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Climate of the Past

A refined TALDICE-1a age scale from 55 to 112 ka before present for the Talos Dome ice core based on high-resolution methane measurements

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Abstract. A precise synchronization of different climate records is indispensable for a correct dynamical interpretation of paleoclimatic data. A chronology for the TALDICE ice core from the Ross Sea sector of East Antarctica has recently been presented based on methane synchronization with Greenland and the EDC ice cores and $\delta^{18}O_{ice}$ synchronization with EDC in the bottom part (TALDICE-1). Using new high-resolution methane data obtained with a continuous flow analysis technique, we present a refined age scale for the age interval from 55–112 thousand years (ka) before present, where TALDICE is synchronized with EDC. New and more precise tie points reduce the uncertainties of the age scale from up to 1900 yr in TALDICE-1 to below 1100 yr over most of the refined interval and shift the Talos Dome dating to significantly younger ages during the onset of Marine Isotope Stage 3. Thus, discussions of climate dynamics at sub-millennial time scales are now possible back to 110 ka, in particular during the inception of the last ice age. Calcium data of EDC and TALDICE are compared to show the impact of the refinement to the synchronization of the two ice cores not only for the gas but also for the ice age scale.

1 Introduction

For a good understanding of the mechanisms at work in the climate system it is indispensable to know the chronology and phase relationships of climate events in the past. Precise dating of climate archives such as ice cores is therefore necessary to optimally utilize the information stored in such archives. Ice cores contain various strains of information on climate and environmental changes in the past. These comprise the water isotopic signature of the ice matrix, dissolved and particulate aerosol tracers as well as the gas composition of the atmosphere all in one climate archive. Accordingly, synthesizing these strains of ice core information circumvents crucial cross-dating issues that affect the comparison of independent climate archives. For the comparison of different ice cores, absolute dating of each core is not necessary, it is sufficient to synchronize the records properly by the use of a global tracer. Air trapped in polar ice cores has the unique property of containing global tracers of the atmosphere, which show the same variations over time at drilling sites on both hemispheres. Thus, it is possible to build relative age scales of different ice cores by synchronizing the respective methane (CH_4) records (Blunier and Brook, 2001; Blunier et al., 1998, 2007; Chappellaz et al., 1997; EPICA, 2006). Methane is particularly well suited for such a synchronization because abrupt concentration changes have been observed over large periods back to 800 thousand years before present (ka BP, i.e. before 1950 AD), not only at glacial-interglacial transitions but also during glacial times, especially during Dansgaard-Oeschger (DO) events (Brook et al., 2000; Chappellaz et al., 1997; Huber et al., 2006; Loulergue et al., 2008; Spahni et al., 2005). These abrupt CH_4 concentration changes are global time markers which have been well archived in all polar ice cores since the interhemispheric mixing time today is about ten times shorter than the atmospheric lifetime of CH_4 and

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was still much shorter during glacial times (Fischer et al., 2008; Lelieveld et al., 1998).

The synchronization of ice cores is limited by the mixing of the air in the firn before bubble close-off which causes different age distributions of the enclosed gas depending on accumulation and temperature at the drilling site. This age distribution as well as the firnification process can be modelled (Goujon et al., 2003; Schwander et al., 1993; Spahni et al., 2003) within its model uncertainties. It has been shown that additional uncertainties of methane tie points of up to 200 yr can be caused by different gas enclosure characteristics at different drilling sites (Köhler et al., 2011). Even larger errors may arise for very low accumulation rate sites (such as Vostok, Dome Fuji or Dome C), where firnification models seem to be in contradiction with $\delta^{15}N_2$ measurements (Landais et al., 2006). Another important limitation usually is the limited resolution of the methane records. Records with higher resolution reflect fast concentration changes in more detail and therefore, tie points can be defined more precisely.

The first official chronology (TALDICE-1) of the deep ice core TALDICE (TALos Dome Ice CorE) at Talos Dome in the Ross Sea sector of East Antarctica (72°47′ S, 159°11′ E), based on an inverse model (Lemieux-Dudon et al., 2010) and methane synchronization with Greenland ice cores (Blunier et al., 2007) (0–50 ka BP) and the EPICA Dome C (EDC) ice core (Loulergue et al., 2008; Spahni et al., 2005) (50–140 ka BP) as well as $\delta^{18}O_{ice}$ synchronization with EDC for ages older than 140 ka, has recently been published by Buiron et al. (2011). The well-resolved (mean resolution of 87 yr) TALDICE methane record was synchronized with the Greenland record back to 50 ka BP. The relative age uncertainty of TALDICE-1 remains lower than 600 yr in this period (except for the Last Glacial Maximum where abrupt methane variations are missing). However, for the time period from 50–140 ka BP where the methane synchronization was made with the EDC ice core, the age uncertainty increases to 2 ka, mainly due to the coarse resolution (mean resolution of 620 yr) of the TALDICE methane record.

The purpose of this paper is to apply a new continuous measurement technique for methane (Schüpbach et al., 2009) and to produce a high-resolution CH_4 record for the early part of the last ice age. In the new record we define 12 new age tie points which result from the high-resolution record. With these additional constraints, we are able to present a refined age scale (TALDICE-1a) for the time period from 55–112 ka BP based on the TALDICE-1 age scale. The impact of the refinement of the age scale to the synchronization of TALDICE and EDC ice cores is shown by a comparison of Calcium (Ca^{2+}) records of the two cores in a selected interval. This provides an independent means of verifying the quality of the revised age scale TALDICE-1a.

The paper is organised as follows: In Sect. 2 we describe the new high-resolution CH_4 data and the construction of the revised age scale. Section 3 presents a discussion of the implications of the new time scale, in particular on ice-based records, and conclusions are given in Sect. 4.

2 Experimental methods and age scale construction

Methane measurements on TALDICE were performed with a new on-line melting technique using a Continuous Flow Analysis (CFA) system (Schüpbach et al., 2009) in the depth interval from 1187 m to 1488 m. These measurements cover the section where TALDICE was synchronized with the EDC ice core (1228 m to 1428 m, Buiron et al., 2011) by the use of discrete methane measurements using a traditional melt-refreeze extraction method (Chappellaz et al., 1997; Spahni et al., 2005). The new on-line record yields a mean depth resolution of 26 cm in the depth interval examined in this study (547 data points from 1239 to 1380 m), compared to a mean depth resolution of 1.52 m of the methane record used for the synchronization with the EDC record by Buiron et al. (2011). Even though the precision of the on-line measurements is lower (1σ of 15–20 ppbv) than the one of the discrete measurements (1σ of 10 ppbv) and absolute calibration is an issue, the new dataset is very well suited for a refined synchronization of the TALDICE and the EDC methane records. This is due to the considerably higher depth resolution of the new dataset, and because the magnitude of atmospheric CH_4 variability (in the range of 350 ppb to 750 ppb during the last glacial period) is much larger than the uncertainty of the measurement. This allows for the definition of more tie points with better precision. Gaps in our high-resolution CH_4 record (see Fig. 3) longer than 1 m were caused either by several distinct ash layers in the ice core that were not measured with CFA (3 m at 86.5–88.5 ka, 2 m at 107–109 ka and 4 m at 111.5–115 ka BP) or maintenance of the GC system (12 m at 61–64 ka BP) while the CFA measurements were continued.

A methane record covering the Antarctic Cold Reversal (ACR) was measured with the same method on TALDICE and presented in Schüpbach et al. (2009). This record features a nominal resolution of 3–10 yr. However, no large concentration variations of methane in the air trapped in ice are possible within such short time periods due to the slow bubble close-off process (Schwander et al., 1993). Therefore, the data were filtered by a binomial 5-point filter to smooth out artificial variations induced by the measurement uncertainty without corrupting the signal during fast concentration increases or decreases. Since these high-frequency variations are a measurement artefact, the filter is not applied on a constant time window but always over five consecutive data points, i.e. on a constant depth interval. This same filter was applied for all the high-resolution data presented in this work featuring similar depth resolution but much lower resolution in time (mean temporal resolution of 103 yr) than the data covering the ACR. In doing so, measurement artefacts were filtered reliably, but atmospheric CH_4 variations were potentially smoothed since the mean temporal resolution of

Table 1. Tie points defined in the age interval from 55–112 ka BP by synchronization of the new high-resolution TALDICE CH_4 data with the EDC CH_4 record on the EDC3 age scale. The indicated uncertainty is from visual matching of TALDICE and EDC only. Additionally indicated are the corresponding depths of the EDML ice core for all the new tie points and the sample resolutions of the EDC and TALDICE CH_4 records, respectively, for each tie point.

EDC depth	TALDICE depth	EDML depth	Gas age EDC3	Resolution EDC/TALDICE	Uncertainty	Comments
(m)	(m)	(m)	(yr BP)	(yr)	(yr)	
44.50	1239.00		55 150		200	*
969.65	1255.50	1663.50	57 400	220/20	220	
980.39	1260.50	1681.03	58 280	150/20	160	onset DO 17
984.52	1262.67	1686.98	58 610	180/50	190	precursor DO 17
1039.51	1287.75	1764.10	64 020	240/30	250	onset DO 18
1105.55	1306.25	1862.50	71 100	200/70	210	onset DO 19
1141.27	1314.57	1914.50	74 630	200/55	200	onset DO 20
1196.27	1326.14	1978.10	79 875	180/55	190	
1234.77	1332.75	2019.80	83 070	170/65	190	peak DO 21
	1334	2425.20	83 650			precursor DO 21
1248.52	1335.25	2031.20	84 230	190/75	200	
1302.70	1345.00		89 500		500	*
1369.3	1356		96 000		500	*
1427.27	1367.1	2196	101 690	220/60	230	onset DO 23
1432.77	1368.4	2199.32	102 240	230/100	250	
1471.27	1374.75	2228.99	106 550	230/80	250	onset DO 24
1515.4	1380.00		112 000		1000	*

* Tie point adopted from Buiron et al. (2011).

the CFA-CH_4 record presented in this study is in the order of magnitude of the bubble close-off time. However, the potential smoothing of atmospheric variations does not have implications on the result of the synchronization of the CH_4 records of TALDICE and EDC as long as tie points can still be clearly identified.

The filtered high-resolution methane record was then synchronized to the EDC methane data by visually matching fast transitions in the two methane records. The tie points were chosen at mid-slope of the transitions at the onset of Dansgaard-Oeschger (DO) events or at the maxima of very short methane peaks (e.g. the very pronounced event at 58 600 ka BP preceding DO 17 in Fig. 1). Due to the high resolution of the new Talos Dome methane record the uncertainty of the visual matching remains always lower than 300 yr (compared to 400–1500 yr in Buiron et al., 2011) in the discussed depth interval. This uncertainty depends only on the resolution of both records and is calculated as the square root of the sum of squares of the EDC and TALDICE time resolution at the respective tie point (see Table 1). Not included in this uncertainty is the additional synchronization error caused by different bubble close-off characteristics of Dome C and Talos Dome. This additional error is lower than the 200 yr calculated by Köhler et al. (2011). This is because Köhler et al. (2011) compare the EDC and NGRIP ice cores where bubble close-off characteristics are very different. The close-off characteristics of TALDICE is more similar to those of EDC, resulting in smaller synchronization uncertainties. In order to obtain the uncertainty of the absolute gas age of each tie point, the uncertainties caused by visual matching have to be added to the inherent uncertainty of the EDC3 age scale of 1–4 ka BP in the interval discussed in this work (Parrenin et al., 2007).

As the TALDICE-1 age scale both for ice and gas is based on gas tie points only (for ages younger than 141 ka BP), shifting the gas tie points has direct implications on the age of the ice. The age difference between the gas and the ice at the same depth (Δage) is largely dependent on the accumulation rate. Since changes in the accumulation rate in the refined age scale caused by shifting tie points do not exceed 16 %, i.e. stay well within the uncertainty of the accumulation rate given by Buiron et al. (2011) ($\pm$20 %), we applied the modeled Δage of TALDICE-1 to the refined gas age scale in order to derive the age of the ice at the corresponding depth.

Soluble calcium (Ca^{2+}), a tracer for mineral dust input, was analyzed on the entire TALDICE with a well-established CFA system used for the determination of aerosol constituents in ice cores (Kaufmann et al., 2008). In the depth interval from 1220 m to 1323 m discussed here, a continuous high-resolution Ca^{2+} record was obtained except for a gap of four meters (1276–1280 m), where Ca^{2+} data were not available. The nominal depth resolution of the continuous Ca^{2+}

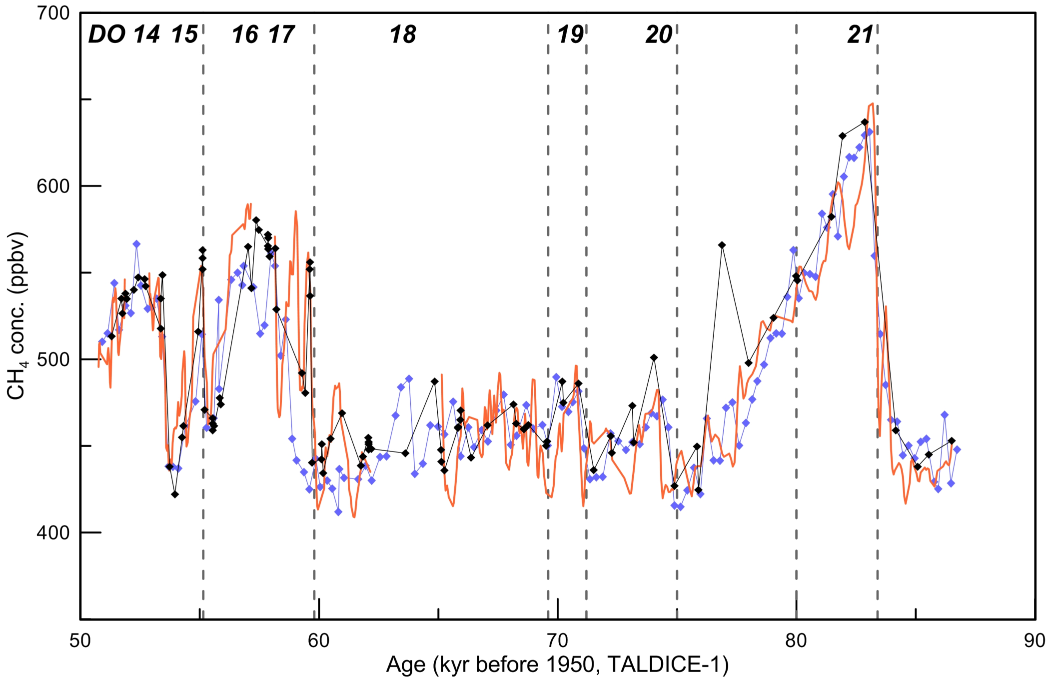

Fig. 1. The EDC CH_4 record (blue diamonds) on the EDC3 age scale is compared to the TALDICE CH_4 record (black diamonds, Buiron et al., 2011) on the TALDICE-1 age scale. The new high-resolution CH_4 record (orange line) is also shown on the TALDICE-1 age scale. Dashed lines indicate the tie points of the TALDICE-1 age scale used by Buiron et al. (2011). Bold italic numbers indicate Dansgaard-Oeschger (DO) events.

record is typically 1 cm (Bigler et al., 2006), for the purpose of this study the high-resolution Ca^{2+} record is down-sampled to a depth resolution of 50 cm to compare with the EDC Ca^{2+} record. The mean measurement error of the Ca^{2+} concentration record is estimated to be less than 10 % (Röthlisberger et al., 2000).

3 Results and discussion

Figure 1 shows the Dome C methane record in the time interval from 50–86 ka BP on the EDC3 age scale (Loulergue et al., 2007; Loulergue et al., 2008) along with the discrete methane data on the TALDICE-1 age scale (Buiron et al., 2011). With the new high-resolution methane data overlaid (orange line), discrepancies between the two age scales appear which could not be unambiguously detected with the discrete measurements only. For example, at the onset of DO 17 preceded by a distinct precursor event the TALDICE-1 gas age is biased 1000 yr towards older ages. Replacing the tie point at 59 800 yr BP with a tie point at the peak of the precursor event (58 600 yr BP on the EDC3 age scale) and thus shifting TALDICE-1 approx. 1000 yr towards younger ages while keeping the tie point at 71 200 yr BP fixed (onset of DO 19) stretches the data in a way that an additional tie point at the onset of DO 18 becomes apparent (see Fig. 2).

The same procedure has been applied for the entire period from 55–112 ka BP shown in Fig. 3. By matching all the fast transitions at the onsets of DO 16–24, precursor events or other distinct signals in the two methane records, 12 new tie points were defined in the age interval from 55–112 ka BP, four of the tie points proposed by Buiron et al. (2011) were adopted unchanged (see Table 1 and Fig. 3). Correlation coefficients between EDC CH_4 and CFA-CH_4 on the TALDICE-1 age scale and on the revised TALDICE-1a age scale have been calculated by linearly interpolating the CFA-CH_4 record to obtain concentration values in the high-resolution record at exactly the same age as the EDC data points. For the 208 data points in the investigated interval correlation on the TALDICE-1 age scale is $r^2 = 0.68$ compared to $r^2 = 0.81$ on the revised age scale. The TALDICE CH_4 data on the whole interval of the refined age scale is shown in Fig. 3 along with the EDC CH_4 data. This new TALDICE-1a age scale is not meant to replace the TALDICE-1 age scale, it is rather a refinement of this age scale in the above mentioned time interval. Figure 4a shows how much the gas age scale has been changed by the construction of the new age scale with respect to the original age scale over the entire depth interval of the age scale refinement. The largest shifts (up to 1200 yr) can be observed in the period from 56–70 ka BP. In the older part, the changes in the age scale are lower than 400 yr. Due to new high-resolution methane data, tie points between the TALDICE

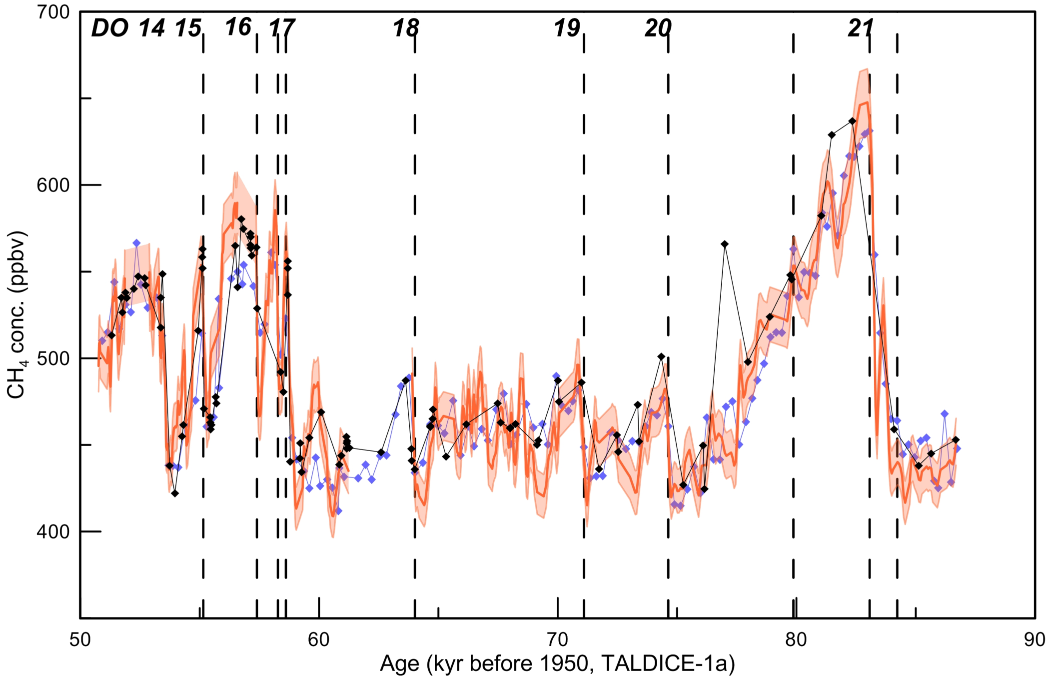

Fig. 2. The TALDICE CH_4 records (black diamonds: discrete data (Buiron et al., 2011); orange line: new high-resolution data with the light orange band indicating a ±3 % error band) plotted on the refined TALDICE-1a age scale in comparison with the EDC CH_4 record (blue diamonds) on the EDC3 age scale. Dashed lines indicate new tie points of the TALDICE-1a age scale; bold italic numbers indicate Dansgaard-Oeschger (DO) events.

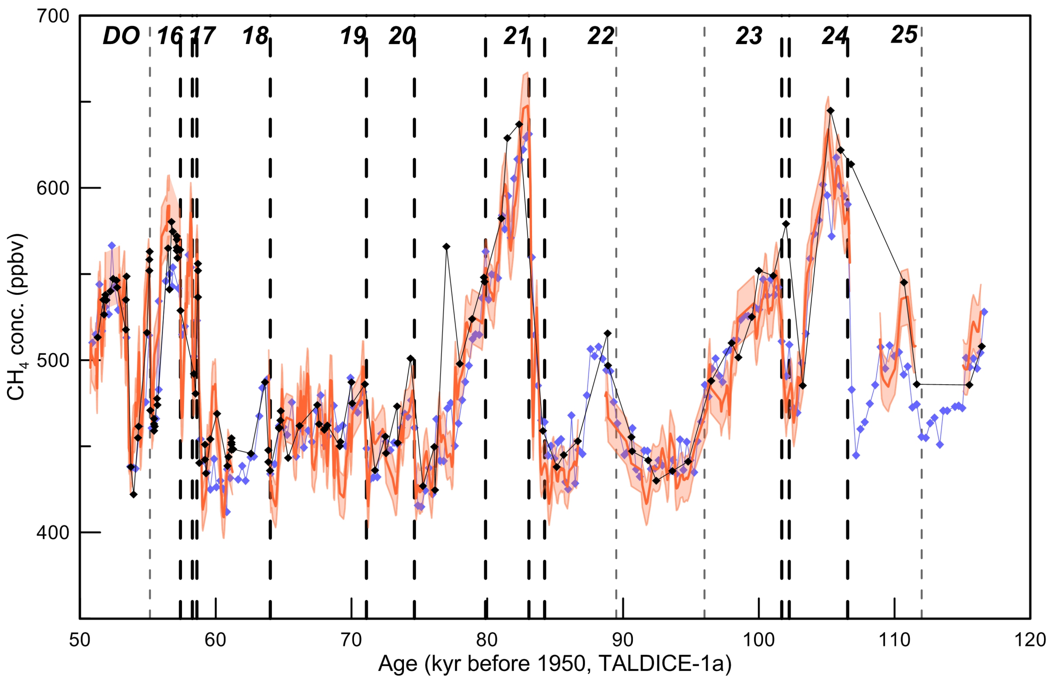

Fig. 3. The CH_4 records (EDC: blue diamonds, discrete TALDICE data: black diamonds, new high resolution TALDICE data: orange line) on the whole interval from 55–112 ka BP where the TALDICE-1 age scale has been refined. Bold dashed lines indicate the new tie point; fine dashed lines indicate tie points adopted from the TALDICE-1 age scale; bold italic numbers indicate Dansgaard-Oeschger (DO) events.

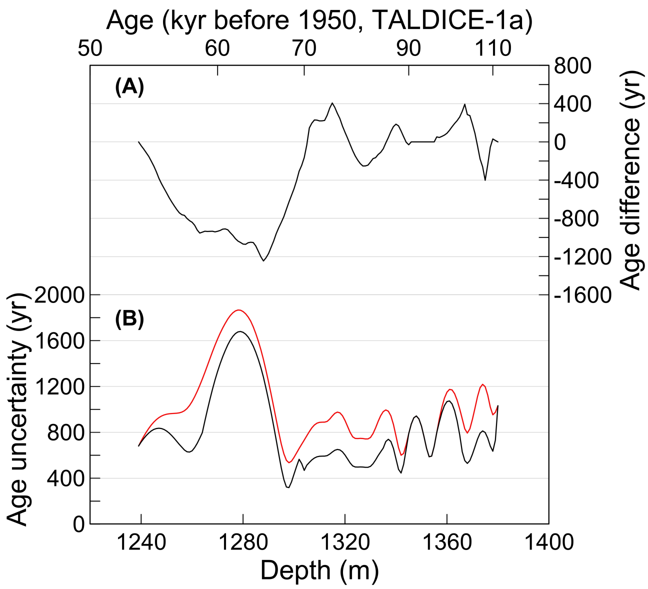

Fig. 4. (A) The ice age differences of the refined TALDICE-1a age scale compared to TALDICE-1 (the age difference is defined as TALDICE-1a age subtracted by the TALDICE-1 age at the respective depth). **(B)** Age uncertainties of the original TALDICE-1 ice age scale (red line), (Buiron et al., 2011) and the reduced uncertainties of the refined TALDICE-1a ice age scale (black line), respectively. The corresponding age (TALDICE-1a) is indicated on top.

and EDC CH_4 records could be significantly constrained, yielding relative age uncertainties of 150–300 yr compared to 400–1500 yr for the tie points in the TALDICE-1 age scale. The uncertainty of the ice age derived from synchronized gas records depends mainly on the Δage uncertainties of both ice cores and of the uncertainty of the CH_4 match. Thus, the better constrained gas tie points also reduce the uncertainty of the ice age scale, leading to relative age uncertainties between TALDICE and EDC of below 1100 yr in the refined interval (except for the depth interval 1267–1290 m corresponding to 60–65 ka BP, where uncertainties reach up to 1500 yr due to missing high-resolution CH_4 data) compared to maximum uncertainties of 1900 yr in the same interval with the TALDICE-1 age scale. The uncertainties of the original TALDICE-1 ice age scale are compared to the new uncertainties of the TALDICE-1a ice age scale in the refined period in Fig. 4b. The new uncertainty is estimated by error propagation with unchanged Δage uncertainties in EDC and TALDICE and the reduced new uncertainty from the gas tie points. While discussions of climate dynamics at sub-millennial time scales were possible back to the Marine Isotope Stage (MIS) 3.3 with the TALDICE-1 age scale, the refined age scale allows for such discussions back to MIS 5.3.

For the first time the precursor event of DO 21 has clearly been detected in methane in an Antarctic ice core (see Fig. 1). It has been measured in high-resolution and discussed before in the GISP2 ice core by Grachev et al. (2007, 2009) and, thus, has been independently verified by our measurements. Also the rapid variations of methane in the NGRIP ice core over DO 16 and 17 discussed in detail by Huber et al. (2006) have not been measured before in such resolution in Antarctica. The existence not only of fast transitions in methane during DO events in both Antarctic and Greenland ice cores, but now also the availability of precursor-like events in the methane records of both hemispheres allows for a discussion of the mechanisms at work at time scales of a few hundred years. However, the EDC CH_4 record does not show all the short events in methane due to limited depth resolution but also due to considerable smoothing of the gas records due to low accumulation and temperature. In contrast, the EDML CH_4 record (Capron et al., 2010; EPICA, 2006; Schilt et al., 2010), which features good depth resolution in the discussed interval, shows the distinct variations over DO 15–17, which allows for even more precise synchronization with the TALDICE CH_4 record. Furthermore, no additional phasing uncertainty due to the bubble close-off characteristics is induced between TALDICE and EDML, since accumulation and temperature at both drilling sites are very similar. In Table 1 the corresponding tie points are also proposed for the EDML ice core based on synchronization with the new TALDICE CH_4 record.

To demonstrate the impact of the refinement of the TALDICE-1 age scale not only in gas records but also in the surrounding ice matrix, the Ca^{2+} concentration records of the TALDICE and EDC ice cores are compared on a selected interval from 54–80 ka BP. This represents an independent validation of our approach and the quality of the revised age scale.

Calcium in East Antarctic ice cores predominantly originates from terrestrial dust from southern South America during the last glacial period (Delmonte et al., 2008; Fischer et al., 2007). Therefore, changes in the flux of Ca^{2+} during this period should be synchronous across East Antarctica and can be used to synchronize ice core records from this region (Mulvaney et al., 2000). Thus, we compare the Ca^{2+} records to demonstrate the impact of the refined age scale on TALDICE. In Fig. 5 Ca^{2+} concentrations from EDC and TALDICE are shown on the time interval from 54–80 ka BP on the EDC3 and the original TALDICE-1 age scales (A), and the refined TALDICE-1a age scale (B), respectively. In general, Ca^{2+} concentrations are approximately three times lower in TALDICE than the respective concentrations in the EDC ice core (note different scales of the ordinates in Figs. 4a and b) over the discussed interval, primarily due to the higher accumulation rate at Talos Dome and secondly because of different transport times of Patagonian dust to Dome C and Talos Dome. The relative variations of the two Ca^{2+} records show high correlation as expected according to Mulvaney et al. (2000). However, the variations are substantially shifted in time when using the original TALDICE-1 age scale (Buiron et al., 2011) (see Fig. 5a). Especially between 60 and

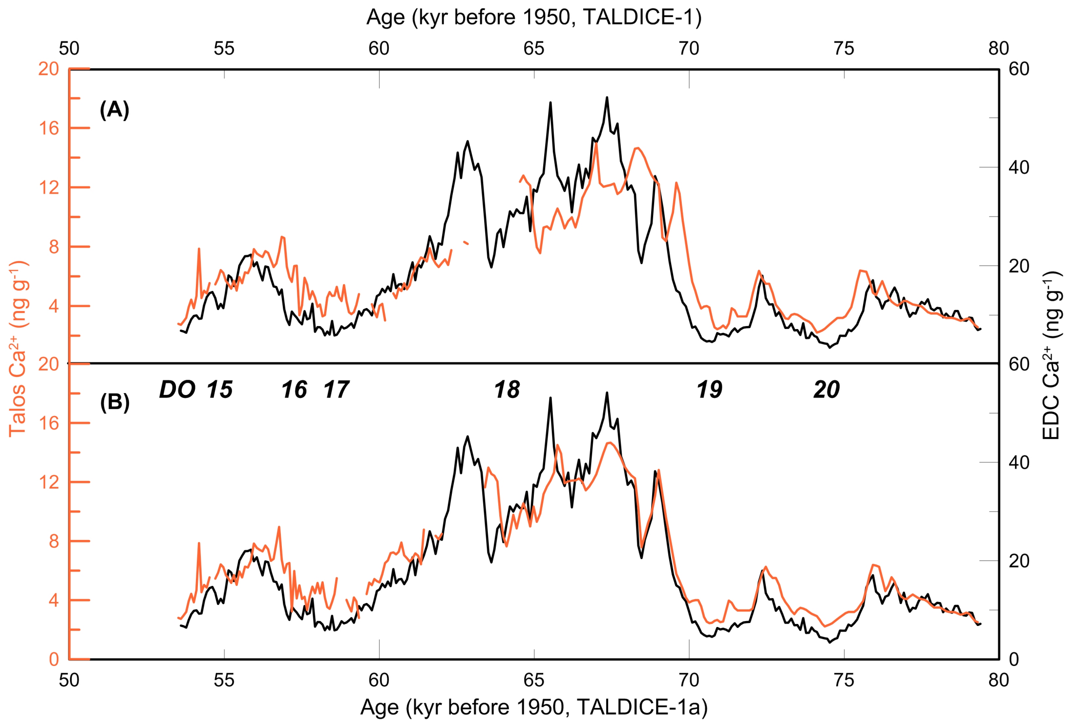

Fig. 5. The Ca^{2+} records from EDC (black line, Bigler et al., 2006) on the EDC3 age scale and from TALDICE (orange line, new data) on the original TALDICE-1 age scale **(A)** and the refined TALDICE-1a age scale **(B)**, respectively, are compared on the interval from 54–80 ka BP. EDC data are shown as 1 m averages, TALDICE data as 50 cm averages. TALDICE data are interpolated to fit the EDC data at the respective ages. Bold italic numbers indicate Dansgaard-Oeschger (DO) events.

70 ka BP (covering DO 17–19) where highest Ca^{2+} concentrations are reached a temporal shift towards older ages in the order of 1000 yr becomes apparent.

When using the refined TALDICE-1a age scale instead (Fig. 5b), the variations in the Ca^{2+} records are in phase within the error limits, confirming the consistency of the TALDICE-1a age scale and the EDC3 age scale in contrast to the TALDICE-1 age scale. Correlation of the TALDICE and EDC Ca^{2+} records (246 data points each) in this interval is increased from $r^2 = 0.71$ using TALDICE-1 to $r^2 = 0.89$ when the refined TALDICE-1a age scale is applied. Thus, not only in the interval where the largest corrections in the gas age scale have been applied (around DO 17, see Figs. 1 and 2), but also in other sections of the refined interval, a substantial improvement of the synchronization in both the gas and the ice age scale has been achieved by the use of the new high-resolution methane data. The first methane tie point of the refined age scale is at 55 150 yr BP (see Table 1) in the gas age, corresponding to an age of the surrounding ice of 56 300 yr BP. Thus, the ice age scale is readjusted only for ages older than 56,3 ka BP as can be seen in Fig. 5b. Δage modeled by Buiron et al. (2011) is slightly overestimated in the age interval 55–67 ka BP, whereas for older ages it seems to fit well with the refined TALDICE-1a age scale.

4 Conclusions

The refined age scale TALDICE-1a presented in this work complements the TALDICE-1 age scale in the age interval from 55–112 ka BP. This refinement is required for investigations of climate dynamics at sub-millennial time scales not only back to 50 ka BP as with the TALDICE-1 age scale but back to MIS 5.3 at 110 ka BP. In particular, precise north-south synchronization is essential for the study of interhemispheric connections (Raisbeck et al., 2007; Stocker and Johnsen, 2003). The availability of such high-resolution CH_4 data allows for more precise synchronizations with future ice cores which are also analyzed with on-line CH_4 measurements. For the present purpose, absolute calibration of the CFA-CH_4 data, which remains a critical issue for on-line CH_4 measurements, is not necessary. This greatly enhances the value of these data. Further improvements concerning the precision of the on-line measurements would then also allow for a better insight in the dynamics of the methane cycle on short time scales and at low concentration variations. With additional methane measurements to achieve higher resolution in the lower part of TALDICE (ages older than 130 ka BP) and using Ca^{2+} for tie points in the ice matrix, the synchronization of TALDICE with EDC could further be improved in the future through the entire length of the ice core by using e.g. the inverse model by Lemieux-Dudon et al. (2010).

Supplementary material related to this article is available online at: http://www.clim-past.net/7/1001/2011/ cp-7-1001-2011-supplement.zip.

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