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Duration of Greenland Stadial 22 and ice-gas Δage from counting of annual layers in Greenland NGRIP ice core

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Received: 23 June 2012 - Accepted: 26 June 2012 - Published: 16 July 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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The NorthGRIP ice core chronology GICC05modelext is composed of the annual-layer counted GICC05 chronology to 60 kyr before 2000 AD (b2k), and an ice flow model dating the deepest part of the ice core to 123 kyr b2k. Determination of annual strata in ice beyond 60 kyr b2k has been challenged by the thinning of annual layers to < 1 cm and the appearance of microfolds in some early glacial strata. We report high-resolution measurements of a 50 m section of the NorthGRIP ice core and corresponding annual layer thicknesses, constraining the duration of the Greenland Stadial (GS-22) between Greenland Interstadials (GIs) 21 and 22 which occurred between approximately 89 (end of GI-22) and 83 kyr b2k (onset of GI-21) depending on the chronology used. Multiple analytes (insoluble dust particles, electrolytic conductivity, ammonium and sodium) were determined in annual layers of ice often thinner than 1 cm. From annual layer counting, we find that GS-22 lasted 2894 ± 198 yr and was followed by a GI-21 pre-cursor event lasting 350 ± 19 yr. Our layer-based counting agrees with the duration of GS-22 determined from the NALPS speleothem record (3250 \pm 526 yr) but not with that of the GICC05modelext chronology (2620 yr). These results show that GICC05modelext overestimates accumulation and/or underestimates thinning in this early part of the last glacial period. We also revise the NorthGRIP ice depth-gas depth $(5.67 \pm 0.18 \,\mathrm{m})$ and ice age-gas age $(550 \pm 52 \,\mathrm{yr})$ differences at the warming onset of GI-21, observing that δ^{15} N increases before CH₄ concentration by no more than a few decades.

1 Introduction

Ice core records are of great importance to paleoclimate studies due to their ability to archive several climate parameters in continuous, precisely dateable stratigraphic sequences. The year-round regularity and relatively high accumulation rate of snowfall in Central Greenland has allowed determination of annual cycles in stable water isotopes,

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ions and dust back to 60 kyr before 2000AD (b2k) (Andersen et al., 2006a). Counting of annual cycles in stratigraphic archives produces constrained durations for temporal sequences but relies on the continuity of the archive for absolute dating. The linear manner of counting is also such that uncertainties accumulate along the length of the seguence. Annual-layer counted chronologies are of great value, especially when combined with absolutely-dated time markers such as known volcanic events and geomagnetic reversals (e.g. Parrenin et al., 2007). Synchronization between ice core records is undertaken using a number of hemispheric or globally homogeneous signals, such as gases (e.g. Blunier and Brook, 2001; EPICA community members, 2006), their isotopic signatures (e.g. Severinghaus et al., 1998; Capron et al., 2010b) or large volcanic eruptions (e.g. Rasmussen et al., 2008; Parrenin et al., 2012). Inverse methods have been employed to produce consistent ice core chronologies combining relative and absolute chronological markers in several synchronized ice core records (Lemieux-Dudon et al., 2010).

The Greenland Ice Core Chronology 2005 (GICC05), of which the most recent extension is GICC05modelext, is based on counting of annual strata in ice cores back to 60 kyrb2k. This common chronology for multiple Greenland ice cores employs annual layer counting of stable water isotopes from the surface to 7.9 kyrb2k, annual layer counting of impurities and visual stratigraphy (greyscale images related to microparticle density) strata back to 60 b2k (Svensson et al., 2005, 2008), and an ice-flow model (ss09sea06bm) chronology back to 123 kyrb2k (Wolff et al., 2010). GICC05modelext offers the paleoscience community a chronological framework for the duration of the Holocene as well as the last glacial period, for which 25 stadial-interstadial oscillations have been identified based on the oxygen isotope ratio in ice ($\delta^{18}O_{ice}$) (NGRIP members, 2004).

The use of Greenland Interstadial (GI) and Greenland Stadial (GS) nomenclature is an attempt to standardize the description of Greenland millennial-scale temperature oscillations first known as Dansgaard-Oeschger (DO) events. The first numbering of DO events employed low-resolution $\delta^{18}O_{ice}$ record from the GRIP ice core, which

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failed to capture rapid, small-scale temperature changes now described as "precursor" and "rebound" events (Capron et al., 2010a). The assignment of precursor events to either the GI following or GS preceding has not yet been standardized, and hence can contribute to the discrepancies between the durations calculated for GS-22; it is important that authors specify whether they include or exclude precursor events from their evaluations of stadial durations. For example, Capron et al. (2010a) evaluated the duration of GS-22 from the mid-point of the $\delta^{18}O_{ice}$ transition at the end of GI-22, to the initial increase of $\delta^{18}O_{ice}$ at the onset of the GI-21 precursor event. In this work, we follow the same approach for evaluating the duration of GS-22. Where possible, we describe durations for both GS-22 and the GI-21 precursor period, which we define here as the duration from the onset of precursor warming (i.e. the end of GS-22 proper) to the mid-point of the δ^{18} O_{ice} transition in the subsequent GI-21 onset. With the recent development of high-resolution techniques for analysis of water isotopologues (Gkinis et al., 2011), impurities (Bigler et al., 2011) and methane content (Stowasser et al., 2012) in ice cores, a systematic nomenclature for identifying stadial and interstadial events and their substructure is clearly required.

Recent studies of Antarctic ice cores and European speleothems have identified discrepancies in the duration of GS-22, suggesting that the current model-based duration is underestimated. GICC05modelext indicates a GS-22 duration of 2620 yr, from 87 680 to 85 060 yr b2k, with a GI-21 precursor duration of 300 yr (Wolff et al., 2010). Capron et al. (2010b) investigated the duration of Antarctic temperature oscillations in the EPICA Dronning Maud Land (EDML) ice core over the same time period and observed that the Antarctic Isotope Maxima that correspond to each set of Greenland stadial-interstadials, which are characteristic of the thermal bipolar seesaw, were misaligned for GS22. Aligning the EDML and NorthGRIP (NGRIP) ice core records by measurements of oxygen isotopes ($\delta^{18}O_{atm}$) and CH₄ concentrations in the air trapped in the ice, they observed that the duration of GS-22 (and warming of the consequent Antarctic Isotope Maxima, AIM21) was discrepant with the linear relationship between GS duration and Antarctic warming proposed by EPICA community

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members (2006). The most recent indication of an underestimation of the duration of GS-22 in *GICC05modelext* is based on radiometrically-dated speleothems from the Northern Alps (Boch et al., 2011). Oxygen isotopes were used to identify the cold and warm stages that correspond to the Greenland stadials and interstadials in the NALPS speleothem record, which were compared to *GICC05modelext*. Based on the speleothem record, the duration of stadial 22 was 3250 ± 526 yr. There are reliable indications that the hemispheric re-organization of the atmospheric circulation associated with GS and GI transitions occurs on the order of years to decades (Steffensen et al., 2008), although the dynamics of atmospheric and oceanic teleconnections between polar and tropical tropic regions has only recently been studied (Cvijanovic et al., 2011). Further modeling is required to better understand the extent to which low- and mid-latitude climate records (such as speleothems) can be compared to the high-latitude ice core climate records. Well-dated, highly-resolved climate records from new speleothem records, such as Sanbao (Wang et al., 2008) and Sofular (Göktürk et al., 2011) caves, are vital to improved understanding.

Continuous flow analysis (CFA) techniques have been developed to improve the reliability and resolution of measurements of ice core impurities (e.g. Röthlisberger et al., 2000; Kaufmann et al., 2008; Bigler et al., 2011). For most analytes, they are replacing the traditional ion chromatographic technique and offering the potential for coupling to online measurements of methane (Stowasser et al., 2012) and water isotopologues (Gkinis et al., 2010). The improved resolution of CFA allows the possibility of direct determinations of annual layer thicknesses in Greenland ice back to the inception of the last glacial climate period (Svensson et al., 2011). Techniques for determination of various climate parameters at high resolution have also been applied to the study of timing and duration of various climate proxies during glacial (Steffensen et al., 2008) and GS terminations (Thomas et al., 2009).

Here we revise the duration of GS-22, based on the high-resolution measurement of insoluble dust particles, ionic impurities and visual stratigraphy in the NGRIP ice core. This technique offers the resolution of annual layers of < 1 cm (Bigler et al., 2011),

sufficient for the counting of annual layers during GS-22 and adjacent GIs. Combined with continuous measurements of CH_4 concentrations, we refine the ice depth-gas depth (Δ depth) and ice age-gas age (Δ age) differences at this depth of the NGRIP record. This technique opens the potential for further refinement of *GICC05modelext* by evaluating annual layers and rapid gas transitions in the deepest sections of Greenland ice cores and synchronizing them with corresponding transitions in Antarctic ice cores.

2 Experimental

2.1 Ice core samples

Samples were obtained from the NorthGRIP ice core drilled in Northwest Greenland between 1997 and 2004 (NGRIP members, 2004). The samples correspond to the depth range 2679.05–2729.65 m of which only two 55 cm sections were unavailable (depths 2682.45–2682.90 and 2684.00–2684.55 m). A 35 × 35 mm section was cut for CFA analysis from the remaining "archive" piece. Optical line-scan images of the full ice core cross-section were collected at the drilling site (Svensson et al., 2005). δ^{18} O data were used to evaluate GS and GI events in the NGRIP (Wolff et al., 2010) and NALPS (Boch et al., 2011) records. As mentioned previously, we define GS-22 here as the cold Greenland stadial period occurring from the mid-point of the δ^{18} O transition at the end of GI-22, to the onset of the warming (δ^{18} O increase) of the GI-21 precursor event.

2.2 Measurements

The CFA system used for the measurements has been described by Bigler et al. (2011) and will be summarized here. The samples were melted on an aluminium melthead with a square inner sampling section ($26 \, \text{mm} \times 26 \, \text{mm}$). A constant ice melting rate of $1.5 \, \text{cm} \, \text{min}^{-1}$ produced meltwater at a rate of $8.4 \, \text{ml} \, \text{min}^{-1}$, of which $6 \, \text{ml}$ was directed

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to the analytical channels. The remaining 2.4 mlmin⁻¹ was used to flush a sealed debubbler to ensure effective removal of air from the CFA analytical channels. The overflow air was delivered to a cavity ring-down spectrometer (Picarro Inc., CFADS36 CO₂/CH₄/H₂O analyzer) for continuous measurements of methane concentrations (Stowasser et al., 2012). The debubbled meltwater was distributed to various analytical channels where continuous measurements of insoluble dust particles (> 1.0 µm diameter), electrolytic conductivity, sodium and ammonium were conducted.

Layer-counting technique

The technique used for layer counting is identical to the one used for the glacial part of GICC05modelext (Rasmussen et al., 2006). The parameters used for assignment of annual cycles included visual stratigraphy, electrolytic conductivity and insoluble dust particle concentration. Annual layers in sodium were not observed due to diffusion in the ice as well as the limited sampling resolution of ~ 3.5 mm for this analyte. Annual cycles in ammonium were identifiable only during the interstadials, when greater concentrations and thicker layers enabled their identification. Three people independently evaluated the data to produce three annual layer counting results. Where an annual layer was uncertain, it was assigned a value of $1/2 \pm 1/2$ yr. The three independent counting results were then evaluated again to produce a consistent final counting result. The Maximum Counting Error (MCE) was calculated as the sum of the "uncertain" annual layers. For the sections where ice was not available to measure, the layer thickness has been linearly interpolated from the adjacent measured sections. A section of NGRIP ice demonstrating the assignment of annual layers is shown in Fig. 1.

Results

Concentrations of ice core impurities determined by high-resolution CFA were consistent with previously reported values for sodium, ammonium and conductivity

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in Greenland glacial ice (Bigler, 2004). We have determined average GS-22 (NGRIP depths 2687.5–2718 m) values of 8.6 ppb for ammonium, 70 ppb for sodium, $1.0\,\mu\text{S\,cm}^{-1}$ for electrolytic conductivity and 56×10^3 insoluble dust particles > $1.0\,\mu\text{m\,ml}^{-1}$. While an impurity record for the whole NGRIP ice core is still in preparation, the results reported here are consistent with available records from GISP2 ice core (Mayewski et al., 1997) and NGRIP GS-5 (Andersen et al., 2006b). From Fig. 1 it can be observed that diffusion has broadened the signals of sodium and ammonium such that annual layers cannot be identified based on these records at this depth in NGRIP. In the sections corresponding to warmer GI-21 and GI-22, greater concentrations of ammonium allowed the detection of annual peaks in this record.

Annual layer thicknesses (λ) were primarily determined from peaks in electrolytic conductivity, insoluble dust particles and visual stratigraphy. Figure 2 shows λ values reported here as well as those calculated by ss09sea06bm. The annual-layer counted λ values were consistently smaller than those calculated by the flow model. We assigned the onset and end of GS-22 as, respectively, depths 2718.0 and 2691.1 m, δ^{18} O values -40.12 and -39.82 and GICC05modelext ages of 87 680 and 85 060 kyrb2k. Based on the annual-layer counting reported here, the duration of GS-22 was 2894 \pm 198 yr. These results are summarized in Table 1 and compared to previously reported durations for GS-22 and the GI-21 precursor period.

4 Discussion

4.1 Implications for Greenland ice core chronologies

The GS-22 duration presented here (2894 ± 198) is inconsistent with that of *GICC05modelext* (2620 yr) and indicates an overestimation of annual layer thickness in deep NGRIP ice. *GICC05modelext* is constrained in the upper section by annual layer counting, but is essentially unconstrained for the lowest 650 m of ice: beyond the 60 kyr limit of annual-layer counted strata, no independent chronological markers are currently

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available. Other lines of evidence exist to suggest that annual layer thicknesses are overestimated by the ss09sea06bm ice flow model: firn densification models used to reconstruct NGRIP temperatures from δ^{15} N measurements required annual snow accumulation rates to be decreased by 20 % to produce a consistent result for GIs 9-17 (Huber et al., 2006); and annual layer counting of NGRIP Eemian and early glacial ice (Svensson et al., 2011) also suggest λ is partly overestimated in the deeper sections of NGRIP. Annual layer thicknesses are essentially dictated by two parameters – snow accumulation and lateral strain – thus an inaccurate evaluation of either parameter will contribute to an overall bias in λ . These findings indicate that GICC05modelext requires revision for the durations of GS-22 and probably also GI-21 and GI-22. To see if other deep sections of NGRIP are also affected by an inaccurate calculation of λ , we compare the record to an independent paleoclimate archive.

A number of precisely-dated speleothem records have recently been reported, allowing the possibility of comparing mid- and low-latitude climate variations to those recorded in the Greenland ice core records. Boch et al. (2011) reported a climate record of the Northern Alpine region of Europe, NALPS, produced from a stack of speleothems dated by high-resolution U-Th measurements. Although there are gaps in the record, it can be seen in Fig. 3 that NALPS replicates some of the DO oscillations observed in NGRIP ice, particularly the transitions at the onset and end of GS-21 (approximately 77 kyr ago) and the entirety of GS-23 (approximately 105 kyr ago). As demonstrated by Boch et al. (2011) GICC05modelext and NALPS are most discrepant between the period 70-90 ky ago, with the maximum difference in chronologies occurring at the onset of GS-22 (1060 yr). The annual-layer counting reported here resolves the discrepancy between chronologies, indicating that the ice-core based duration of GS-22 should be increased by approximately 350 yr (14% greater than the current GICC05modelext duration). If the overall agreement between the speleothem and ice core chronologies in the earliest part of the glacial is to be maintained, the implication of this work is that the duration of GI-22 is overestimated in GICC05modelext.

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Implications for Antarctic ice core synchronization

Constraints to GICC05modelext have also been proposed using isotopic markers and gas-based synchronization to the well-resolved EPICA Dronning Maud Land (EDML) ice core. Capron et al. (2010b) reported CH₄ concentrations, δ^{15} N and δ^{18} O_{air} values in NGRIP and EDML ice, using these proxies to provide an alternative chronology for the deepest sections of NGRIP. Both CH_4 and $\delta^{18}O_{air}$ are globally homogenous on decadal timescales while $\delta^{15}N$ has been demonstrated to respond to changes in the firn column temperature and thickness and thus can be employed to identify rapid warming events such as the onsets of GIs. CH_4 and $\delta^{18}O_{air}$ allow accurate synchronization between ice core gas records but uncertainties are introduced when transferring between gas and ice ages, denoted as Δage, for each ice core. Various models have been proposed to account for firn-column diffusion processes (summarized in Buizert et al., 2012) and it has recently been reported that also impurity content plays a significant role in firn densification processes (Hörhold et al., 2012). Synchronization of ice cores through gas tracers is most precise when both records feature a small Δage, and hence high snow accumulation rate, such as at NGRIP and EDML. Earlier attempts to synchronize NGRIP with Vostok ice core experienced substantial difficulty due to the large Δ age associated with the low-accumulation site of Vostok (Landais et al., 2006).

The EDML-synchronized NGRIP chronology reported by Capron et al. (2010b), hereafter referred to as NGRIP-EDML, has a GS-22 duration over 700 yr longer than that determined here. The NGRIP-EDML duration (3625 ± 325 yr) is also longer than other estimates for GS-22 shown here, although it is consistent with the NALPS duration of 3250 ± 526 yr. Regarding the absolute ages, NGRIP-EDML and GICC05modelext agree on the onset of GS-22 (respectively 87756 ± 230 yrb2k and 87680 yrb2k) although the two chronologies are discrepant by 1 kyr by the onset of GI-21. One of the largest uncertainties associated with NGRIP-EDML during GS-22 is the matching of δ^{15} N and CH₄ records, which is used to constrain Δ age and transfer EDML gas ages to

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NGRIP ice depths. In Fig. 4, we show CH₄ concentrations determined in high-resolution as well as the δ^{15} N values reported by Capron et al. (2010b) in order to better constrain Δdepth and Δage for this part of NGRIP. Due to solubility effects in the extraction lines the online CH₄ data was calibrated using contemporary values reported in the GISP2 ice core (Grachev et al., 2007). The start of $\delta^{18}O_{ice}$ increases at the onset of the GI-21 was found at an NGRIP depth of 2687.8 m whereas the start of the associated CH₄ concentration increase can be attributed to the range 2693.3-2693.6 m (a gap in the CH_4 record precludes a more precise depth evaluation). This corresponds to a Δ depth of 5.67 ± 0.18 m and Δ age of 550 ± 52 yr, based on the annual-layer counting reported here. This evaluation was also undertaken for the onset of the GI-21 precursor warming and corresponding CH₄ concentration increase, as shown in Fig. 4, and found to have a slightly longer Δ age of 589 \pm 66 yr. Figure 4 also shows the relative phasing of δ^{15} N and CH₄ at the onset of GI-21, between NGRIP depths of 2693.3 m (latest possible CH₄ increase) and 2693.9 m (earliest possible δ^{15} N increase). The annual-layer counted chronology presented here shows that the maximum possible difference between δ^{15} N and CH₄ is 69 ± 5 yr, although the difference is most likely on the order of a few decades, consistent with the range of 25 to 70 yr proposed by Huber et al. (2006).

Our revision of the duration of GS-22 gives further support to the thermal bipolar seesaw theory of heat exchange between the Northern and Southern Hemispheres via oceanic circulation. Adapted from Capron et al. (2010a), Fig. 5 displays a strong correlation between the duration of Greenland cooling (GS duration) and the amplitude of Antarctic warming (temperature change during AIM events) for most of the past glacial period. The relationship is an empirical confirmation of the thermal bipolar seesaw model proposed by Stocker and Johnsen (2003) although it is apparent that GS 3, 19 and 22 are outliers from this relationship. It is of interest to note that the duration of GS-22 is only consistent with the linear fit in Fig. 5 if the duration of the GI-21 precursor period is not included. This suggests that the trigger of accelerating Atlantic meridional overturning circulation and associated heat transport from the Southern Ocean to the North Atlantic may lie with the climatic reorganization occurring during the precursor

event, rather than that of the following GI onset. In summary, our findings suggest that the thermal capacity of the Southern Ocean heat reservoir is not exhausted during longer stadials such as GS-22 and instead implies that other climatic processes may have been responsible for the unexpectedly slight warmings of Antarctica during GS-3 and GS-19.

5 Conclusions

The development of a high-resolution CFA system has enabled the identification of thin (<1 cm) annual layers in early glacial ice from the Greenland NGRIP ice core. We demonstrate that during GS-22 the annual layer thickness λ calculated by the ss09sea06bm model is overestimated by approximately 10 %, indicating a need to revise this section (including GIs 21 and 22) of the GICC05modelext chronology. The revised GS-22 duration presented here is not consistent with the gas-synchronized NGRIP-EDML chronology although it does agree with that of an independent U-Th dated speleothem record from the Northern Alps. Our proposed GS-22 duration is consistent with a strong correlation between GS duration and Antarctic warming as proposed by Stocker and Johnsen (2003). This work opens the possibility for annual layer counting in other polar ice cores for which absolute chronological markers are lacking. The combination of these data with high-resolution gas measurements in NGRIP will also help to constrain the Δ age relationship in the ice core, thus allowing ice flow models and understanding of firn densification processes to be improved.

Acknowledgements. We thank Bo Vinther, Emelie Capron, Amaelle Landais and Myriam Guillevic for helpful discussions. This work is a contribution to the NorthGRIP ice core project, which is directed and organized by the Centre for Ice and Climate at the Niels Bohr Institute, University of Copenhagen. It is being supported by funding agencies in Denmark (SNF/FNU), Belgium (FNRS-CFB), France (IFRTP and INSU/CNRS), Germany (AWI), Iceland (Rannls), Japan (MEXT), Sweden (SPRS), Switzerland (SNF) and the United States of America (NSF).

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Table 1. Summary of absolute ages of onset and end transitions associated with GS-22, and calculated durations from various NorthGRIP ice core chronologies as well as the NALPS speleothem record.

Archive	GI-21 onset ^a	±	GI-21 precursor onset ^a	±	GI-22 end ^a	±	GS-22 Duration ^a	±
NGRIP (ss09sea ^b) NGRIP (EDML synchronized ^c)	84 760 83 634	230	85 060 84 131	230	87 680 87 756	230	2620 3625	325 ^d
NGRIP (this work) NALPS ^f	85 030	410	85 440	410	88 690	330	2894 3250	198 ^e 526 ^d

^a Definitions of onsets, ends and durations of Greenland Interstadial (GI) and Greenland Stadial (GS) events are given in the text.

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^b From Wolff et al. (2010).

^c From Capron et al. (2010b).

^d Uncertainties are calculated as root-sum-of-squares of the GI onset and end uncertainties.

^e Uncertainty is the Maximum Counting Error, as described in the text.

f From Boch et al. (2011).

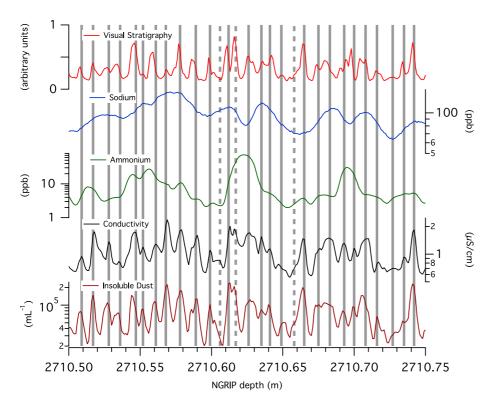


Fig. 1. Example of Continuous Flow Analysis (CFA) measurements of NorthGRIP glacial ice and assignment of annual layers. Visual stratigraphy was measured by optical scanning at the drilling site, not by CFA. Vertical grey bars indicate "certain" (solid line) and "uncertain" (dotted line) years. Note that sodium, ammonium, conductivity and insoluble dust are plotted on logarithmic scales.

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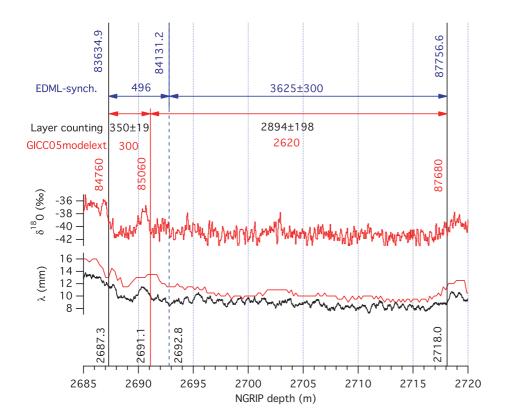


Fig. 2. Comparison of NorthGRIP ice core chronologies over the interval between GI-21 and GI-22. Also shown are NGRIP δ^{18} O_{ice} and annual layer thicknesses (λ) from the ss09sea06bm iceflow model and from annual layer counting (this study). Numbers shown horizontally correspond to event durations in years calculated from GICC05modelext in red (Wolff et al., 2010), EDMLsynchronized NGRIP chronology in blue (Capron et al., 2010b) and annual layer counting in black (this study). Vertical numbers show NGRIP depths (black) corresponding to absolute ages in years before 2000AD from GICC05modelext (red) and EDML-synchronized NGRIP (blue) chronologies.

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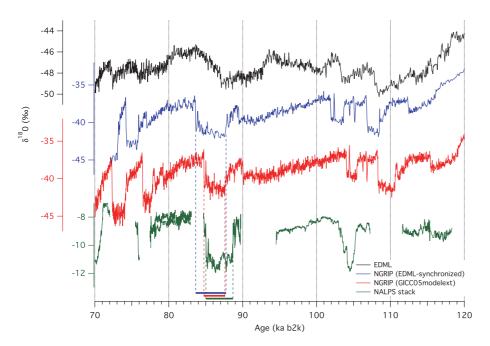


Fig. 3. Comparison of temperature proxy records from Greenland, Europe and Antarctica. The Antarctic EPICA Dronning Maud Land (EDML) ice core $\delta^{18}O_{ice}$ record is shown in black (EPICA community members, 2006). The Greenland NorthGRIP ice core $\delta^{18}O_{ice}$ record is shown in blue (EDML-synchronized chronology, Capron et al., 2010b) and red (*GICC05modelext* chronology, Wolff et al., 2010). The Northern Alps (NALPS) speleothem record is shown in green (Boch et al., 2011). Coloured markers at the bottom of the graph show the different timings and durations of GS-22 according to each archive and chronology.

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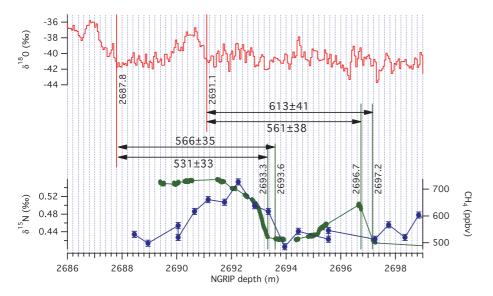


Fig. 4. Comparison of NorthGRIP ice core $\delta^{18}O_{ice}$ and trapped gas species for the determination of Δage. $\delta^{18}O_{ice}$ is shown in red (*GICC05modelext* chronology, Wolff et al., 2010) while $\delta^{15}N$ is shown in blue (Capron et al., 2010b) and CH₄ concentration is shown in green (this study). Horizontal numbers indicate depth differences between ice (red) and gas (green) transitions, while vertical numbers specify the depths assigned to temperature and gas features.

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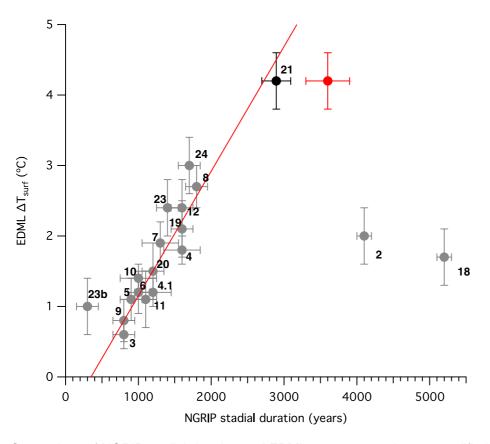


Fig. 5. Comparison of NGRIP stadial duration and EDML temperature change, modified from Capron et al. (2010a). Numbers indicate corresponding GI and AIM events, where the stadial duration is determined from the GS prior to the numbered GI. The durations of GS-22 (together with GI-21 corresponding to AIM21 in the figure) are shown for both EDML-synchronized (red, Capron et al., 2010b) and annual-layer counted (black, this study) NGRIP chronologies.

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