T_2}{V_2}. \quad (3)$$

125 substituting this in equation 2 we get:

$$TAC = \frac{T_0 \cdot p_{\text{exp}}}{m \cdot p_0} \cdot \left( \frac{V_1}{T_1} + \frac{V_2}{T_2} \right). \quad (4)$$

Note that the parameter  $T_1$  may slightly vary with lab temperature and also with different extraction vessels. Assuming errors of  $0.5 \text{ }^\circ\text{C}$  for  $T_1$  and  $T_2$ ,  $0.2 \text{ ml}$  for  $V_1$  and  $V_2$  and  $0.01 \text{ g}$  for the mass  $m$  of

the ice sample (Baumgartner, 2013) and 50 Pa for  $p_{\text{exp}}$  (at an average  $p_{\text{exp}}$  of 4000 Pa for a sample)  
 130 the resulting uncertainty in  $TAC$  is  $1.3 \text{ mL kg}^{-1}$ , which corresponds to about 1.5% of the  $TAC$   
 value in NGRIP ice.

The error used for the 2010, 2011 and 2012 data in the plots and for the interpretation was also deter-  
 mined by reproducibility measurements. Five adjacent samples were measured at 15 depth levels. In  
 each of the 15 depths, we measured  $TAC$  randomly distributed over the different extraction vessels  
 135 and duration of the measurement series. The pooled standard deviation of the residuals of the 75  
 samples is  $2.2 \pm 0.8 \text{ mL kg}^{-1}$  (about 2.5 % of the  $TAC$  value in NGRIP ice), which is higher than  
 the calculated analytical error of  $1.3 \text{ mL kg}^{-1}$ . This is expected due to natural variations of  $TAC$   
 in the ice along the 25 cm of ice core used for the reproducibility measurements (see also section 3  
 below) and variations in the number and size of the air bubbles opened on the sides of the ice cube  
 140 during cutting. In order to minimize the latter effect, we cut all samples the same way, in pieces of  
 $\sim 40 \text{ g}$ .

The whole  $TAC$  dataset has a mean value of  $93.4 \text{ mL kg}^{-1}$  with a standard deviation of  $4.5 \text{ mL kg}^{-1}$ .  
 The measured  $TAC$  data show notable high-frequency variability which is much larger than the de-  
 rived analytical error of  $1.3 \text{ mL kg}^{-1}$  (see Fig. 3). We infer that a considerable part of the scattering  
 145 in neighbouring samples seems to results from the small-scale variability of the  $TAC$  signal in the  
 ice itself. One option to verify this is to check whether the scattering diminishes with depth and  
 therefore decreasing annual layer thickness, as described in Baumgartner et al. (2014). If the scatter-  
 ing is a signal in the ice itself, the standard deviation of the values in the 5 adjacent reproducibility  
 samples should get smaller with increasing depth, since high-frequency variations will be smoothed  
 150 by the increasing time interval per sample due to layer thinning with depth. In Fig. 3 the standard  
 deviation over the reproducibility measurements is plotted vs. depth. There is a clear trend to lower  
 scattering with depth (although not with a high correlation coefficient) indicating that part of the  
 scatter is embedded in the ice itself. Martinerie et al. (1992) found seasonal peaks with up to 10-  
 25 % amplitude in  $TAC$ , so we can assume most of the scattering to be caused by seasonal cycles  
 155 or inter-annual variability. If we do so, we average over more cycles with an increasing age interval  
 covered in the 25 cm of the adjacent reproducibility samples. The measured variation should there-  
 fore decrease with  $1/N$ ,  $N$  being the number of years contained in one sample and the 5 samples in  
 each 25 cm interval provide us with an information on the analytical error according to:

$$\sigma_{\text{measured}}^2 = \frac{\sigma_{\text{ice}}^2}{N} + \sigma_{\text{analytical}}^2. \quad (5)$$

160 If  $N$  approaches infinity we get an independent estimate of our analytical error. In Fig. 3 in the right  
 panel we display the variation in the reproducibility samples versus  $1/N$  with the best linear fit. We  
 get a y-intersect (corresponding to  $N = \infty$ ) of  $1.4 \text{ mL}^2 \text{ kg}^{-2}$ . Taking the square root this independent  
 estimate leads to an analytical error of  $1.2 \text{ mL kg}^{-1}$ , very close to the  $1.3 \text{ mL kg}^{-1}$  we calculated in  
 section 2.1.1.

165 Most of our  $TAC$  data (years 2010-2012) were measured using the above described method, while  
data obtained between 2002 and 2004, 287 samples in total, were measured with a slightly differ-  
ent procedure as described in Flückiger et al. (2004). The main difference is that at that time the  
evacuation step after loading the ice into the vessel lasted for two hours instead of about 30 min,  
and the released air was expanded three times in sequence into a smaller, unchilled sampling loop  
170 for analysis. For those measurements the  $TAC$  was determined three times per sample and the ana-  
lytical error of  $TAC$  was estimated as the standard deviation of the three measurements, leading to  
individual errorbars for each data point with an average error of  $2.86 \text{ mL kg}^{-1}$ .

### 2.1.2 Offset correction in the melt-refreeze data

The 2002/2004 and 2010-2012 data are slightly offset from each other, so a method to intercalibrate  
175 the two data sets was developed. Also between the measurement periods of 2010, 2011 and 2012  
minor changes in the instrument could lead to small offsets which have to be accounted for. Data  
pairs of corresponding sample depths in the NGRIP ice core from the different measuring periods  
were identified, the measuring period of 2012 was taken as a reference. Reference data points are  
compared with interpolated values of the other dataset. Only the data from 2010 could not be com-  
pared directly to 2012 because they cover different sections of the ice core and hence the 2010 data  
180 set was compared to the 2011 data. The mean of the offset values are displayed in table 2 together  
with its standard error. The age differences to the closest points of the reference values are also  
shown in table 2, with the interpolations providing better results if the data points are closer to each  
other, as expected from the natural variability of  $TAC$  in the ice. Based on this comparison the data  
185 from 2002 were shifted by  $3.4 \text{ mL kg}^{-1}$ , those from 2004 by  $6.1 \text{ mL kg}^{-1}$ , and those from 2011 by  
 $-2 \text{ mL kg}^{-1}$ . The 2010 data are not significantly different ( $1.2 \pm 1.4 \text{ mL kg}^{-1}$ ) from 2012, so no cor-  
rection was made. This corrected melt-refreeze data set was used to compare with the vacuum-melt  
data and showed no significant offset, as described in section 2.1.

## 3 The NGRIP $TAC$ record

190 Our new NGRIP record contains 1688  $TAC$  data points and is shown in Fig. 2 on the AICC2012  
gas age scale (Veres et al., 2013), along with  $\delta^{18}\text{O}_{\text{ice}}$ . The depth range is 133.81 to 3082.23 m, which  
corresponds to 294 to 119555 yrs in gas age on the AICC2012 timescale.

### 3.1 Comparison with GRIP $TAC$

Raynaud et al. (1997) presented a lower resolution Greenland  $TAC$  data set from the GRIP ice  
195 core. GRIP is located 316 km south-southeast of NGRIP, at an altitude of 3232 m, compared to  
2919 m at NGRIP (Dahl-Jensen et al., 1997). Today there is essentially no temperature difference  
between NGRIP and GRIP as the altitude effect is compensated by the higher latitude of the for-

mer. Therefore, and because insolation differences being insignificant between the two sites due to their geographic proximity, we expect also no difference in pore volume  $V_c$  (Martinerie et al. (1992)).

200 Accordingly, assuming the temperature consistency did also not change in the past, the only factor influencing the  $TAC$  difference between the two sites is altitude (and possibly wind (Martinerie et al., 1994), which is neglected here). The GRIP data mainly cover the Holocene with measurements back to 40.6 kyr BP. In Fig. 4 we show the  $TAC$  from Raynaud et al. (1997), along with our two  $TAC$  records (melt-refreeze and vacuum-melt) in the time interval 0.2 to 45 kyr BP on gas age.

205 The GRIP and NGRIP data are given on a synchronized ice age scale for the Greenland records (Seierstad et al., 2014). The data show good agreement, the GRIP  $TAC$  air content is on average slightly lower. To quantify the difference, each point from GRIP was compared with at most the two nearest neighbours of the NGRIP data in each time direction, if they lay within 250 yrs of the GRIP data point. Up to 11.5 kyr (Holocene) GRIP data were only compared to vacuum-melt data since no

210 melt-refreeze data were available. The Holocene GRIP  $TAC$  is about  $1.7 \pm 0.3 \text{ mL kg}^{-1}$  lower than NGRIP and glacial GRIP in the interval 11.5 to 45 kyr is  $2.4 \pm 0.3 \text{ mL kg}^{-1}$  lower, where the error is the standard error of the mean. This is generally in line with the expectations: a higher altitude at the deposition site should lead to lower  $TAC$ . Our results leave, on the brink of significance, room for small relative altitude changes from the LGM to Holocene between the two sites, although

215 other studies (e.g. NGRIP Project Members (2004)) state that the relative altitude changes are believed to be small. Assuming a mean annual temperature of  $-46 \text{ }^\circ\text{C}$  ( $-31.5 \text{ }^\circ\text{C}$ ) for stadial (Holocene) conditions (Kindler et al., 2014) at NGRIP and using the barometric formula, leads to a pressure-elevation gradient of  $\delta P/\delta Z = 10.5 \text{ hPa}/100 \text{ m}$  ( $9.9 \text{ hPa}/100 \text{ m}$ ). Ignoring temperature, pore volume and upstream correction, Eq. (1) gives an expected  $TAC$  difference of  $4.2 \text{ mL kg}^{-1}$  ( $4 \text{ mL kg}^{-1}$ ) at

220 an average of  $90 \text{ mL kg}^{-1}$  and NGRIP bubble close-off pressure of  $699 \text{ hPa}$  (*pers. comm. K. Steffen University of Colorado, Boulder*). This is more than what we observe in our data. Moreover, in reality the pressure-elevation gradient could be larger (11 to  $15 \text{ hPa}/100 \text{ m}$ ), as automatic weather stations located in the GRIP area suggest (Raynaud et al., 1997). Accordingly, we can not quantitatively explain the absolute  $TAC$  difference between the two sites and therefore also refrain from

225 interpreting the relative change in  $TAC$  difference between the sites from the LGM to the Holocene.

## 4 Discussion

### 4.1 Low-frequency variations in TAC

$TAC$  in Antarctica is known to show an anti-correlation with the integrated local summer insolation ( $ISI$ ) as shown by Raynaud et al. (2007) for approximately the last 400,000 years in the EPICA

230 Dome C record. We define  $ISI$  as

$$ISI = \sum_{i=1}^{365} w_i \cdot \theta(w_i - w_0). \quad (6)$$

Where  $w_i$  is the daily insolation in  $\text{W m}^{-2}$ ,  $\theta$  is the Heavyside stepfunction, and  $w_0$  denotes a threshold insolation. This threshold had been defined by tuning the correlation between  $ISI$  and  $TAC$ . A similar dependency emerges for our Greenland ice core calculating a local summer insolation for the NGRIP drill site. A maximum correlation between  $TAC$  and  $ISI$  is found for  $w_0 = 390 \text{ W m}^{-2}$ , compared to  $380 \text{ W m}^{-2}$  used by Raynaud et al. (2007) for the Antarctic EPICA Dome C (EDC) ice core. The correlation difference between 380 and  $390 \text{ W m}^{-2}$  is however small and the threshold does not alter the shape of the  $ISI$  much.

Martinierie et al. (1992) found an empirical relationship between the pore volume  $V_c$  at bubble close-off and the temperature for recent equilibrium densification conditions with,

$$V_c = 0.76 \cdot \left( \frac{\text{ml}}{\text{K} \cdot \text{kg}} \right) \cdot T_s - 57 \cdot \left( \frac{\text{ml}}{\text{kg}} \right), \quad (7)$$

where  $T_s$  is the snow temperature in Kelvin, here assumed to be the same as the temperature at bubble close-off depth,  $T_c$ , when the firn column is in thermal equilibrium. Like in Raynaud et al. (2007), we defined the non-thermal residual term  $V_{cr}$  as:

$$V_{cr} = TAC \cdot \frac{T_c}{P_c} \cdot \frac{P_0}{T_0} - V_c(T_s). \quad (8)$$

Where  $T_c$  and  $P_c$  are the temperature and pressure at bubble close-off depth. For the temperature at bubble close-off we used values by Kindler et al. (2014) which are derived from a heat conduction model and surface temperature variations using the  $\delta^{15}\text{N}$  thermo-diffusion technique (Severinghaus and Brook (1999), Lang et al. (1999), Kindler et al. (2014)), providing data from 10 to 120 kyr. For the pressure at bubble close-off we use a constant value of 699 hPa.  $T_0$  and  $P_0$  are the standard temperature (273 K) and standard atmospheric pressure (1013 hPa), respectively. Analogous to Raynaud et al. (2007) and Lipenkov et al. (2011) we define a standardized version of  $TAC$  and  $V_{cr}$

$$TAC^* = - \frac{TAC - \overline{TAC}}{\sigma(TAC)} \quad (9)$$

and

$$V_{cr}^* = - \frac{V_{cr} - \overline{V_{cr}}}{\sigma(V_{cr})}. \quad (10)$$

Splines with a 750 year cut-off period (Enting, 1987) through  $TAC^*$  and  $V_{cr}^*$  are shown together with the standardized  $ISI$  ( $sISI$ ), splined with a 3 kyr cut-off period, in Fig. 5.

The  $r^2$  between  $TAC^*$  and  $V_{cr}^*$  for the spline is 0.95, so the temperature effect on firnification processes quantified according to Martinierie et al. (1992) is responsible for only 5% of the  $TAC$  variance, in accordance with Raynaud et al. (2007). These authors derived an  $r^2$  of 0.86 and estimated the temperature induced  $TAC$  variations to 10% of the total signal. The strong covariance of  $TAC^*$  and local insolation for both Greenland and Antarctic ice cores provides independent evidence of an  $ISI$  effect on pore volume as the temporal evolution of  $ISI$  in both hemispheres differs significantly. As can be seen in Fig. 5 the shape of the  $sISI$  is highly covariant with the low-frequency variations



265 of  $TAC^*$  and  $V_{cr}^*$ , while higher-frequency variations seem to correlate with temperature on the ice sheet (see Fig. 2). Note that during the glacial, temperature changes in Greenland are dominated by fast DO events, and a spline through the data filters out some of the variations.

Investigations on the higher frequency variations and  $TAC$  relation to climate changes during DO events are discussed in section 4.3.2. In table 3 the correlations between the  $sISI$ ,  $V_{cr}^*$ ,  $T_c$  and  $TAC^*$  270 are shown. For the best linear fit we estimate a sensitivity of  $TAC$  on the local integrated summer insolation's energy input above  $390 \text{ W m}^{-2}$  of  $-5.7 \times 10^{-9} \text{ mL kg}^{-1} \text{ J}^{-1}$  with an  $r^2$  of 0.3.

Fig. 5 shows that the correlation of  $ISI$  and  $TAC^*$  is absent before about 109 kyr, i.e. at the glacial inception at the end of the Eemian. Raynaud et al. (2007) associated the 100 kyr cycle in the Antarctic EDC  $TAC$  record to pressure differences induced by surface elevation changes. The question 275 arises whether the  $TAC$  deviations from the expected insolation effect at the glacial inception in our NGRIP record are also related to ice sheet changes. Models for Greenland ice sheet coverage and surface height in the Eemian show little difference to the present. Born and Nisancioglu (2012), based on ice sheet modelling, estimate at NGRIP a maximum lowering of 200 m in the last glacial maximum (LGM) compared to the Holocene. Using the same calculations as in section 3.1, this 280 would account for a  $TAC$  change of  $2.4 \text{ mL kg}^{-1}$ , while the observed  $TAC$  changes at the very end of the  $TAC$  record are in the order of  $10 \text{ mL kg}^{-1}$ .

Note that the correlation breakdown between  $TAC$  and  $ISI$  before 109 kyr mainly results from only two data points (see Fig. 2), at 118.8 and 119.4 kyr with very low  $TAC$ , and the robustness of the  $TAC/ISI$  decoupling can therefore be questioned. If we exclude these two points and correlate 285 the  $sISI$  with the  $TAC^*$  from the top only until 109 kyr,  $r^2$  increases to 0.45, while the absolute changes in  $TAC$  are still larger than expected from altitude changes in models.

It has to be taken in to account that the time scale of  $ISI$  is absolute, while the AICC2012 age scale used in this study is fundamentally based on an ice-flow model and in particular shows younger ages for the lowest part of the ice core, compared to other time scales (Veres et al., 2013), with an 290 uncertainty of around 5000 yrs in the lowest part of the ice core. Accordingly, if the older part of the  $TAC$  record were shifted to somewhat older ages, the correlation would increase. This would imply that the lowest part of the NGRIP ice core contains not the end of the Eemian but its maximum. The comparison of the NGRIP and NEEM ice and gas records over the Eemian compiled by Landais et al. (2016) shows that such a stretching of the NGRIP record's lowest part would then lead to 295 consistency problems between the NEEM gas records and their Antarctic counterparts, which were used as template to date the bottom-most ice at NEEM. Accordingly, a simple shift of the AICC2012 age scale used for the NGRIP ice core in Fig. 5 seems incompatible with the NEEM ice core. We therefore refrain from providing a new orbitally tuned age scale for the oldest part of the NGRIP record. Instead, other factors than the age scale appear to be responsible for the deviation of  $TAC$  300 from  $ISI$  at that time.

## 4.2 Spectral analysis

Following Raynaud et al. (2007) we performed a wavelet analysis on the  $TAC$  data (Fig. 6). Between 20-70kyrs the obliquity effect on  $TAC$  is dominant, while for 80-110kyrs the precession cycle dominates. This is in agreement with the findings for EDC, displayed in the right panel of Fig. 6.

305 Since both Antarctic EDC and Greenland NGRIP  $TAC$  show the same pattern of either obliquity or precession dominance, we performed a cross-wavelet analysis between the  $TAC$  and the respective local  $ISIs$ . This analysis allows us to find common spectral signals in the time series (see e.g. Grinsted et al. (2004)). (Fig. 7).

Our results for NGRIP support the findings by Raynaud et al. (2007) and Lipenkov et al. (2011) on  
310 Antarctic  $TAC$  being related to  $ISI$ . Both records show coherence in the obliquity and precession bands. Antarctic  $TAC$  and  $O_2/N_2$  ratio (Lipenkov et al., 2011) were known to contain an  $ISI$  signal as was the  $O_2/N_2$  ratio in Greenland (Suwa and Bender, 2008). Now we show for the first time that Greenland  $TAC$  also contains an  $ISI$  signature, similarly to Antarctic  $TAC$  records.

## 4.3 Higher-frequency TAC variations and DO events

### 315 4.3.1 Relation to $Ca^{2+}$ /dust

Based on recent studies (Freitag et al., 2013) small-scale firn density is known to correlate with  $Ca^{2+}$  concentrations in the ice representative of mineral dust concentration. Accordingly, a firnification effect of dust on pore volume has been proposed (Hörhold et al., 2012), which should be most pronounced for stadial/interstadial variations, when dust concentrations in Greenland changed by  
320 a factor of about 15 (Fischer et al., 2007). As the  $TAC$  is a result of the competing process of densification and water vapour transport/recrystallization, also an influence of  $Ca^{2+}$  concentration on  $TAC$  could be hypothesized. In Fig. 8 the NGRIP  $TAC$ , dust and  $Ca^{2+}$  (Ruth, 2007),  $CH_4$  and  $\delta^{18}O_{ice}$  records are shown on the depth scale for selected DO events. No simple relation from  $TAC$  with the dust concentration can be observed. Moreover, the  $TAC$  variations on their depth scale are  
325 not in phase with dust and  $Ca^{2+}$  concentrations, as would be expected from a direct firnification effect of dust concentrations in the ice matrix on pore volume at bubble close-off. Instead, the high-frequency variations in  $TAC$  seem to change in parallel with  $CH_4$  and therefore on the gas age scale, suggesting a direct influence of temperature on the number of moles of air enclosed in the pore volume during bubble close-off. We will discuss this anti-correlation in the next section.

### 330 4.3.2 Relation to climate changes during DO events

The  $TAC$  data (Fig. 2) not only show low-frequency variations as discussed in section 4.1 but reveal a strong high-frequency signal. Making use of the unprecedented resolution of our record, we investigate the high-frequency variations and take a closer look on what happens to the  $TAC$  during DO events.

335 The temperature effect (Eq. (7)) on the pore volume created during steady-state densification would lead to a very small increase in pore volume with rising temperatures. Using the ideal gas law we obtain:

$$TAC = V_{\text{mol}} \cdot n = V_{\text{mol}} \cdot \frac{P_c \cdot V_c(T_s)}{R \cdot T_s} = \frac{P_c \cdot V_{\text{mol}}}{R} \cdot \left(0.76 - \frac{57\text{K}}{T_s}\right). \quad (11)$$

Where  $V_{\text{mol}}$  is the volume of one mol at STP,  $V_c(T)$  the pore volume at close off,  $R$  is the gas  
 340 constant ( $8.31 \text{ J mol}^{-1} \text{ kg}^{-1}$ ),  $T_s$  the snow temperature and  $n$  the number of moles of air enclosed in the bubbles. Therefore, a slight increase in  $TAC$  with increasing temperature is expected from the pore volume effect. However, the formula for pore volume changes, derived in Martinerie et al. (1992) based on steady-state Holocene conditions is most likely not applicable during DO events where a transient change in densification occurs. It is reasonable to assume that the pore volume in  
 345 the firm does not follow this temperature relationship (Eq. (7)) directly at the onsets of DO events. If we assume that the pore volume remains constant during the very first stage of a DO event, the first-order effect of slowly increasing temperatures in the firm would lead to a decrease in  $TAC$ , as supported by our data (Fig. 2). To test objectively whether there is a coherent pattern of decreasing  $TAC$  at the onset DO events, we developed a method to find significant  $TAC$  decreases. To remove  
 350 noise in the  $TAC$  raw data, 1000 Monte Carlo splines (varying the datapoints randomly within their error before calculating each spline fit) with a cut-off period of 750 years were calculated on the AICC2012 gas age scale, and the mean of the 1000 splines was taken as our best-guess representation of true  $TAC$  variations (Monte Carlo Average, MCA). This MCA-spline is then searched for maxima and minima. A detected minimum is considered significant if the difference between the  
 355 last maximum and the minimum is larger than 1.5 times the added standard deviation of the spline at both points. The result is shown in Fig. 9. With these criteria and parameters the routine finds 23 significant minima, out of which 17 are related to a DO event in  $\delta^{18}\text{O}_{\text{ice}}$ . The significant minima unassociated with a DO event occur at the onset of the Younger Dryas, two in the LGM and one during DO event 25. There is another one before DO event 24, which is due to a wiggle in the spline  
 360 fit, leading to two significant minima in the descent preceding DO event 24 (see Fig. 9). Using the above mentioned parameters, the routine fails to find significant minima related to DO events 8, 9, 16-18, 20, 22, 23 and 25, although, for many of these cases there exists a decline in  $TAC$ , which, however, did not satisfy our significance criterion. For DO events 9, 18 (and the event p18, in Fig. 9 regarded as a precursor event of DO event 18), 20, 23 and 25 this is due to the threshold of  $1.5 \sigma$   
 365 being too high, while 16-17 follow each other very closely so the  $TAC$  response signal is not visible. For DO event 22 the detected minimum is more than a thousand years before the  $\delta^{18}\text{O}_{\text{ice}}$  maximum, so we considered this not to be related to the warming. DO event 22 has a small amplitude in  $\delta^{18}\text{O}_{\text{ice}}$  compared to the background and the other DOs, thus only a small  $TAC$  response is expected. Apparently,  $TAC$  shows an anti-correlation not only to  $ISI$  but also to rapid DO warmings. Again  
 370 a comparison to the  $O_2/N_2$  ratios is of interest, since Suwa and Bender (2008) found not only a correlation of  $O_2/N_2$  to insolation, but as well a correlation of  $O_2/N_2$  ratios with DO warmings.

We speculate that both proxies are influenced by the same not yet fully understood firnification processes. Of interest is also the phasing of the  $TAC$  compared to the  $\delta^{18}O_{ice}$ . In table 4 the timing of the  $TAC$  minima on the AICC2012 gas age scale and the maxima in the rises of  $\delta^{18}O_{ice}$  on the  
375 AICC2012 ice age scale are shown. On average, the  $TAC$  minimum is synchronous to the  $\delta^{18}O_{ice}$  maximum within the error ( $12\pm 290$  yrs) on the AICC2012 age scale. However, as stated by Baumgartner et al. (2014), the AICC2012 gas age scale suffers from inconsistency with the AICC2012 ice age scale for several DO events as gas and ice have been synchronized between different ice cores to some extent independently. This leads to a dephasing of  $CH_4$  and  $\delta^{18}O_{ice}$  records in some cores  
380 on the AICC2012 age scale which is absent in the original age scales, where gas age scale has been determined by adding the gas age/ice age difference to the ice age scale. For this reason Kindler et al. (2014) published a new gas age scale for NGRIP, based on the ss09sea06bm (NGRIP Project Members, 2004) ice age scale, defined from 10 to 120 kyrs. Being aware of this inconsistency, we also derived the corresponding  $\delta^{18}O_{ice}$  maxima on ss09sea06bm ice age and the  $TAC$  spline minima  
385 on the gas age scale by Kindler et al. (2014). On those age scales the  $\delta^{18}O_{ice}$  maximum is reached on average  $111\pm 232$  yrs earlier than the minimum in  $TAC$  and only two DO events show the  $TAC$  minimum earlier than the  $\delta^{18}O_{ice}$  maximum. Neglecting DO 13, the  $\delta^{18}O_{ice}$  maximum leads  $TAC$  by  $162\pm 108$  yrs ( $37\pm 217$  yrs on the AICC2012 age scales). Due to the considerable analytical and small-scale scatter of our  $TAC$  data it is difficult to pinpoint the temporal evolution of the  $TAC$  and  
390 its phase relationship to other climate proxies in the ice core for individual DO events. Moreover, when comparing  $\delta^{18}O_{ice}$  in the ice matrix and a direct temperature related signal in  $TAC$ , the uncertainty in the ice age-gas age difference has to be taken into account. Therefore, in the following we compare the  $TAC$  behaviour to other proxies only on the same age scales.

To figure out how the  $TAC$  reacts in general to DO event warmings we calculated a stack of  $TAC$   
395 variations during DO events and compared it to other gas phase parameters. Since the  $TAC$  seems to react in the time window where also the  $CH_4$  shows changes, we stacked the  $TAC$  around the  $CH_4$  onsets. For this we defined a criterion for the rise in  $CH_4$ . The analytical error in the  $CH_4$  data is 5.9 ppbv (Baumgartner et al., 2014). The start of the  $CH_4$  increase was defined by Baumgartner et al. (2014) in the middle between the first two data points during the onset of stadial/interstadial transitions which did not agree anymore within their  $3\sigma$  uncertainty. We used the same definition and  
400 translated the depth values on the AICC2012 gas age scale. Additionally, we defined the onset for DO 3 and 22 by applying only a  $2\sigma$  criterion, since with  $3\sigma$ , no onset could be defined. These criteria give the onsets given in table 4, except for DO 2 and 25, for which the onset could not be defined. The same stacking analysis was performed for  $\delta^{15}N$  (Kindler et al., 2014) indicating temperature  
405 gradients across the firn column caused by rapid warming at the surface. The  $TAC$  [this study] and the  $\delta^{15}N$  time series from Kindler et al. (2014) were then cut out in age windows  $+400$  and  $-1000$  yrs around the DO onsets in  $CH_4$ . For each window we subtracted the mean value over this time span to remove the long-term trend in the data. Note that we neglected the temperature effect on pore vol-

ume as discussed in section 4.1, as this effect is small (Fig. 5) and does not occur in the gas itself but  
410 acts on the firm matrix. Due to gas age-ice age difference, the latter process is, therefore, not in phase  
with changes in temperature but affects  $TAC$  several hundred years later. The resulting data were  
then stacked and for each, the  $CH_4$ , the  $TAC$ , and  $\delta^{15}N$  data, a spline with a COP of 200yrs was  
calculated. The result is displayed in the left panel of Fig. 10. Relative to  $CH_4$ , the measured  $TAC$   
decrease starts around 100yrs earlier. Within the error,  $\delta^{15}N$  starts to increase synchronously with  
415  $TAC$ . This 100 year lag of  $CH_4$  to temperature is somewhat more than the  $25-70\pm 25$  yrs calculated  
for DO events in Marine Isotope Stage 3 in previous studies (Huber et al., 2006), and clearly more  
than the  $4.5^{+21}_{-24}$  yrs for the Bølling-Allerød (BA) calculated in Rosen et al. (2014). This difference  
may partly be attributed to the different methods used in the various publications to detect the onset  
in the  $CH_4$  rise, and/or may be specific to the BA warming. Note that the stacked  $TAC$  data show a  
420 two-step decrease that lasts over several hundred years. When the  $\delta^{15}N$  signal reaches its maximum,  
 $TAC$  is still decreasing; shortly before the  $\delta^{15}N$  stabilizes the  $TAC$  slightly rises and then drops in  
a second step to lower values than before the event.

The total amplitude of the  $TAC$  response in Fig. 10a is  $-4.7\pm 0.7$  mL kg<sup>-1</sup>. Using Eq. (1) with all  
parameters but the temperature fixed, we can calculate the expected physical  $TAC$  response accord-  
425 ing to the ideal gas law (Fig. 10b). The temperature influencing the  $TAC$  is the bubble close-off  
temperature, as derived by Kindler et al. (2014) using a heat transport model with the surface tem-  
perature determined by  $\delta^{15}N$  thermodiffusion thermometry. To get an average behaviour of bubble  
close-off temperature, we also stacked this modelled firm temperature at bubble close-off for the DO  
events in windows of +200 to -800 yrs relative to the onset in close-off temperature (see table 4). We  
430 then calculated the mean over 50 yrs intervals from +175 to -775 yr around the starting points of the  
temperature increase at bubble close-off (red points in Fig. 10b). The starting points were defined as  
the onset in bubble close-off temperature provided by (Kindler et al., 2014) on depth scale, translated  
to the AICC2012 ice age scale. With a starting temperature and  $TAC$  of 227.15 K and 90 mL kg<sup>-1</sup>,  
respectively, we computed the expected  $TAC$  response (blue crosses in Fig. 10b). Also shown in  
435 Fig. 10b are the measured  $TAC$  values on ice age scale for comparison with the modelled  $TAC$  and  
the temperature at the surface. The calculated amplitude of the direct temperature effect through the  
ideal gas law (number density of molecules per volume) at bubble close-off is 1.4 mL kg<sup>-1</sup>, which is  
only about a third of the measured one. The amplitude difference indicates that other effects than the  
temperature at bubble close-off influence  $TAC$  on short timescales and especially during the second  
440 step of the  $TAC$  decrease, where in situ gas temperature changes are already quite small.

One possibility to explain the larger  $TAC$  amplitude than expected from the direct temperature  
effect, could be co-occurring changes in surface pressure, for example related to synoptic pressure  
pattern changes related to DO events. To explain the full amplitude in DO event  $TAC$  changes, how-  
ever, a pressure decrease at the NGRIP site of around 17 hPa would be required during interstadial  
445 warmings, potentially related to a northward shift of North Atlantic storm tracks (Kageyama et al.,

2009) connected to a drastic reduction of sea ice during DO events which would also lead to a lowering of synoptic pressure over Greenland (Zhang et al.). However, compared to currently observed spatial gradients in mean annual sea level pressure over the North Atlantic the size of this effect appears too large and, moreover, should occur synchronously to the onset of the DO events, thus is unlikely to explain the  $TAC$  changes in later stages of the DO events. In contrast a transient effect of changes in firnification, hence pore volume, during Greenland interstadials appears more likely to explain our observations. We suggest that such an effect can be induced by the rapidly increasing accumulation rate at the onset of the DO event. This leads to a higher load and thus enhanced deformation of the snow grains at depth at a time when the temperature in the firn column is still cold. A simple transient firnification model experiment (section 4.3.3) supports this hypothesis by reducing  $TAC$  by several  $\text{mL kg}^{-1}$  as in our observations. In the following we attempt to quantify an upper limit of this transient firnification effect using a standard firnification model (Schwander et al., 1997).

#### 4.3.3 Transient firnification model experiment

Empirical equations for estimating bubble close-off densities and bubble close-off depths have been derived for steady-state conditions (Martinerie et al. (1992), Martinerie et al. (1994)). However, especially at the beginning of a DO event the firn layer is far from being in a steady state condition. Fast artificial densification experiments of snow by applying high pressures resulted in very low  $TAC$  compared to natural firnification (*B. Stauffer, pers. comm.*). The reason for low  $TAC$  in artificially densified ice is most likely that, due to the extremely high densification rate, there is not enough time to form spherical cavities, which are a result of minimizing surface energy by slow mass redeposition through vapor diffusion. At the beginning of a DO event, accumulation increases in a step-like fashion, causing (less drastically but analogous to the artificial experiments) additional pressure in the bubble close-off zone by the increasing load of snow. We therefore expect a pore volume reduction and expulsion of air from the firn, yielding to lower  $TAC$  compared to steady-state conditions. We estimate the upper limit of this effect by assuming that for some 140 annual layers above the firn-ice transition in the firnification model the time required to reach bubble close-off remains unchanged after a transition into a DO event. This assumption is based on the fact that the temperature at the depth of bubble close-off remains near the cold state during the first 140 years of a DO event (less than 20% temperature response compared to the surface temperature change, Fig. 10) and on the hypothesis that time is more important for finalizing the bubble close-off than the additional hydrostatic pressure.

We have used a standard dynamic firn densification model (Schwander et al., 1997) to calculate this upper limit for a typical DO event. In addition to computing the time and depth where the steady-state close-off density is reached (as in the normal usage of the model) the model provides the density that a firn layer reaches after a certain number of years. This number of years was set to the duration

needed to reach close-off under interstadial conditions. Under the above mentioned assumption of an initially constant duration to reach close-off, this density reflects the true close-off density and corresponding  $TAC$  better than values obtained for steady-state stadial conditions. Stadial temperature is set to  $-46^{\circ}\text{C}$  and ice accumulation rate to  $0.05\text{ m a}^{-1}$ . At the beginning of the simulated DO event we increase the temperature from  $-46^{\circ}\text{C}$  to  $-36^{\circ}\text{C}$  and the ice accumulation rate from  $0.05\text{ m a}^{-1}$  to  $0.1\text{ m a}^{-1}$  within 100 years, based on the model data by Kindler et al. (2014). The resulting  $TAC$  of the simulation is shown in Fig. 11. We interpret the resulting decrease in  $TAC$  as the upper limit scenario for the first 140 years of a DO event. The real effect might be smaller. Later, when the temperature at the firn-ice transition increases further,  $TAC$  will slowly approach the new equilibrium value. As there exists no physical model describing this dynamic behavior of densification and bubble close-off to date, we cannot provide a more precise modeled evolution of  $TAC$  during a DO event, but the decrease in  $TAC$  as observed in the NGRIP ice core seems to be compatible with the simulation.

## 5 Conclusions

We present the first high-resolution  $TAC$  record from the Greenland NGRIP ice core covering the last 120 kyr. In line with previous studies in Antarctica (Raynaud et al. (2007), Lipenkov et al. (2011)) we find the low-frequency variations to depend on local summer insolation and thus the orbital parameters. Those effects act on the firn matrix controlling the pore volume during bubble close-off and, thus, operate on the ice age scale, (e.g. Raynaud et al. (2007), Bender (2002)), although the underlying processes are not yet understood. Additionally, in steady-state, the pore volume is known to correlate with firn temperature (Martinerie et al., 1992), which is also an ice property leading to  $TAC$  changes. Our study shows that this temperature effect imprinted on pore volume during densification in steady-state is small compared to the insolation effect operating at the surface, and also small compared to a direct temperature effect on  $TAC$  imposed by the change in density of the gas during bubble enclosure that we clearly observe during DO events.

Comparison of  $\delta^{15}\text{N}$ ,  $\text{CH}_4$  and  $TAC$ , all on the gas age scale, provides evidence that surface temperature warming, or an effect synchronous to surface warming, has a direct imprint on the  $TAC$ . The immediate decrease in  $TAC$  at an onset of a DO event could have two possible sources according to the ideal gas law: decreasing air pressure or less amount of substance per volume due to rising temperature. However, both effects appear to be too small to explain the measured  $TAC$  decline. Large changes in the height of the ice sheet are ruled out for such very short-term variations as the  $TAC$  change occurs immediately with the DO event warming, while the ice sheet response would be slow and delayed. However, the increasing accumulation rate during DO events leads to an increase in firn thickness of several tens of meters, which, through the additional weight on the firn column, leads to a temporarily enhanced densification. This could reduce  $TAC$  for several centuries

after the onset of the DO event. After 500-1000 yrs, the firm column reaches a new equilibrium with ambient temperature, accumulation and pore volume, and  $TAC$  reaches again its steady-state value. With the  $TAC$  signal being influenced by effects on the ice age and gas age scale, this also limits the precision of deriving orbital timescales from  $TAC$  for Greenland ice cores which experience the rapid millennial scale DO variability which is absent for Antarctic ice cores.

*Acknowledgements.* Continuing support by the Swiss National Science Foundation for ice core research at the University of Bern is gratefully acknowledged. NGRIP is coordinated by the Department of Geophysics at the Niels Bohr Institute for Astronomy, Physics and Geophysics, University of Copenhagen. It is supported by Funding Agencies in Denmark (SHF), Belgium (FNRS-CFB), France (IPEV and INSU/CNRS), Germany (AWI), Iceland (RannIs), Japan (MEXT), Sweden (SPRS), Switzerland (SNF) and the United States of America (NSF, Office of Polar Programs). We thank J. Freitag for fruitful discussion on firnification and bubble enclosure processes.



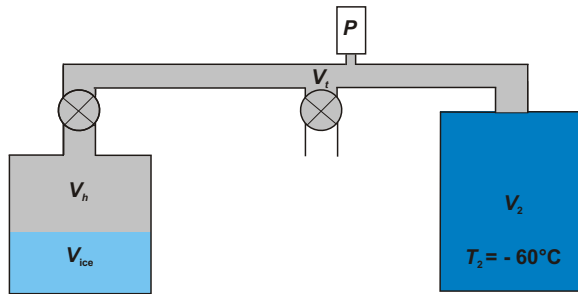
## References

- 530 Baumgartner, M.: Bipolar reconstructions of atmospheric methane and nitrous oxide during the last glacial-interglacial cycle, Ph.d. thesis, Physics Institute, University of Bern, Switzerland, 194 pp., 2013.
- Baumgartner, M., Schilt, A., Eicher, O., Schmitt, J., Schwander, J., Spahni, R., Fischer, H., and Stocker, T. F.: High-resolution inter-polar difference of atmospheric methane around the Last Glacial Maximum, *Biogeosciences*, 9, 3961–3977, doi:10.5194/bg-9-3961-2012, <http://www.biogeosciences.net/9/3961/2012/>, 2012.
- 535 Baumgartner, M., Kindler, P., Eicher, O., Floch, G., Schilt, A., Schwander, J., Spahni, R., Capron, E., Chappellaz, J., Leuenberger, M., Fischer, H., and Stocker, T. F.: NGRIP CH<sub>4</sub> concentration from 120 to 10 kyr before present and its relation to a  $\delta^{15}\text{N}$  temperature reconstruction from the same ice core, *Climate of the Past*, 10, 903–920, doi:10.5194/cp-10-903-2014, <http://www.clim-past.net/10/903/2014/>, 2014.
- Bender, M. L.: Orbital tuning chronology for the Vostok climate record supported by trapped gas composition, *Earth and Planetary Science Letters*, pp. 275–289, 2002.
- 540 Born, A. and Nisancioglu, K. H.: Melting of Northern Greenland during the last interglaciation, *The Cryosphere*, 6, 1239–1250, doi:10.5194/tc-6-1239-2012, <http://www.the-cryosphere.net/6/1239/2012/>, 2012.
- Dahl-Jensen, D., Gundestrup, N., Keller, K., Johnsen, S., Gogineni, S., Allen, C., Chuah, C., Miller, H., Kipfstuhl, S., and Waddington, E.: A search in north Greenland for a new ice-core drill site, *Journal of Glaciology*, pp. 300–306, 1997.
- 545 Enting, I. G.: On the Use of Smoothing Splines to Filter CO<sub>2</sub> Data, *JGR*, 92, 10977–10984, 1987.
- Fischer, H., Siggaard-Andersen, M.-L., Ruth, U., Röthlisberger, R., and Wolff, E.: Glacial/interglacial changes in mineral dust and sea-salt records in polar ice cores: Sources, transport, and deposition, *Reviews of Geophysics*, 45, n/a–n/a, doi:10.1029/2005RG000192, <http://dx.doi.org/10.1029/2005RG000192>, rG1002, 2007.
- 550 Flückiger, J., Blunier, T., Stauffer, B., Chappellaz, J., Spahni, R., Kawamura, K., Schwander, J., Stocker, T., and Dahl-Jensen, D.: N<sub>2</sub>O and CH<sub>4</sub> variations during the last glacial epoch: Insight into global processes, *Global Biogeochem. Cycles*, 18, 10.29/2004GB002122, 14 pp., 2004.
- Freitag, J., Kipfstuhl, S., Laepple, T., and Wilhelms, F.: Impurity-controlled densification: a new model for stratified polar firn, *Journal of Glaciology*, 59, 1163–1169, doi:10.3189/2013JG13J042, <http://www.igsoc.org/journal/59/218/j13J042.html>, 2013.
- 555 Grinsted, A., Moore, J. C., and Jevrejeva, S.: Application of the cross wavelet transform and wavelet coherence to geophysical time series, *Nonlinear Processes in Geophysics*, 11, 561–566, doi:10.5194/npg-11-561-2004, <http://www.nonlin-processes-geophys.net/11/561/2004/>, 2004.
- Hörhold, M., Laepple, T., Freitag, J., Bigler, M., Fischer, H., and Kipfstuhl, S.: On the impact of impurities on the densification of polar firn, *Earth and Planetary Science Letters*, 325–326, 93–99, doi:<http://dx.doi.org/10.1016/j.epsl.2011.12.022>, <http://www.sciencedirect.com/science/article/pii/S0012821X11007424>, 2012.
- 560 Huber, C., Leuenberger, M., Spahni, R., Flückiger, J., Schwander, J., Stocker, T. F., Johnsen, S., Landais, A., and Jouzel, J.: Isotope calibrated Greenland temperature record over Marine Isotope Stage 3 and its relation to CH<sub>4</sub>, 243, 504–519, 2006.
- 565 Hutterli, M., Schneebeli, M., Freitag, J., Kipfstuhl, J., and Röthlisberger, R.: Impact of local insolation on snow metamorphism and ice core records, *Low Temperature Science*, pp. 223–232, 2009.

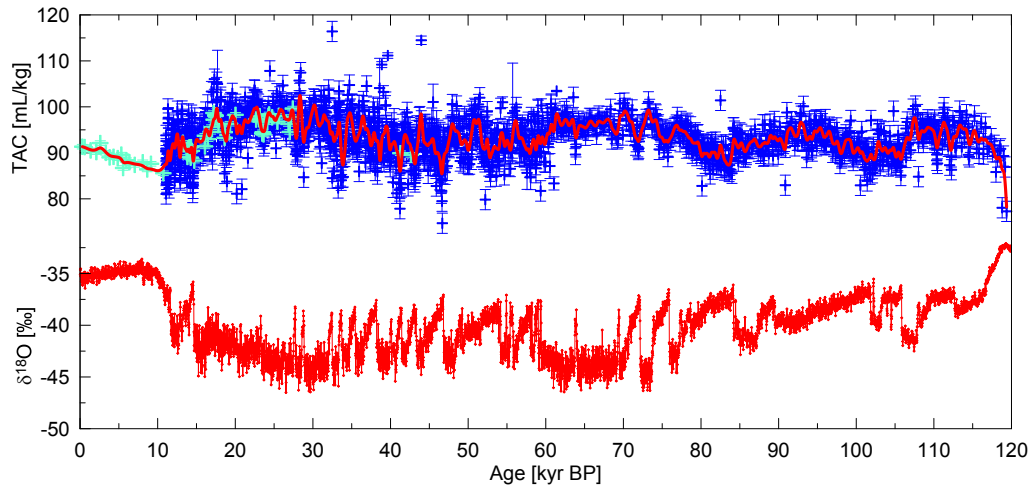
- Kageyama, M., Mignot, J., Swingedouw, D., Marzin, C., Alkama, R., and Marti, O.: Glacial climate sensitivity to different states of the Atlantic Meridional Overturning Circulation: results from the IPSL model, *Climate of the Past*, 5, 551–570, doi:10.5194/cp-5-551-2009, <http://www.clim-past.net/5/551/2009/>, 2009.
- Kindler, P., Guillevic, M., Baumgartner, M., Schwander, J., Landais, A., and Leuenberger, M.: NGRIP temperature reconstruction from 10 to 120 kyr b2k from NGRIP ice core, *Climate of the Past Discussions*, 10, 887–902, doi:10.5194/cpd-9-4099-2013, <http://www.clim-past-discuss.net/9/4099/2013/>, 2014.
- Krinner, G., Raynaud, D., Doutriaux, C., and Dang, H.: Simulations of the Last Glacial Maximum ice sheet surface climate: Implications for the interpretation of ice core air content, *Journal of Geophysical Research: Atmospheres*, 105, 2059–2070, 2000.
- Landais, A., Masson-Delmotte, V., Capron, E., Langebroek, P. M., Bakker, P., Stone, E. J., Merz, N., Raible, C. C., Fischer, H., Orsi, A., Prié, F., Vinther, B., and Dahl-Jensen, D.: How warm was Greenland during the last interglacial period?, *Climate of the Past Discussions*, 2016, 1–27, doi:10.5194/cp-2016-28, <http://www.clim-past-discuss.net/cp-2016-28/>, 2016.
- Lang, C., Leuenberger, M., Schwander, J., and Johnsen, S.: 16°C Rapid Temperature Variation in Central Greenland 70,000 Years Ago, *Science*, 286, 934–937, doi:10.1126/science.286.5441.934, <http://www.sciencemag.org/content/286/5441/934.abstract>, 1999.
- Lipenkov, V., Raynaud, D., Loutre, M., and Duval, P.: On the potential of coupling air content and O<sub>2</sub>/N<sub>2</sub> from trapped air for establishing an ice core chronology tuned on local insolation, *Quaternary Science Reviews*, 30, 3280 – 3289, 2011.
- Lorius, C., Raynaud, D., and Dolle, L.: Densité de la glace et Étude des gaz en profondeur dans un glacier antarctique, *Tellus*, 20, 449–460, 1968.
- Martinerie, P., Raynaud, D., Etheridge, D. M., Barnola, J. M., and Mazaudier, D.: Physical and climatic parameters which influence the air content in polar ice, *Earth and Planetary Science Letters*, 112, 1–13, 1992.
- Martinerie, P., Lipenkov, V. Y., Raynaud, D., Chappellaz, J., Barkov, N. I., and Lorius, C.: Air content paleo record in the Vostok ice core (Antarctica): A mixed record of climatic and glaciological parameters, *J. Geophys. Res.*, 99, 10 565–10 576, 1994.
- NEEM community members: Eemian interglacial reconstructed from a Greenland folded ice core, *Nature*, 493, 489–494, doi:10.1038/nature11789, <http://dx.doi.org/10.1038/nature11789>, 2013.
- NGRIP Project Members: High-resolution record of Northern Hemisphere climate extending into the last interglacial period, *NATURE*, 431, 147–151, doi:10.1038/nature02805, 2004.
- Parrenin, F., Barnola, J.-M., Beer, J., Blunier, T., Castellano, E., Chappellaz, J., Dreyfus, G., Fischer, H., Fujita, S., Jouzel, J., Kawamura, K., Lemieux-Dudon, B., Loulergue, L., Masson-Delmotte, V., Narcisi, B., Petit, J.-R., Raisbeck, G., Raynaud, D., Ruth, U., Schwander, J., Severi, M., Spahni, R., Steffensen, J. P., Svensson, A., Udisti, R., Waelbroeck, C., and Wolff, E.: The EDC3 chronology for the EPICA Dome C ice core, *Climate of the Past*, 3, 485–497, doi:10.5194/cp-3-485-2007, <http://www.clim-past.net/3/485/2007/>, 2007.
- Raynaud, D. and Lebel, B.: Total gas content and surface elevation of polar ice sheets, *Nature*, 281, 289–291, 1979.
- Raynaud, D. and Lorius, C.: Climatic implications of Total Gas Content in Ice at Camp Century, *Nature*, 243, 283–284, 1973.

- Raynaud, D., Chappellaz, J., Ritz, C., and Martinerie, P.: Air content along the Greenland Ice Core Project core: A record of surface climatic parameters and elevation in Central Greenland, *J. Geophys. Res.*, 102, 26 607–26 613, 1997.
- 610 Raynaud, D., Lipenkov, V., Lemieux-Dudon, B., Duval, P., Loutre, M.-F., and Lhomme, N.: The local insolation signature of air content in Antarctic ice. A new step toward an absolute dating of ice records, *Earth and Planetary Science Letters*, 261, 337 – 349, doi:<http://dx.doi.org/10.1016/j.epsl.2007.06.025>, <http://www.sciencedirect.com/science/article/pii/S0012821X0700413X>, 2007.
- Rosen, J. L., Brook, E. J., Severinghaus, J. P., Blunier, T., Mitchell, L. E., Lee, J. E., Edwards, J. S., and  
615 Gkinis, V.: An ice core record of near-synchronous global climate changes at the Bolling transition, *Nature Geoscience*, 7, 459–463, doi:10.1038/ngeo2147, <GotoISI>://WOS:000337164400019, n/a, 2014.
- Ruth, U.: Dust concentration in the NGRIP ice core, doi:10.1594/PANGAEA.587836, <http://doi.pangaea.de/10.1594/PANGAEA.587836>, supplement to: Ruth, Urs; Bigler, Matthias; Röthlisberger, Regine; Siggaard-Andersen, Marie-Louise; Kipfstuhl, Josef; Goto-Azuma, Kumiko; Hansson, Margareta E; Johnsen, Sigfus J;  
620 Lu, Huayu; Steffensen, Jörgen Peder (2007): Ice core evidence for a very tight link between North Atlantic and east Asian glacial climate. *Geophysical Research Letters*, 34, L03706, doi:10.1029/2006GL027876, 2007.
- Schilt, A., Baumgartner, M., Schwander, J., Buiron, D., Capron, E., Chappellaz, J., Loulergue, L., Schüpbach, S., Spahni, R., Fischer, H., and Stocker, T. F.: Atmospheric nitrous oxide during the last 140,000 years, *Earth and Planetary Science Letters*, 300, 33–43, 2010.  
625
- Schilt, A., Baumgartner, M., Eicher, O., Chappellaz, J., Schwander, J., Fischer, H., and Stocker, T.: The response of atmospheric nitrous oxide to climate variations during the last glacial period, *Geophysical Research Letters*, 40, 1888–1893, doi:10.1002/grl.50380, <http://dx.doi.org/10.1002/grl.50380>, 2013.
- Schmitt, J., Schneider, R., and Fischer, H.: A sublimation technique for high-precision measurements of  $\delta^{13}\text{CO}_2$  and mixing ratios of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  from air trapped in ice cores, *Atmospheric Measurement Techniques*, 4, 1445–1461, doi:10.5194/amt-4-1445-2011, <http://www.atmos-meas-tech.net/4/1445/2011/>, 2011.  
630
- Schmitt, J., Seth, B., Bock, M., and Fischer, H.: Online technique for isotope and mixing ratios of  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , Xe and mixing ratios of organic trace gases on a single ice core sample, *Atmospheric Measurement Techniques*, 7, 2645–2665, doi:10.5194/amt-7-2645-2014, <http://www.atmos-meas-tech.net/7/2645/2014/>, 2014.
- 635 Schwander, J., Sowers, T., Barnola, J. M., Blunier, T., Malaizé, B., and Fuchs, A.: Age scale of the air in the Summit ice: Implication for glacial-interglacial temperature change, *J. Geophys. Res.*, 102, 19 483–19 494, 1997.
- Seierstad, I. K., Abbott, P. M., Bigler, M., Blunier, T., Bourne, A. J., Brook, E., Buchardt, S. L., Buizert, C., Clausen, H. B., Cook, E., Dahl-Jensen, D., Davies, S. M., Guillevic, M., Johnsen, S. J., Pedersen, D. S.,  
640 Popp, T. J., Rasmussen, S. O., Severinghaus, J. P., Svensson, A., and Vinther, B. M.: Consistently dated records from the Greenland GRIP, GISP2 and NGRIP ice cores for the past 104 ka reveal regional millennial-scale delta O-18 gradients with possible Heinrich event imprint, *Quaternary Science Reviews*, 106, 29–46, doi:10.1016/j.quascirev.2014.10.032, <GotoISI>://WOS:000348010900003, n/a, 2014.
- Severinghaus, J. P. and Brook, E. J.: Abrupt Climate Change at the End of the Last Glacial Period Inferred from Trapped Air in Polar Ice, *Science*, 286, 930–934, doi:10.1126/science.286.5441.930, <http://www.sciencemag.org/content/286/5441/930.abstract>, 1999.  
645

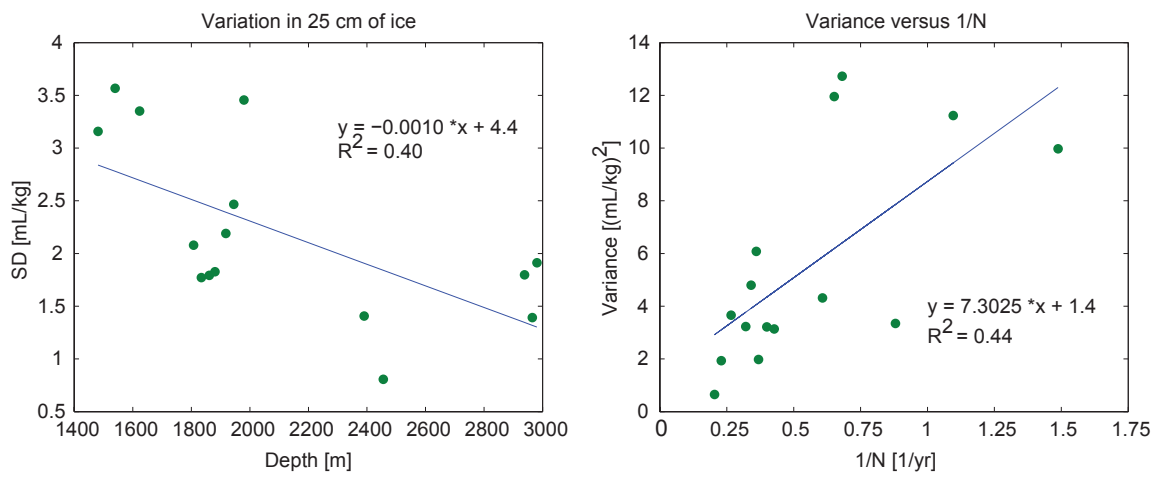
- Suwa, M. and Bender, M. L.: O<sub>2</sub>/N<sub>2</sub> ratios of occluded air in the GISP2 ice core, *Journal of Geophysical Research: Atmospheres*, 113, doi:10.1029/2007JD009589, <http://dx.doi.org/10.1029/2007JD009589>, d11119, 2008.
- 650 Veres, D., Bazin, L., Landais, A., Toyé Mahamadou Kele, H., Lemieux-Dudon, B., Parrenin, F., Martinerie, P., Blayo, E., Blunier, T., Capron, E., Chappellaz, J., Rasmussen, S. O., Severi, M., Svensson, A., Vinther, B., and Wolff, E. W.: The Antarctic ice core chronology (AICC2012): an optimized multi-parameter and multi-site dating approach for the last 120 thousand years, *Climate of the Past*, 9, 1733–1748, doi:10.5194/cp-9-1733-2013, <http://www.clim-past.net/9/1733/2013/>, 2013.
- 655 Zhang, X., Lohmann, G., Knorr, G., and Purcell, C.: Abrupt glacial climate shifts controlled by ice sheet changes, *Nature*, 512, 290–294.



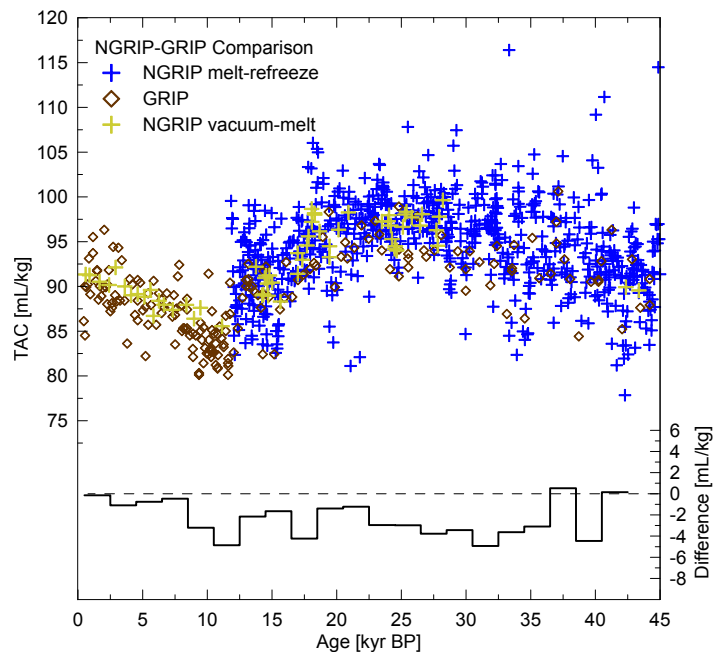
**Figure 1.** Scheme of the volumes involved in the  $TAC$  measurements. The gas from the refrozen melt water in the vessel on the left is confined in the headspace volume  $V_h$ . It is then expanded in the Volume  $V_{exp} = V_1 + V_2 = V_h + V_t + V_2$ . The temperature  $T_2$  in  $V_2$  is held at  $-60^\circ\text{C}$ .



**Figure 2.** The NGRIP  $TAC$  record of this study on the AICC2012 gas age scale (Veres et al., 2013), using two different methods. In blue the melt-refreeze data, in turquoise the vacuum-melt  $TAC$ . The red line represents a spline with a 750 yr cut-off period, according to Enting (1987). At the bottom, the  $\delta^{18}O_{ice}$  for the NGRIP ice core (NGRIP Project Members, 2004) is given.

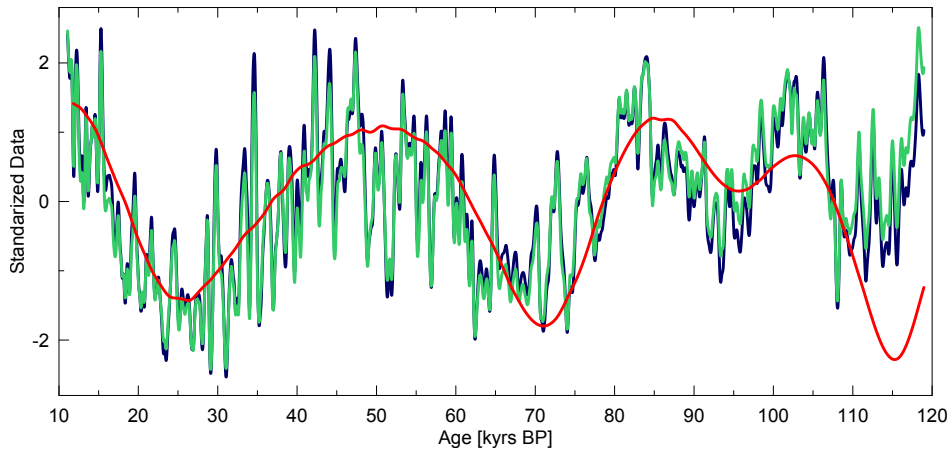


**Figure 3.** Left: Standard deviation of reproducibility measurements in the *TAC* dependent on depth. Each point represents the mean over 5 adjacent samples. As expected, the variations get smaller with the smoothing due to thinner annual layers. Right: The variation of the reproducibility measurements versus  $1/N$ , where  $N$  is the number of annual cycles in the sample.

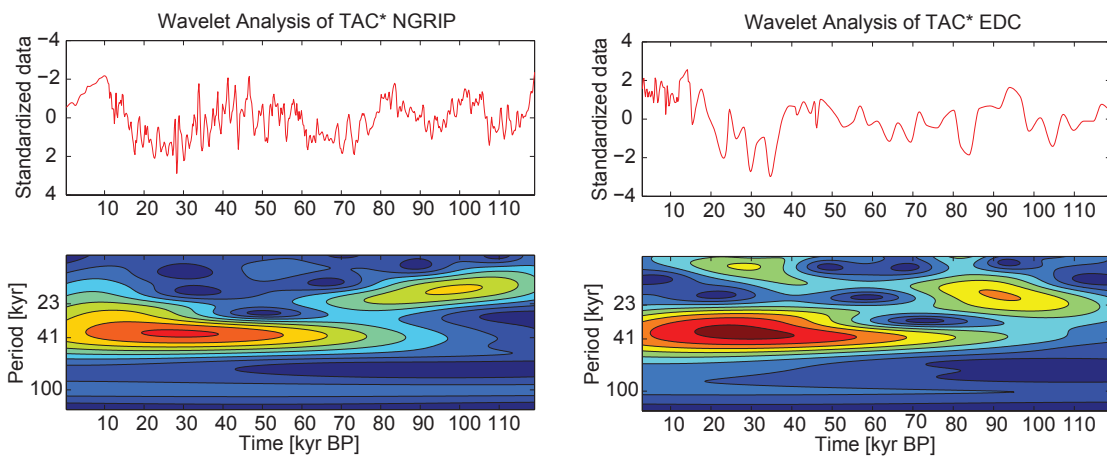


**Figure 4.** GRIP *TAC* data (Raynaud et al., 1997) in brown, vacuum-melt *TAC* data in yellow, melt-refreeze *TAC* data in blue. All data on the synchronized ice age scale for GRIP and NGRIP, according to Seierstad et al. (2014). The black curve at the bottom represents the difference between GRIP and NGRIP *TAC* data in 2 kyr intervals.

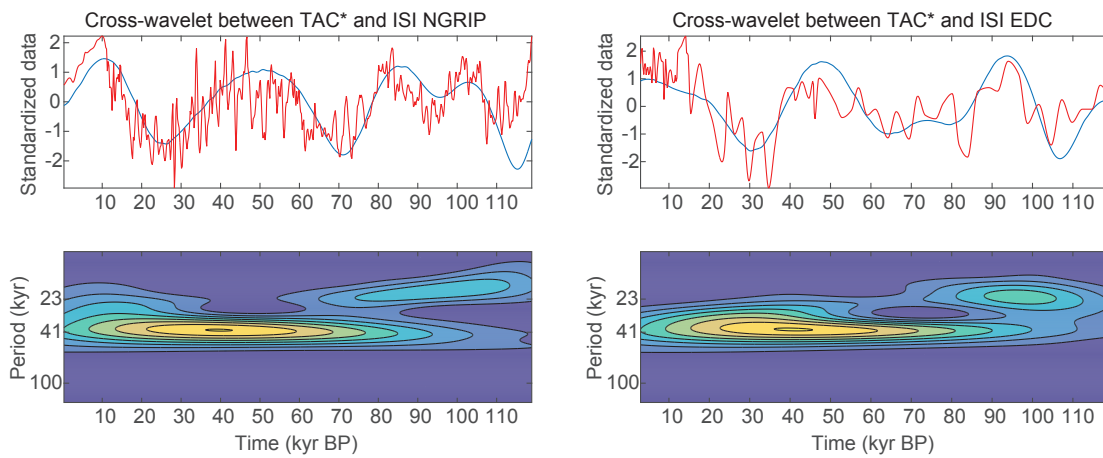




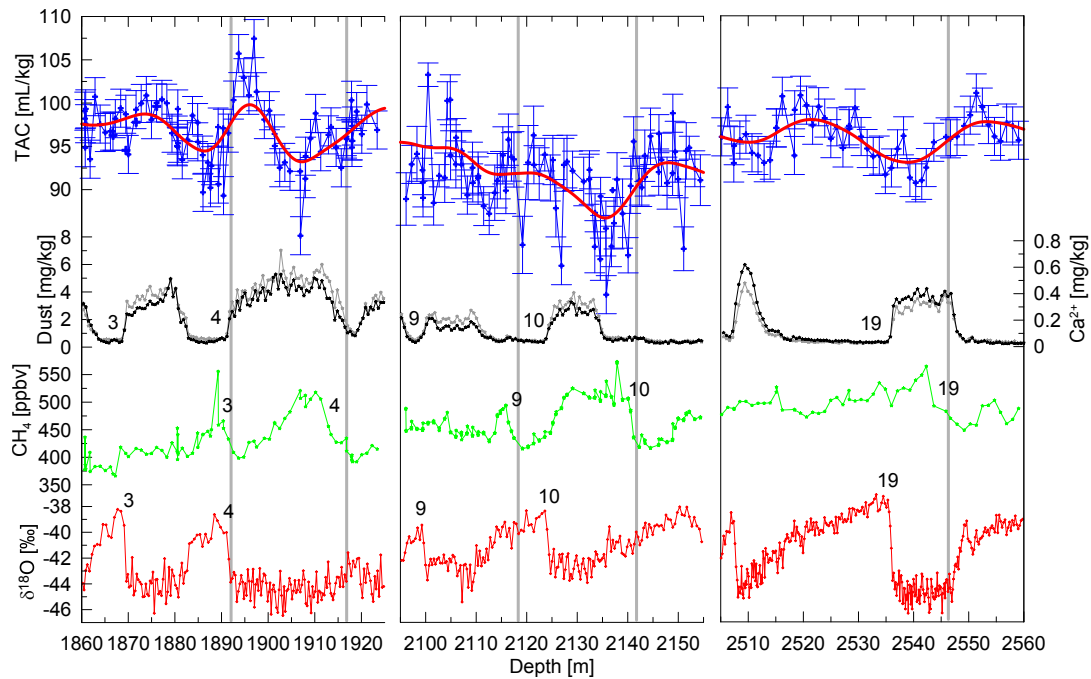
**Figure 5.** In red the standardized  $75.1^{\circ}\text{N}$  integrated summer insolation  $sISI$  on days with more than  $390\text{ W m}^{-2}$ , splined with a 3 kyr cut-off period. In blue a standardized spline with a 750- year cut-off of the  $TAC^*$  record. In green, analogous to Raynaud et al. (2007) the  $TAC^*$  data after correcting for the temperature effect on pore volume  $V_{cr}$  (Martinerie et al., 1992). Note that the ice core data are given on the glaciological AICC2012 ice age scale (as solar insolation acts on the snow matrix and therefore on changes in  $TAC$  on the ice age scale), while  $ISI$  is on the absolute astronomical age scale.



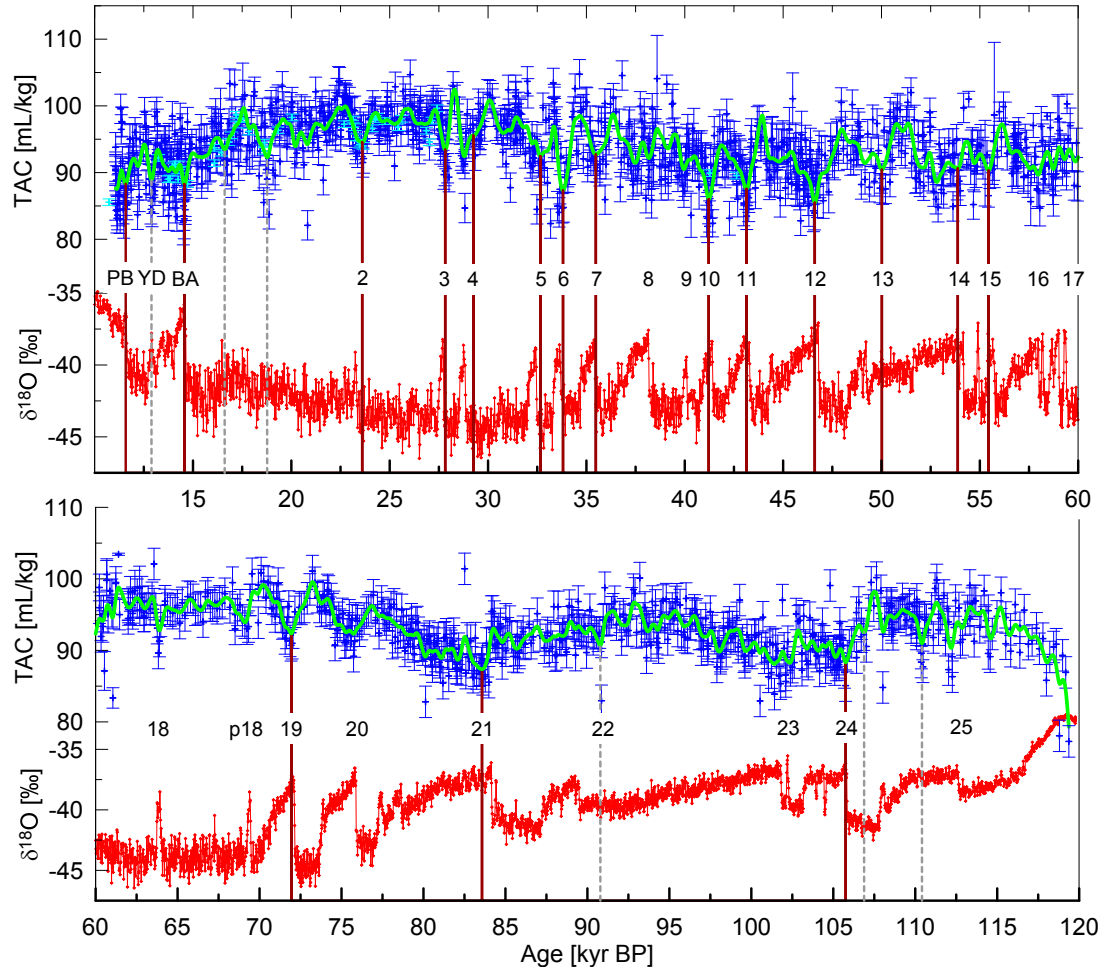
**Figure 6.** Left: The  $TAC^*$  data in red, re-sampled at an age step of 0.2 kyr and wavelet analysis of this spline. Right: EDC  $TAC^*$  data (Raynaud et al., 2007), re-sampled at 0.2 kyr and its wavelet analysis in the same time window.



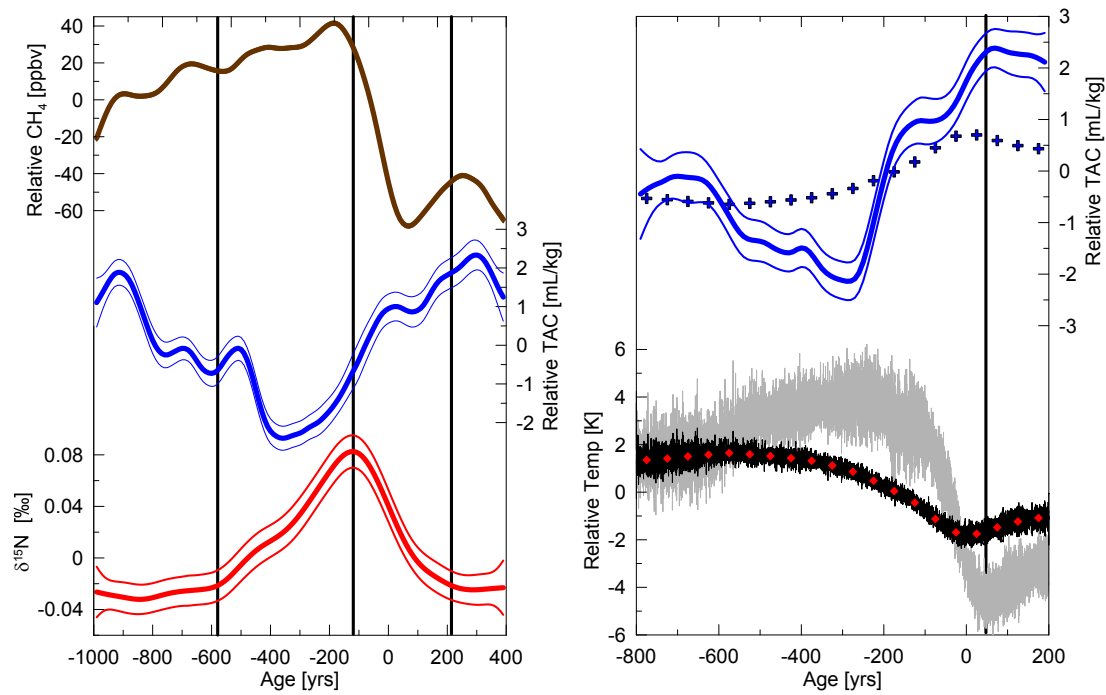
**Figure 7.** Left: The  $TAC^*$  data, re-sampled at 0.2 kyr in red,  $sISI$  with a threshold of  $390 \text{ W m}^{-2}$  in blue, splined with a 3 kyr cut-off period, and cross-wavelet analysis thereof. Both records show coherence in the obliquity and precession bands. Right: EDC  $TAC^*$  (Raynaud et al., 2007) re-sampled at 0.2 kyr,  $sISI$  ( $75.1^\circ \text{ S}$ ) with a threshold of  $380 \text{ W m}^{-2}$  and cross-wavelet analysis of the EDC and  $sISI$



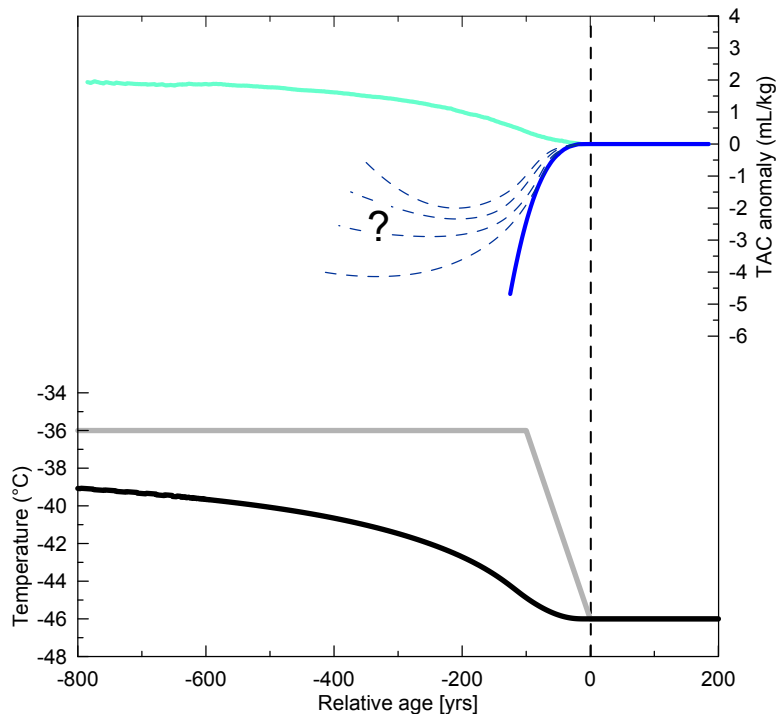
**Figure 8.** Zoom into DO events 3&4, 9&10 and 19 on depth scale. In blue the *TAC*, including a spline with a 120 m cut-off (thick red line). In black the dust and in grey the  $\text{Ca}^{2+}$  concentration (Ruth, 2007). In green the  $\text{CH}_4$  and in red the  $\delta^{18}\text{O}_{\text{ice}}$ . Grey lines indicate the beginning of the DO events in  $\text{CH}_4$ . More on the timing of *TAC* changes in section 4.3.2 and in Fig. 9 and 10



**Figure 9.** The significant minima in the  $TAC$  spline with 750yr cut-off from 10 to 120kyr BP. The measured  $TAC$  on AICC2012 gas age scale in blue, the spline in green. Minima marked by ruby lines are considered significant by the algorithm described in the text, while significant minima without a close-by DO event are indicated by grey, dashed lines. In red the  $\delta^{18}O_{ice}$  on the AICC2012 ice age scale.



**Figure 10.** Stacked data over the onsets of all DO events except DO event 2 and 25 (Table 4). Left: In red the stacked  $\delta^{15}\text{N}$  model data (Kindler et al., 2014), in blue the  $TAC$  and in brown the  $\text{CH}_4$ . Full lines represent the spline, thin lines the  $1\sigma$  error range. Note that the variability in the stacked concentration only refers to the analytical error and not the variability between different DO events. Grey lines indicate the start, the maximum and the end of the  $\delta^{15}\text{N}$  signal. All three on AICC2012 gas age scale. Right: Running mean over the modelled bubble close-off temperature (Kindler et al., 2014) in black, red squares indicate a 50 year mean. In grey the modelled surface temperature. Blue crosses represent the calculated  $TAC$  values dependent on bubble close-off temperature only. The blue lines represent the measured  $TAC$  on ice age scale. Note that the amplitude of the  $TAC$  response differs for the left and right plot, since the stack was established on a different age scale and thus not over the same time windows and with different starting points. The grey line indicates the onset of the surface temperature warming.



**Figure 11.** Modelled behaviour of  $TAC$  for an idealised DO event with a  $10\text{ }^{\circ}\text{C}$  linear surface warming during 100 yrs after the onset of the event. At the bottom, in grey, the assumed surface temperature and in black the temperature at bubble close-off depth. On top, in turquoise the  $TAC$  model output for steady-state firnification conditions (Eq. (11)). In blue the transient firnification model (Schwander et al., 1997)  $TAC$  output for a constant bubble-close-off time. Dashed lines indicate the range of measured  $TAC$  anomalies.

**Table 1.** List of abbreviations used, in order of appearance

Abbreviation(s)	Denotation
$TAC$	Total air content (in literature also called $V$ )
$V_c, P_c, T_c$	Volume, pressure and temperature at close-off
$P_0, T_0$	Standard pressure and temperature
$m$	Mass of the ice sample
$n$	Mole number
$V_2$	Volume of the sampling loop
$V_1, V_h, V_t$	Volumes in the apparatus, with $V_1=V_h+V_t$ and $h$ for headspace, $t$ for transition
$T_1, T_2$	The temperature in the above mentioned volumes $V_1$ and $V_2$
$ISI, sISI$	Integrated summer insolation, standardized $ISI$
$V_{cr}$	Non-thermal residual term of the pore volume
$TAC^*$	$-\frac{TAC-\overline{TAC}}{\sigma(TAC)}$
$V_{cr}^*$	$-\frac{V_{cr}-\overline{V_{cr}}}{\sigma(V_{cr})}$
$V_{mol}$	The volume of one mol at STP

**Table 2.** Table with the offsets between the data from different measuring periods. The second number in the intervals column is the reference period. Offset values are the median of all data points compared. The given error is the standard error.  $n$  is the number of points compared. Av. age offset denotes the average difference to the closer endpoint of the interpolation interval. The 2010 data could not be compared directly to 2012, so the offset values in the table are calculated from the other offsets.

Intervals [yrs]	Offset [mL kg <sup>-1</sup> ]	$n$	Av. age offset [yrs]
2004 & 2012	-6.1±0.6	33	196
2002 & 2012	-3.4± 2.1	24	348
2010 & 2011	3.16± 0.9	37	47
2012 & 2011	-2.0± 1.1	24	344
2010 & 2012	1.2± 1.4	-	-



**Table 3.** Table with the squared correlation coefficients between data and calculated parameters  $TAC^*$ ,  $sISI$ ,  $V_{cr}^*$  and  $T_c$ .

	$TAC^*$	$sISI$	$V_{cr}^*$	$T_c$
$TAC^*$	-	0.31	0.95	0.26
$sISI$	0.31	-	0.24	0.01

**Table 4.** Timing of the DO events and related features. The time value in  $\delta^{18}\text{O}_{\text{ice}}$  denotes the maximum of the rise in  $\delta^{18}\text{O}_{\text{ice}}$  on the AICC2012 ice age scale, defined by eye. The time point in  $TAC$  is the time of the minimum, found with the method described in section 4.3.2. On average the  $\delta^{18}\text{O}_{\text{ice}}$  rise is younger by  $-12\pm 290$  yrs with a median of  $-10$  yrs on the AICC2012 age scale. The corresponding values on the sso9sea06bm ice age scale and the gas age scale published by Kindler et al. (2014) are also shown in the second block of the table. On average the  $\delta^{18}\text{O}_{\text{ice}}$  rise is older by  $111\pm 233$  yrs with a median of  $140$  yrs on this age scales. The third block shows the timing of the onset in  $\text{CH}_4$  used for the stacking in Fig. 10a, on the AICC2012 gas age scale (Veres et al., 2013). In the forth block, the onsets in bubble close-off temperature  $T_{\text{cod}}$  used for the stacking in Fig. 10b on the AICC2012 ice age scale are displayed.

DO	$\delta^{18}\text{O}_{\text{ice}}$		TAC	Diff.	$\delta^{18}\text{O}_{\text{ice}}$		Diff.	$\text{CH}_4$	$T_{\text{cod}}$
	[AICC2012 ice]	[AICC2012 gas]			ss09sea06bm	[kindler gas]			
PB	11570	11580	-10		11464	11390	74	-	-
BA	14551	14560	-9		14534	14439	95	14904	15780
2	23251	23600	-349		22669	22569	100	-	22100
3	27691	27820	-129		27364	27264	100	28117	29060
4	28751	28790	-39		28462	28303	158	29280	30440
5	32410	32660	-250		32217	32064	153	33062	33740
6	33630	33810	-180		33519	33384	134	34246	34960
7	35390	35480	-90		35335	35199	136	35918	36880
8	-	-	-		-	-	-	38303	40120
9	-	-	-		-	-	-	40273	41120
10	41391	41220	171		41728	41560	168	41521	42580
11	43270	43140	130		43657	43459	198	43445	44560
12	46789	46610	179		47355	47215	140	46851	47960
13	49210	50020	-810		49782	50504	-722	49341	50120
14	54151	53880	271		55056	54745	311	54294	55200
15	55651	55440	211		56516	56314	202	55837	56740
16	-	-	-		-	-	-	58106	58980
17	-	-	-		-	-	-	59086	-
18	-	-	-		-	-	-	64059	65520
19	72087	71940	147		72957	72815	142	72095	73320
20	-	-	-		-	-	-	75860	76820
21	84130	83570	560		85421	84925	496	84101	84780
22	-	-	-		-	-	-	89402	90040
23	-	-	-		-	-	-	101844	102320
24	105747	105760	-13		108882	108886	-4	106065	10660
25	-	-	-		-	-	-	-	113240
		Average	$-12\pm 290$			Average	$111\pm 233$		
		Median	$-10$			Median	$140$		