

1 Dear Editor,

2

3 Thank you for careful reading and positive evaluation of our revised manuscript. Below
4 we addressed how we revised our manuscript. We hope this could help our updated
5 manuscript to be published.

6

7 **Editor Decision: Publish subject to minor revisions (review by Editor)** (27 Jul
8 2017) by Eric Wolff

9 Comments to the Author:

10 Thank you again for your constructive response to the reviewers. Although I think your
11 method of calculating the uncertainty remains open to question, I think (based also on
12 the data in Table 1) the value you are using is probably reasonable, and that there is no
13 value in pursuing this further. I am therefore not sending the paper back for further
14 review but instead accepting it subject to minor changes.

15

16 I have a couple of points about the English (copy editors may have more):

17 Page 3, line 27, remove "Since" so that the sentence makes sense

18 Line 36, replace "Despite" with "Although"

19 → The sentences were modified as below:

20 → ~~Since~~ There is no high-resolution reconstruction of past population and land use area, and consequently
21 large uncertainties of CH₄ emission from land use change impede identification of any shorter scale
22 changes.

23 → ~~Although~~ ~~Despite~~ Rhodes et al. (2015) reported a very high-resolution record from WAIS Divide ice core
24 that extends from the last glacial period to the earliest Holocene (~9.8 ka), the authors do not deal with the
25 early Holocene CH₄ variability.

26 Page 10, line 39. This should surely read "Fig 7" not "Fig 6"

27 → The sentences were modified as below:

28 → Given the IPD-2 is better constrained than IPD-1, we use IPD-2 curve from 9.9 to 11.5 ka interval and IPD-
29 1 for the rest of the studied period (Fig. ~~7~~6).

30 You have moved much material from SI into main text but you left duplicate figures in SI.
31 This is not needed, please remove them: Fig S1 is Fig 3; Fig S2 is Fig 5; the material in
32 Fig S3 is in Fig 8; and Fig S4 is Fig 4.

33 → Regarding the Supplement, we did not upload any material for SI, but it seems
34 that the SI of the old version of this manuscript still remains. We asked this to

Copernicus Editorial Support, and they replied us that we cannot delete the uploaded SI, but if we do not submit a new one, they will not use the old one.

Table 1: It would be useful to add a column showing the difference between the mean of the 1st measurement and the mean of the 2nd measurement, as this is the statistic that indicates that your error estimate might be OK.

→ We added a column in Table 1 showing the difference between the means of duplicate samples from the 1st and 2nd measurements The Table 1 was changes as below:

→ **Table 1. Summary of results of replicate analysis from 8 depth intervals. The rightmost two columns show the difference between the means of the first- and the second measurements. The depth difference between the first- and second replicate samples is 10 cm.**

Depth (m)	1 st measurement				2 nd measurement				Difference in means <u>1st - 2nd</u> (ppb)
	Dup.1 (ppb)	Dup.2 (ppb)	Mean <u>± 1σ</u> (ppb)	Date (dd/mm/yy)	Dup.1 (ppb)	Dup.2 (ppb)	Mean <u>± 1σ</u> (ppb)	Date (dd/mm/yy)	
523.150	634.8	634.7	634.7 <u>± 0.1</u>	27-01-14	637.5	634.3	635.9 <u>± 0.1</u>	24-02-14	-1.2
530.950	669.0	665.8	667.4 <u>± 1.6</u>	03-02-14	669.4	670.7	670.0 <u>± 0.1</u>	24-02-14	-2.6
558.295	682.5	678.2	680.3 <u>± 2.2</u>	14-03-14	687.5	678.3	682.9 <u>± 0.1</u>	02-04-14	-2.6
559.850	689.8	680.3	685.0 <u>± 4.7</u>	03-02-14	683.8	690.0	686.9 <u>± 0.1</u>	26-03-14	-1.9
561.150	687.8	689.2	688.5 <u>± 0.7</u>	14-03-14	684.0	690.4	687.2 <u>± 0.1</u>	02-04-14	1.3
562.407	687.2	685.5	686.4 <u>± 0.8</u>	26-03-14	689.4	686.4	687.9 <u>± 0.1</u>	02-04-14	-1.5
575.913	679.2	679.2	679.2 <u>± 0.0</u>	07-02-14	686.7	678.9	682.8 <u>± 0.1</u>	28-03-14	-3.6
<u>578.150</u>	<u>675.6</u>	<u>685.1</u>	<u>680.4</u> <u>± 4.7</u>	<u>04-02-14</u>	<u>676.0</u>	<u>680.7</u>	<u>678.3</u> <u>± 0.1</u>	<u>24-04-14</u>	<u>2.0</u>

1 Atmospheric methane control mechanisms during the early 2 Holocene

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7 **Abstract.** Understanding processes controlling the atmospheric methane (CH₄) mixing ratio is crucial to
8 predict and mitigate future climate changes in this gas. Despite recent detailed studies of the last ~1000 to 2000
9 years, the mechanisms that control atmospheric CH₄ still remain unclear, partly because the late Holocene CH₄
10 budget may be comprised of both natural and anthropogenic emissions. In contrast, the early Holocene was a
11 period when human influence was substantially smaller, allowing us to elucidate more clearly the natural
12 controls under interglacial conditions more clearly. Here we present new high resolution CH₄ records from Siple
13 Dome, Antarctica, covering from 11.6 to 7.7 thousands of years before 1950 AD (ka). We observe four local
14 CH₄ minima on a roughly 1000-year spacing, which correspond to cool periods in Greenland. We hypothesize
15 that the cooling in Greenland forced the Intertropical Convergence Zone (ITCZ) to migrate southward, reducing
16 rainfall in northern tropical wetlands. The inter-polar difference (IPD) of CH₄ shows a gradual increase from the
17 onset of the Holocene to ~9.5 ka, which implies growth of boreal source strength following the climate warming
18 in the northern extratropics during that period.

19 1 Introduction

20 Methane (CH₄) is a potent greenhouse gas whose atmospheric mixing ratio has increased more than 2.5 times
21 since the Industrial Revolution (Dlugokencky et al., 2009). Although lower in abundance compared to carbon
22 dioxide (CO₂), CH₄ has ~28 times higher global warming potential (GWP) on a 100 year time scale and even
23 higher GWP on shorter time scales due to its short atmospheric lifetime (Stocker et al., 2013). Hence
24 understanding the controls on atmospheric CH₄ is important to predict and mitigate future climate and
25 environmental changes.

26 Naturally, CH₄ is mainly produced from microbial decomposition by methanogens in anaerobic environments,
27 such as waterlogged soil, wetlands, or sediments of lakes and rivers. Even though a part of CH₄ is oxidized, and
28 can be emitted in the form of CO₂, a considerable amount of CH₄ is still released into the atmosphere through
29 vascular plants, diffusion and ebullition processes (e.g., Joabsson and Christensen, 2001). Other, more minor
30 sources include geological CH₄ released from mud volcanoes and gas seepages through faults (e.g., Etiope et al.,
31 2008 and references therein), pyrogenic sources such as wildfire and biomass burning (Andreae and Merlet,
32 2001; Ferretti et al., 2005; Hao and Ward, 1993), and microbial digestion by wild animals and termites (e.g.,
33 Sanderson, 1996). The CH₄ flux from the ocean to the atmosphere is considered as too small to create a
34 significant change in global budget compared to the other sources (e.g., Rhee et al., 2009). The major sink of

1 atmospheric CH₄ is photochemical reactions (oxidation) with the hydroxyl radical (OH), which is mainly
2 controlled by atmospheric temperature, humidity, and the mixing ratio of CH₄ itself and non-methane volatile
3 organic compound (NMVOC) (e.g., Levine et al., 2011 and references therein). Air temperature affects
4 humidity thereby limiting the production of OH. Oxidation of both NMVOCs and CH₄ compete for OH, that is,
5 an increase in NMVOC emission reduces the available OH, and increases the atmospheric lifetime of CH₄
6 (Valdes et al., 2005). Further, since the OH is produced by photo-dissociation reaction, the CH₄ sink strength is
7 affected by light availability and tropospheric ozone (e.g., Levy, 1971). However, recent model studies
8 suggested that CH₄ changes between glacial- and interglacial conditions were driven mostly by source changes,
9 rather than sink changes (Weber et al., 2010; Levine et al., 2011).

10 Polar firn and ice are the unique archives that preserves the ancient atmosphere for the research of fossil air
11 older than the 20th century. Paleoatmospheric CH₄ levels have been reconstructed for the last 800 ka from
12 Antarctic- and Greenland ice cores (Louergue et al., 2008). Given the relatively long lifetime in troposphere
13 (11.2 ± 1.3 years at present, e.g., Prather et al., 2012) compared to atmospheric mixing time, ice core CH₄
14 records represent well-mixed global signatures. The 800 ka record shows that past CH₄ change generally
15 followed glacial-interglacial cycles, with low concentrations during glacial periods and high concentrations in
16 interglacials, as well as the shorter orbital cycles of obliquity and precession (e.g., Spahni et al., 2005; Louergue
17 et al., 2008). Those earlier studies suggested that the changes in climate and hydrology in the tropics induced by
18 orbital forcing controlled CH₄ emissions. The resemblance between water stable isotope records from Greenland
19 ice cores, a proxy for Greenland temperature change, and global CH₄ mixing ratios on millennial time scales is
20 also well known. This implies that local temperature change around Greenland is linked to the major CH₄
21 sources in low latitudes (e.g., Brook et al., 1996; Chappellaz et al., 1993; Huber et al., 2006; EPICA Community
22 Members, 2006; Grachev et al., 2007, 2009).

23 Intensive precipitation changes in the low latitude summer monsoon regions, caused by insolation changes
24 (e.g., Asian monsoon) have been suggested as an important CH₄ control during the glacial period (e.g.,
25 Chappellaz et al., 1990). From time series analysis of past CH₄ records, Guo et al. (2012) found that the tropical
26 monsoon circulation is a primary control of relatively shorter (millennial) time scale variability, while long-term
27 (multi-millennial to orbital scale) variations are dominated by solar insolation changes. It has been found that
28 tropical monsoon activity is closely related to orbital-scale CH₄ change (e.g., Brook et al., 1996; Chappellaz et
29 al., 1990), especially Asian monsoon (e.g., Louergue et al., 2008) and South American monsoon (e.g., Cruz et
30 al., 2005). However, no direct correlation between CH₄ and tropical monsoon signals has been reported for the
31 early Holocene, although positive relationships between Greenland climate and tropical monsoon intensity (e.g.,
32 Chiang et al., 2008), as well as between Greenland climate and CH₄ (e.g., Spahni et al., 2005; Wang et al., 2005;
33 Mitchell et al., 2011) have been reported.

34 The relationship between the latitudinal shift of the ITCZ and CH₄ emissions varies with time scales. Landais
35 et al. (2010) and Guo et al. (2012) suggested that ITCZ migration is not a dominant control of glacial-
36 interglacial CH₄ cycle because long-term CH₄ trend does not follow the precessional insolation change in the
37 northern hemisphere (NH) well. Modelling studies found the southward shift of the ITCZ coincides with
38 reduced CH₄ in Last Glacial Maximum (LGM) and Heinrich Stadial (HS) events, even though changes in
39 wetland area and surface hydrology were limited (Weber et al., 2010; Hopcroft et al., 2011). These authors
40 instead suggested that changes in temperature and/or plant productivity affected CH₄ production during those

1 events. ITCZ migration does appear to be related to millennial- or sub-millennial scale CH₄ change, however.
2 Brook et al. (2000) found that sub-millennial CH₄ minima during the last deglaciation correspond with reduced
3 precipitation recorded in Cariaco Basin sediment data, which indicates southward displacement of ITCZ
4 (Hughen et al., 1996). This hypothesis is supported by spectral analysis of CH₄ during the past 800 ka record
5 that found that ITCZ change becomes an important driver of millennial scale CH₄ change (Tzedakis et al., 2009;
6 Guo et al., 2012).

7 For the Holocene, high-resolution CH₄ records from Law Dome and West Antarctic Ice Sheet (WAIS) Divide
8 ice cores in Antarctica show characteristic variability on multi-decadal to centennial time scale during the late
9 Holocene (MacFarling-Meure et al., 2006; Mitchell et al., 2011). The high-resolution records have been
10 compared with various temperature- and precipitation proxies, but previous work found no strong correlations
11 that explain the observed decadal- to centennial scale variabilities. This may be because the late Holocene CH₄
12 budget was comprised of both natural and anthropogenic terms, making it difficult to distinguish between them.
13 Mitchell et al. (2011) pointed out that some of the abrupt CH₄ decreases could have had anthropogenic causes.
14 Later, Mitchell et al. (2013) made simultaneous measurement of Antarctic (WAIS Divide) and Greenland
15 (Greenland Ice Sheet Project 2; GISP2) ice cores to derive an IPD record, and extended their high-resolution
16 records back to ~4 ka. They used eight-box atmospheric methane model (EBAMM) and anthropogenic- and
17 natural emission scenarios to investigate CH₄ control factors. Their results showed that the late Holocene CH₄
18 evolution can be explained by a combination of natural- and anthropogenic emissions. In principle, stable
19 isotope ratios of CH₄ help us to distinguish the types of sources – biogenic, pyrogenic, and geologic. Sowers
20 (2010) reconstructed the CH₄ mixing ratio and stable isotopic composition ($\delta^{13}\text{C-CH}_4$ and $\delta\text{D-CH}_4$) throughout
21 the entire Holocene. He suggested several possible control factors, such as boreal wetlands and thermokarst
22 lakes, changing C₃/C₄ plant ratio of CH₄-emitting ecosystems, and changing composition of methanogenic
23 communities. Previous studies have shown reduction of pyrogenic emission and increased agricultural emission
24 during the last millennium (Ferretti et al., 2005; Mischler et al., 2009). In later work using $\delta^{13}\text{C-CH}_4$ records
25 from North Greenland Eemian Ice Drilling (NEEM) ice core, Sapart et al. (2012) found that the centennial-scale
26 variations during the last two millennia were caused by changes in pyrogenic- and biogenic emissions.
27 Ruddiman et al. (2011) and Sapart et al. (2012) estimated CH₄ emission change due to anthropogenic land use
28 changes, which shows a good agreement with the trends from ice core measurement. ~~Since there is no high-~~
29 ~~resolution reconstruction of past population and land use area, and consequently large uncertainties of CH₄~~
30 ~~emission from land use change impede identification of any shorter scale changes.~~

31 The early Holocene is a suitable period to study natural CH₄ controls under Holocene interglacial climate
32 condition. Since there was only negligible human population and relevant CH₄-emitting anthropogenic activities
33 (e.g., Goldewijk et al., 2010; Kaplan et al., 2011) during this time, the early Holocene CH₄ changes must have
34 occurred mostly due to natural causes. Understanding natural controls could contribute to better constraints on
35 human-induced CH₄ changes. However, high-resolution studies that covers the entire early Holocene have not
36 been carried out extensively so far, except for studies of the prominent cooling event at ~~8.2 ka~~~~2000 years BP~~
37 (Spahni et al., 2003; Kobashi et al., 2007; Ahn et al., 2014). ~~Although~~~~Despite~~ Rhodes et al. (2015) reported a
38 very high-resolution record from WAIS Divide ice core that extends from the last glacial period to the earliest
39 Holocene (~9.8 ka), the authors do not deal with the early Holocene CH₄ variability. Earlier studies mainly
40 focused on long-term change, attributing the major control to low latitude hydrology based on regional climate

1 records that show wetter climate in tropics during the early Holocene (Blunier et al., 1995; Brook et al., 2000;
2 Chappellaz et al., 1993, 1997). Therefore, in this study we present a new high-resolution CH₄ record from the
3 early Holocene and investigate natural control mechanisms under interglacial condition. It should be noted that
4 environmental boundary conditions of the early Holocene were not identical to those of the late Holocene.
5 Global sea level rose throughout the early Holocene while remnant ice sheets in North America disappeared.

6 **2 Materials and Methods**

7 In this study we used ice samples from the Siple Dome deep ice core (SDMA) drilled from 1997 to 1999 on
8 the Siple Coast, West Antarctica (81.65°S, 148.81°W; 621 m elevation) (Taylor et al., 2004). The SDMA
9 samples were collected and cut at National Ice Core Laboratory (NICL, Denver, Colorado, USA) from January
10 to February of 2013. The brittle zone of SDMA ice starts below 400 m and continues to the bottom of the core at
11 1004 m (Gow and Meese, 2007) and samples from this region are more likely to be fractured. Hence, the
12 samples were carefully collected from unbroken subsections during sample preparation at NICL. The samples
13 were packed in insulated foam boxes with numerous eutectic gels, and shipped to South Korea via expedited
14 airfreight. Temperature loggers showed the temperatures were maintained below -25°C. The boxes were picked
15 up directly just after custom clearance at the airport and then the ice samples were stored in a walk-in freezer at
16 Seoul National University (SNU, Seoul, South Korea) that was maintained below -20°C. We measured 295
17 individual ice samples from 156 depth intervals from 518.87 to 718.83 m, covering from 8.36 to 20.25 ka after
18 synchronizing to the Greenland Ice Core Chronology 2005 (GICC05, Rasmussen et al., 2006), of which 256 ice
19 samples from 120 depth intervals from 518.87 to 623.38 m are used in this study. All samples were duplicated,
20 so that our final CH₄ data were presented by averaging the results of duplicate analysis from the same depth.
21 The analytical uncertainty of our data set is estimated by the uncertainty of individual ice measurement divided
22 by square root of 2 (see below). We rejected data that show difference between duplicate measurements larger
23 than 10 ppb, and 9 data points were rejected in the studied period. The results of SNU measurement (111 points)
24 are plotted in Figure 1. The 16 samples from 8 depths were used for reproducibility check on different days
25 (Table 1). The air occluded in ice was extracted by a melting and refreeze process under vacuum. Ice samples
26 were prepared in a walk-in freezer in the morning of each experiment day, the outermost >2 mm was trimmed
27 off to eliminate potential contamination by ambient air during the storage. The samples were then moved to the
28 laboratory and placed in glass sample containers. The sample flasks were custom-made glass flasks welded to
29 stainless steel flanges, and attached to the vacuum line with copper gaskets. The sample flasks were partially
30 submerged in a chilled ethanol bath while being attached to the vacuum line. Flasks were evacuated for at least
31 40 minutes, then the ice samples were melted by submerging the sample flasks in a warm water bath. Melting
32 was usually completed within 30 minutes. The sample flasks were then submerged in the cold ethanol bath
33 chilled to around -82°C for more than an hour to refreeze. During refreezing, we carried out daily calibration of
34 the gas chromatograph system, normally taking ~90 minutes. The ethanol temperature normally rose to -55°C
35 just after submerging the flasks, and recovered to -65°C before expansion of the air in the flasks. The extracted
36 air in the headspace was expanded into the evacuated vacuum line and sample loop of a gas chromatograph (GC)
37 equipped with a flame ionization detector (FID) to measure CH₄ mixing ratio. After detecting the CH₄ peak in
38 the GC chromatogram (retention time of ~1.6 minutes), the vacuum line and sample loop is evacuated again

1 prior to the next injection. The GC linearity was tested by a series of inter-tank calibration using four working
2 standard air cylinders (395.5, 721.3, 895.0, and 1384.9 ppb CH₄ on NOAA04 scale, Dlugokencky et al., 2005).
3 A daily GC calibration curve was determined by measurements of a working standard having the closest CH₄
4 mixing ratio of expected value from the samples; in this study, we used the 721.3 ppb CH₄ standard for samples
5 of the early Holocene. We calibrated with a standard air six times before and after sample measurements. The
6 detailed configuration of the vacuum line and GC is described in another paper (Yang et al., in preparation).

7 Different solubilities of each air component cause preferential dissolution during melting procedure. As the
8 solubility of CH₄ is higher than the other major components of air – nitrogen (N₂), oxygen (O₂), Argon (Ar), the
9 CH₄ mole fraction of the extracted air is lower than originally enclosed air (solubility effect). The CH₄ mole
10 fraction of air enclosed in ice sample is estimated from residual gas fraction and CH₄ mixing ratio in air
11 remained in refrozen meltwater (retrapped air). Residual gas fraction is a measure of how much air is retrapped
12 during refreeze, which is defined as ratio of amount (pressure) of air extracted from the 2nd gas extraction to the
13 1st extraction. The 2nd gas extraction was carried out using leftover refrozen meltwater samples after the 1st
14 extraction finished. Mean residual gas fraction is $1.05 \pm 0.13\%$ (1σ , $n = 60$) for SDMA ice samples and $0.38 \pm$
15 0.08% (1σ , $n = 40$) for bubble-free ice. The test with ice samples from Styx glacier, Antarctica revealed that
16 CH₄ mixing ratio in retrapped air is enriched 3.1 times ($n = 12$) for glacial ice and 3.0 times ($n = 7$) for bubble-
17 free ice. Then the solubility effect is corrected by using a simple mass balance calculation.

18 Daily systematic offset correction was applied to account for the daily-varying system condition. To do this,
19 we measured four bubble-free ice samples every day with SDMA ice samples. The experimental procedures for
20 the bubble-free ice were identical to the SDMA ice. After the sample flasks are evacuated, standard air is
21 injected into the flasks containing bubble-free ice, so that it returns similar air pressure to the typical size of
22 SDMA ice when the extracted air inside the bubble-free ice flasks is expanded into the sample loop. The
23 solubility correction for the bubble-free ice was done by the same formula as SDMA ice samples, but using
24 different residual gas fraction. After corrected for solubility effect, the daily systematic offset is calculated by
25 difference between CH₄ mixing ratio of the injected standard air and results from the four flasks containing
26 bubble-free ice. The systematic offset ranges from 5 to 15 ppb during the SDMA measurement period. A daily
27 offset is subtracted from the ice samples corrected for gas solubility effect. This is one of the major differences
28 with OSU wet extraction system, where the systematic offset is interpolated from the results of blank tests
29 carried out between several days (Mitchell et al., 2011).

30 The bubble-free ice was made by chilling the degassed ultrapure water (resistivity $>18.2 \text{ M}\Omega\text{-cm}$ at 25°C)
31 slowly from the bottom in a closed stainless steel chamber. From gas extraction test using our bubble-free ice
32 without injecting standard air, we observed that no significant pressure increase at the pressure gauge with a
33 detection limit of 0.01 Torr (corresponding to less than 0.03% of sample air pressure in the extraction line) after
34 melting-refreezing the bubble-free ice. Mass dependent (gravitational) fractionation within the firn (Craig et al.,
35 1988; Schwander, 1989) was corrected by using the nitrogen isotope ratio ($\delta^{15}\text{N}$) of atmospheric N₂ occluded in
36 bubbles. Siple Dome $\delta^{15}\text{N}$ records show a mean enrichment of $0.23 \pm 0.01\%$ during the early Holocene
37 (Severinghaus et al., 2009) and result in a slight decrease of CH₄ by 1.97 ± 0.15 ppb, which we applied to all of
38 our measurements.

39 Here we consider two types of uncertainty sources: uncertainty in (1) estimating daily systematic offset and (2)
40 other causes. The former indicates uncertainty of the daily systematic offset ($e1$). As the daily systematic offset

1 is calculated from the mean of the four flasks with bubble-free ice and standard air, scattering of the bubble-free
2 ice samples can induce uncertainty in the systematic offset correction. The daily $e1$ is estimated with standard
3 error of the mean (SEM, $n = 4$), because the daily systematic offset is calculated from the mean of the four
4 bubble-free ice samples. The average of daily $e1$ is 1.9 ppb. The latter ($e2$) includes uncertainty due to solubility
5 correction and inhomogeneous distribution of CH_4 . Given our solubility correction uses the mean value of
6 residual gas fraction and the ratio at which CH_4 enriches in retrapped air, different solubility effect and/or
7 inhomogeneous CH_4 distribution in individual ice causes offset between adjacent duplicate ice samples analysed
8 on the same day. As the duplicates from same depths were measured on the same day, we estimated the $e2$ with
9 pooled standard deviation (PSD) between duplicate measurements from entire depths, which yields 3.3 ppb.
10 Taking the $e1$ and $e2$ into account together, the final uncertainty of individual measurement is given as 3.8 ppb
11 by error propagation. The uncertainty for the mean of duplicate results is obtained by dividing the individual
12 uncertainty by square root of 2, yielding 2.7 ppb. Further details on the correction method is found in our
13 manuscript in preparation (Yang et al., in preparation).

14 We made additional measurements using adjacent samples (depth difference of 10 cm) at randomly selected 8
15 depth intervals to examine reproducibility and long-term stability of our system. The second measurements of
16 duplicates were performed 8 to 80 days after the first analysis. Table 1 displays quadruplicate results at each
17 depth. PSD between the mean of duplicate analyses of the first and second measurements on different days
18 yields 1.1 ppb. The good agreement between duplicate means indicates good reproducibility of our system. In
19 the meanwhile, PSD of the quadruplicate measurements is 3.0 ppb, which is similar to PSD of duplicate samples
20 for the entire data set (3.3 ppb).

21 To check reliability of the record we compared our data set with previous SDMA measurements at Oregon
22 State University (OSU) for 8.4 to 9.1 ka period when the two records overlap. The OSU CH_4 record was
23 measured with a temporal resolution of 8 years with precision of 2.8 ppb (Mitchell et al., 2011; Ahn et al., 2014).
24 The average offset between the two data sets is 0.1 ppb, which lies within analytical uncertainty range of data
25 sets. Therefore, we created a composite record by using the OSU data for 499.49 – 537.20 m interval (7.6 to 9.0
26 ka) because mean temporal resolution of OSU data (~22 years) is lower than SNU data (~37 years) during this
27 period (Fig. 1). Our new SDMA CH_4 composite data have mean temporal resolution of ~26 years. The WAIS
28 Divide continuous CH_4 records show much higher resolution (~2 years), but does not cover the entire early
29 Holocene period (Rhodes et al., 2015).

30 **3. Result and Discussion**

31 **3.1 Millennial scale variability**

32 We carried out spectral analysis of SDMA composite record using the REDFIT program (Schulze and
33 Mudelsee, 2002). Moderate (over 90% significance level) spectral power was found at ~1340, 401, 309, and 96-
34 year periods. Given the ~42 years of gas age distribution of SDMA (Ahn et al., 2014), it would not reliable to
35 study centennial scale variability. Therefore, we smoothed the data by a 250-year running average to remove
36 centennial- to multi-centennial scale components and then detrended by a high-pass filter with a cut off period
37 of 1800 years to isolate millennial scale variability. For comparison, the same processing scheme was applied to

1 WAIS Divide time series and we observed that Siple Dome and WAIS Divide CH₄ anomalies share similar
2 millennial scale variability, confirming the reliability of both our data and observed millennial scale changes
3 (Fig. 2).

4 The high-pass filtered CH₄ time series demonstrates millennial scale minima at ~8.2, 9.3, 10.2 and 10.9 ka,
5 which occurred with nearly 1000-year spacing. The REDFIT results for 7.6 to 11.2 ka interval that excludes [the](#)
6 [Preboreal Oscillation \(PBO\)](#) shows moderate (80% significance level) powers at ~731 and 430 (860)-year
7 periods. Each minimum is accompanied by depletion of water stable isotope ratio ($\delta^{18}\text{O}_{\text{ice}}$) from North
8 Greenland Ice Core Project (NGRIP) ice core, which implies climate cooling in Greenland. A close relationship
9 between CH₄ and Greenland $\delta^{18}\text{O}_{\text{ice}}$ has been previously reported in glacial-interglacial cycles and Dansgaard-
10 Oeschger (DO) events during the last glacial period (e.g., Brook et al., 1996, 2000; Blunier and Brook, 2001;
11 Chappellaz et al., 1993, 2013; EPICA Community Members, 2006). However, it has not been confirmed for
12 interglacial climate conditions during the Holocene. Mitchell et al. (2011) found no significant correlation with
13 Greenland climate in multi-decadal scale during the late pre-industrial Holocene (LPIH), possibly because LPIH
14 CH₄ budget is also affected substantially by anthropogenic emissions (e.g., Ferretti et al., 2005; Mischler et al.,
15 2009; Mitchell et al., 2013; Sapart et al., 2012). In contrast, we observe a significant positive correlation ($r =$
16 0.57 , $p = 0.06$) between the millennial-scale change of Siple Dome CH₄ and NGRIP $\delta^{18}\text{O}_{\text{ice}}$ during the early
17 Holocene. The correlation coefficient between the smoothed- and filtered time series of SDMA CH₄ (before
18 synchronization to GICC05) and NGRIP $\delta^{18}\text{O}_{\text{ice}}$ was calculated for the 7.8 - 11.5 ka by interpolating to the
19 original ages of SDMA CH₄ composite, with a reduced degree of freedom.

20 The gas chronology of SDMA was developed based on CH₄ and $\delta^{18}\text{O}$ of air ($\delta^{18}\text{O}_{\text{atm}}$) correlation
21 (Severinghaus et al., 2009). In this study, we improved the chronology by synchronization of the previous
22 chronology to GICC05 age scale by setting 3 age tie-points with stable water isotope ($\delta^{18}\text{O}$) record from the
23 ~~North Greenland Ice Core Project (NGRIP)~~ ice cores during the abrupt climate change events of ~~the Preboreal~~
24 ~~Oscillation (PBO)~~ and the 8.2 ka event, given that both events have been proved to be synchronous with CH₄
25 change (Kobashi et al., 2007, 2008). Ages between tie-points were inferred by linear interpolation of the age
26 offset of nearest tie-points, which range from -114 to 28 years. After synchronizing to the GICC05 scale, the
27 correlation coefficient between SDMA CH₄ composite and the NGRIP $\delta^{18}\text{O}_{\text{ice}}$ increases to $r = 0.74$ ($p < 0.01$) It
28 implies that natural CH₄ budget is closely connected with Greenland climate on millennial timescales, even
29 though this conclusion is less robust as there is no age tie-points between the 8.2 ka episode and PBO (Fig. 3).
30 The positive correlation implies that the natural CH₄ budget is connected with Greenland climate on millennial
31 timescales.

32 The uncertainty of the modified chronology was examined by comparing with a tentative age scale
33 determined by CH₄ correlation with NEEM CH₄ discrete measurement data. NEEM CH₄ data follow
34 GICC05modelext-NEEM-1 scale (Rasmussen et al., 2013). The detailed method for CH₄ correlation is
35 described in Section 3.2. The age difference between the two chronologies is plotted in Figure 4, showing the
36 maximum age difference of 105 years. In addition, we include the maximum layer counting uncertainty of 99
37 years (Rasmussen et al., 2006) and delta-age uncertainty of 30 years (Rasmussen et al., 2013) during the early

1 Holocene. Therefore, error propagation of the above three errors indicate that the maximum error of SDMA gas
2 age used in this study is ~147 years.

3 According to atmospheric modelling studies, abrupt cooling in the North Atlantic regions can alter
4 atmospheric circulation and to cause southward migration of the mean latitudinal position of the ITCZ (e.g.,
5 Chiang and Bitz, 2005; Broccoli et al., 2006; Cvijanovic and Chiang, 2012). Climate proxies demonstrate the
6 climatic teleconnection between northern North Atlantic and low latitude regions. Sediment reflectance record
7 from Cariaco Basin shows increased rainfall and humidity – which is due to southward displacement of ITCZ –
8 corresponding to the 8.2, 9.3, and 10.9 ka abrupt cooling event, as revealed in previous studies for the different
9 time periods (Peterson et al., 2000; Haug et al., 2001; Fleitmann et al., 2007; Deplazes et al., 2013). The
10 southward displacement of the ITCZ leads further weakening of Asian and Indian summer monsoons and
11 probably reduces CH₄ emission from northern tropical wetlands. The ¹⁸O enrichment in speleothems from
12 Dongge Cave (China), Qunf Cave (Oman), and Hoti Cave (Oman, not shown, Neff et al., 2001) occurred at
13 similar timing with abrupt cooling in Greenland at 8.2, 9.3, and 10.9 ka, which indicates the reduction of
14 monsoonal rainfall in northern tropical wetlands. The speleothem records from Chinese and Oman caves seem
15 to lag by ~100 – 200 years after the CH₄ change at ~9.3 ka, but this lies within chronological uncertainties of
16 ~200 – 400 years at around ~9.0 ka (Dykoski et al., 2005; Fleitmann et al., 2007). Moreover, sediment Ba/Ca
17 ratio from Gulf of Guinea demonstrates concurrent decrease of West African monsoon (Weldeab et al., 2007).
18 In contrast, an inverse relationship is observed from the Eastern Brazilian speleothem data (Lapa Grande Cave,
19 Strikis et al., 2011) that suggest an increase in precipitation at the time of abrupt CH₄ decreases. Rhodes et al.
20 (2015) pointed out that strong southward migration of the ITCZ could induce an abrupt CH₄ increase from
21 southern hemisphere (SH) during the HS 1, 2, 4, and 5 events. Sperlich et al. (2015) also suggested that a sharp
22 CH₄ peak at Greenland Interstadial 21.2 (~85 ka) was caused by emission from Asian and Amazon wetlands.
23 However, considering the orbital parameters that indicate maximum summer insolation in NH while minimum
24 in SH during the early Holocene, it can be inferred that contribution of SH wetland emission was relatively
25 weak and overcompensated by reduction of NH emission.

26 The possibility that the observed CH₄ minima were caused by reduction of northern extra-tropical sources is
27 not supported by previous modelling studies. Zürcher et al. (2013) found that abrupt cooling in Greenland and
28 northern high latitudes by large freshwater input to the North Atlantic causes boreal peatland CH₄ emission to
29 decrease substantially, which can explain ~23% of abrupt CH₄ decrease (~80 ppb) during the 8.2 ka event.
30 Given the meltwater pulses during the early Holocene before the 8.2 ka event were probably much weaker
31 (Teller and Leverington, 2004) than that corresponding to the 8.2 ka event, we suggest that boreal emission
32 change is not the major cause of the CH₄ local minima.

33 Previously, Björck et al. (2001) found that climate cooling in the northern Atlantic and Santa Barbara Basin
34 occurred associated with a change in solar-forcing at ~10.3 ka. However, the proxy data in Figure 2 show no
35 clear indication of southward migration of the ITCZ and changes in Asian, Indian, African, and South American
36 summer monsoon intensity associated with the ~10.2 ka cooling and CH₄ decrease. (Fig. 2b-f). Furthermore,
37 speleothem $\delta^{18}\text{O}$ records from Mawmluh Cave (not shown) show no weakening of the Indian monsoon
38 (Berkelhammer et al., 2012), and there was no distinct change in $\Delta\epsilon_{\text{LAND}}$, a proxy of global terrestrial respiratory
39 fractionation of atmospheric O₂ at this time, which is affected by low latitude surface hydrology (Severinghaus

1 et al., 2009). These evidences suggest that precipitation and surface hydrology in the northern tropics may have
2 not changed significantly during around the 10.2 ka. Instead, there are two small decreases at ~9.9 and ~10.6 ka
3 as shown in Dongge cave deposit record (Fig. 2d), but it is difficult to tell, given dating uncertainties, if these
4 events correlate with the 10.2 ka cooling. Although there appears to have been no strong change in low latitude
5 hydrology at 10.2 ka, the amplitude of CH₄ decrease at 10.2 ka is similar order to the other millennial events.
6 Given that no clear reduction of the Asian, Indian, and African monsoon intensity is observed, it is possible that
7 the CH₄ decrease at 10.2 ka was controlled by other processes, outside of the northern tropics.

8 Previous studies have suggested an important role of solar forcing during the Holocene (e.g., Björck et al.,
9 2001; Bond et al., 1997, 2001). Bond et al. (1997) reported four large ice-rafted debris (IRD) drifts occurred at
10 ~8.1, 9.4, 10.3 and 11.1 ka caused by surface cooling of North Atlantic Ocean. They found that the ocean
11 surface cooling and the IRD events are closely related to cooling over the Greenland. Figure 2 shows that each
12 IRD event (maxima in hematite stained grain) occurred concurrently with minima of NGRIP $\delta^{18}\text{O}_{\text{ice}}$ record
13 within age uncertainty. We postulate that the Greenland cooling leads to southward shift of the ITCZ and in turn
14 it changes wetland CH₄ emission in low latitudes. Bond et al. (2001) found that IRD maxima during the
15 Holocene coincide with solar activity minima and suggested that solar forcing could affect the climate change
16 around the North Atlantic Ocean (and Greenland), through amplification by changes in sea ice and/or deep
17 water formation. A close interplay between solar activity and monsoon intensity has been observed in previous
18 studies using the Chinese and Oman speleothem records during the Holocene (Neff et al., 2001; Wang et al.,
19 2005; Gupta et al., 2005), even on multi-decadal time scales (Agnihotri et al., 2002). However, the forcing
20 mechanism of solar activity on the North Atlantic and global climate is not well understood. Jiang et al. (2015)
21 found positive correlations between North Atlantic SST and solar forcing inferred from paleo-proxies (¹⁴C and
22 ¹⁰Be) for the last 4000 years, although the correlation disappears during the mid- and early Holocene. They
23 hypothesized that climate sensitivity to solar forcing is high for cooler climate. The above evidence suggests that
24 the early Holocene CH₄ minima may be linked to anomalies in solar activity, but future study is needed to make
25 it more conclusive.

26 Meanwhile, a shift to an El Niño-like SST state was suggested as another mechanism that changes tropical
27 rainfall patterns (Marchitto et al., 2010). According to modern atmospheric observations, El Niño conditions
28 lead to drying conditions in low latitude wetlands in Africa, Asia, and the Americas (e.g., Dai and Wigley, 2000;
29 Lyon and Barnston, 2005; Hodson et al., 2011), which reduces tropical CH₄ emissions. Thus, we could
30 speculate that both the ITCZ migration and El Niño-like SST change affected the tropical surface hydrology and
31 CH₄ emission. According to Holocene ENSO activity reconstructions by Moy et al. (2002), no ENSO event was
32 recorded during the early Holocene until around 7 ka, except weak ENSO events during 10.4 – 10.1 ka, where
33 we observe a CH₄ drop apparently unrelated to monsoon proxies. Mitchell et al. (2011) observed a significant
34 positive correlation between CH₄ and Pacific Decadal Oscillation (PDO) variability during the late Holocene. It
35 has been reported that PDO modulates the wet/dry impact of ENSO depending on phase relationship between
36 ENSO and PDO (e.g., Wang et al., 2014 and references therein). Using a Holocene PDO reconstruction from
37 sediment grain size analysis by Kirby et al. (2010) shows PDO-related drying intervals in North America during
38 9.5 – 9.1, 8.9 – 8.6, and 8.3 – 7.8 ka, which overlap the CH₄ minima at 8.2 and 9.3 ka present in this study.

3.2 Inter-polar difference of CH₄ during the early Holocene

We calculated the inter-polar difference (IPD) of CH₄ to trace the latitudinal source distribution change during the early Holocene. The currently available high-resolution CH₄ records covering the early Holocene are SDMA discrete (this study), WAIS Divide discrete (WAIS Divide project members, 2015), WAIS Divide continuous (Rhodes et al., 2015), NEEM discrete (Chappellaz et al., 2013) and NEEM continuous data (Chappellaz et al., 2013). Among the Antarctic records, we consider WAIS continuous records most reliable from ~9.9 to 11.5 ka interval. For the rest of the studied period, SDMA discrete records are better constrained than WAIS discrete data, because SDMA records have better analytical precision, as well as comparison with OSU measurements reveals a minimal offset for the early Holocene interval. Before IPD calculation, WAIS continuous data were calibrated to SDMA data, given the discrete measurements generally have better accuracy than continuous ones. Regarding the Greenland side, we use NEEM discrete records because not only there are discrepancies between continuous- and discrete data in some intervals, but also because NEEM discrete records were measured by similar wet extraction technique at OSU (Chappellaz et al., 2013).

Precise synchronization is crucial for direct comparison between data sets which have high frequency variations. For synchronizing between Antarctic (Siple Dome and WAIS Divide continuous) and NEEM records, the NEEM CH₄ record (~11 years resolution on average) is chosen as reference. Synchronization was done by two steps: First, we made initial synchronization between the Antarctic and NEEM data by setting match points at the midpoint of abrupt CH₄ change, and then we linearly interpolated the age offset of each match point for the rest of data points. Then we applied a Monte Carlo simulation to find a maximum correlation. Both data sets were resampled every 30 years, and each point was randomly perturbed (assuming a normal distribution with 1 sigma of 30 years). By doing so 1000 different time series were created, and the set having a maximum correlation with NEEM data was chosen. Criteria for “best fit” is correlation coefficient of 0.8 with NEEM original age scale, so that a maximum correlation less than 0.8 was discarded. This procedure was repeated to make 20 sets of maximum correlation time series, and the mean ages of 20 replicate simulations were set to synchronized age scale. The uncertainty range of IPD was calculated from synchronization uncertainty and CH₄ data uncertainty. To estimate synchronization uncertainty, we created 20 IPDs from the 20 sets of maximum correlation time series, and the standard deviation of the 20 records was taken as synchronization uncertainty for each of the data points. The CH₄ data uncertainty was estimated with the stated uncertainty of each data set (4.3 ppb for NEEM discrete / 2.7 ppb for SDMA / 1.5 ppb for WAIS continuous, 1 sigma). To check the sensitivity of the uncertainties, we carried out Monte Carlo simulations. We produced 1000 different sets of IPD, which vary randomly with Gaussian propagation in their ages and CH₄ concentration uncertainties. Each IPD was annually interpolated and smoothed by a 1/1000 year⁻¹ low-pass filter. The cut-off frequency of 1000 years was chosen to examine multi-centennial to millennial scale change, because the IPD calculation is very sensitive to high frequency variability of CH₄ records from both poles. To report 95% confidence interval, we multiplied the standard deviation by 1.96 and enveloped the IPD.

Figure 6 displays the IPDs calculated from various pairs of data set with 95% significant interval. The two IPD records derived from most reliable data sets are plotted in red (NEEM discrete – Siple Dome, IPD-1 hereafter) and green (NEEM discrete – WAIS continuous, IPD-2 hereafter). Both IPD-1 and IPD-2 show a long-term increase from 11.5 to 9.9 ka, which indicates that boreal source contribution enhanced. However, IPD-1

1 shows a sharper increase during the PBO followed by decrease until ~10.7 ka, and in the latter case both IPDs
2 differ beyond 95% envelope (from 10.4 to 10.8 ka). Although these differences are significant, and are probably
3 due to small errors in the time scale and absolute concentrations differences, for example, due to uncertainties in
4 blank corrections or solubility corrections, or core quality, they do not affect our basic interpretation of the
5 trends. Instead, we combined the two IPDs to resolve this. Given the IPD-2 is better constrained than IPD-1, we
6 use IPD-2 curve from 9.9 to 11.5 ka interval and IPD-1 for the rest of the studied period (Fig. 76). The
7 combined IPD shows ~13 ppb increase from 11.5 to 9.5 ka. It displays similar trend with the NH extratropical
8 (30°N – 90°N) temperature reconstruction (Marcott et al., 2013) and the modelled CH₄ emission from boreal
9 thermokarst lakes (Walter et al., 2014), indicating that NH extratropical source strength increased during this
10 period.

11 To quantify the source strength of low- and high latitude sources, we employed a simple 3-box CH₄ source
12 distribution model used in previous studies (Chappellaz et al., 1997; Brook et al., 2000). Briefly, the model
13 contains 3 boxes; northern extra-tropical latitude (30°N – 90°N, N-box), tropical (30°S – 30°N, T-box), and
14 southern extra-tropical latitude boxes (30°S – 90°S, S-box). CH₄ mixing ratios in 3 boxes (in Tg box⁻¹) were
15 determined from CH₄ mixing ratio of Antarctica and Greenland. The mean CH₄ mole fraction of N-box (30°N –
16 90°N) is not identical to that of Greenland ice core record, given the latitudinal CH₄ distribution (e.g., Fung et
17 al., 1991). To derive the N-box CH₄, we followed the assumption of Chappellaz et al. (1997), where the authors
18 assumed that difference between Greenland and the mean N-box CH₄ is 7% of IPD. Hence here the N-box CH₄
19 is calculated by subtracting 7% of IPD from the Greenland mixing ratio. T-box mixing ratio is inferred by
20 assuming that the S-box emission is constant of 15 Tg yr⁻¹ (Fung et al., 1991). Emission from each box (Tg yr⁻¹)
21 is then estimated by using the mixing ratios of the boxes, lifetime of CH₄ in each box, and transport times
22 among the boxes. Following Chappellaz et al. (1997), we assume the lifetime of 18.7, 8.1, and 26.8 years in N,
23 T, and S-box, respectively, and transport time of 9 months. The modelled emission changes are plotted in Figure
24 8. The model results reveal that tropical sources decrease (accounting for the largest portion in CH₄ budget),
25 while NH extratropical emissions increase. The T-box emission is reduced from ~118 Tg yr⁻¹ to ~109 Tg yr⁻¹,
26 and the N-box source strength increases from ~60 Tg yr⁻¹ to ~71 Tg yr⁻¹ during the 11.5 – 9.5 ka interval (Fig. 8).
27 The long-term decrease of tropical emission follows the NH summer insolation change. This covariation may
28 reflect the insolation-driven changes in emissions on multi-millennial timescale (e.g., Loulergue et al., 2008;
29 Guo et al., 2012). Also plotted in Figure 8 is the boreal source fraction, defined as ratio of N-box emission to
30 total source emissions, showing 5% increase (from 31.5 to 36.5%) during the same interval. The box model
31 results at 9.0, 9.5, and 11.5 ka time slices are summarised in Table 2.

32 Our results are supported by proxy-based temperature reconstructions that indicate a gradual warming in
33 northern extratropical regions (30°N – 90°N) until ~9.6 ka, while tropical temperature remains stable (Marcott
34 et al., 2013). The climate warming in northern high latitudes caused ice sheet retreat (e.g., Dyke, 2004) and may
35 have enhanced CH₄ emission by forming new wetlands in permafrost regions (e.g., Gorham et al., 2007; Yu et
36 al., 2013) and accelerating microbial decomposition of organic material (e.g., Christensen et al., 2004; Schuur et
37 al., 2015). Thermokarst lakes created by thawing ice wedges and ground ice in Alaskan- and Siberian
38 permafrost has been suggested as a source of CH₄ (e.g., Walter et al., 2006, 2007; Brosius et al., 2012). The
39 modelled enhancement of NH extratropical emission of ~11 Tg yr⁻¹ is similar to the CH₄ release of 8.2 Tg yr⁻¹
40 from thermokarst lake thawing, which is estimated based on present-day observations (Walter et al., 2014).

1 Since most thermokarst lakes are located in NH high latitude regions (e.g., Walter et al., 2006, 2014), it may
2 support the box model results. Our results are consistent with previous findings based on CH₄ stable isotope
3 analysis. Fischer et al. (2008) found that increase of boreal source contribution is required to explain the more
4 depleted $\delta^{13}\text{C-CH}_4$ during Preboreal period than the Younger Dryas interval. Sowers (2010) extended the CH₄
5 isotopic ratio into the entire Holocene and showed a gradual decrease of $\delta^{13}\text{C-CH}_4$ by ~2‰ from 10.5 to 4 ka,
6 which was attributed to progressive expansion of NH high latitude sources.

8 **4. Conclusion and summary**

9 We reconstructed a new high resolution CH₄ record during the early Holocene from Siple Dome ice core,
10 Antarctica, to study millennial CH₄ variability and its natural controls under Holocene interglacial condition.
11 The new Siple Dome record agrees well with previous records measured at OSU within analytical uncertainty,
12 showing a mean difference of 0.1 ppb. By combining the two data sets, we present a SDMA CH₄ composite
13 record covering from ~7.7 to 11.6 ka. We observed four millennial scale CH₄ minima having 10–20 ppb of
14 amplitude with 300–400 years duration. It is found that these CH₄ minima were accompanied with Greenland
15 cooling, changes in ITCZ position and reduced Asian and Indian monsoon intensities. The observed evidences
16 suggest that low latitude hydro climate changes were closely related to millennial scale CH₄ minima. Further,
17 this study presented the millennial scale change of IPD, which was calculated from high resolution discrete data
18 set of NEEM and SDMA, and a continuous record of WAIS Divide. Here we reported that the IPD increased by
19 ~13 ppb from the onset of the Holocene to ~9.5 ka following the temperature rise in NH extra-tropical regions.
20 The three-box model demonstrates that NH extratropical emissions elevated by ~11 Tg yr⁻¹, while tropical
21 emission was reduced by ~9 Tg yr⁻¹, resulting the increased contribution of the NH extra-tropical sources by
22 ~5%.

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34 **Data availability**

35 The early Holocene Siple Dome CH₄ data will be available on NOAA Paleoclimatology database and
36 PANGAEA data repository.

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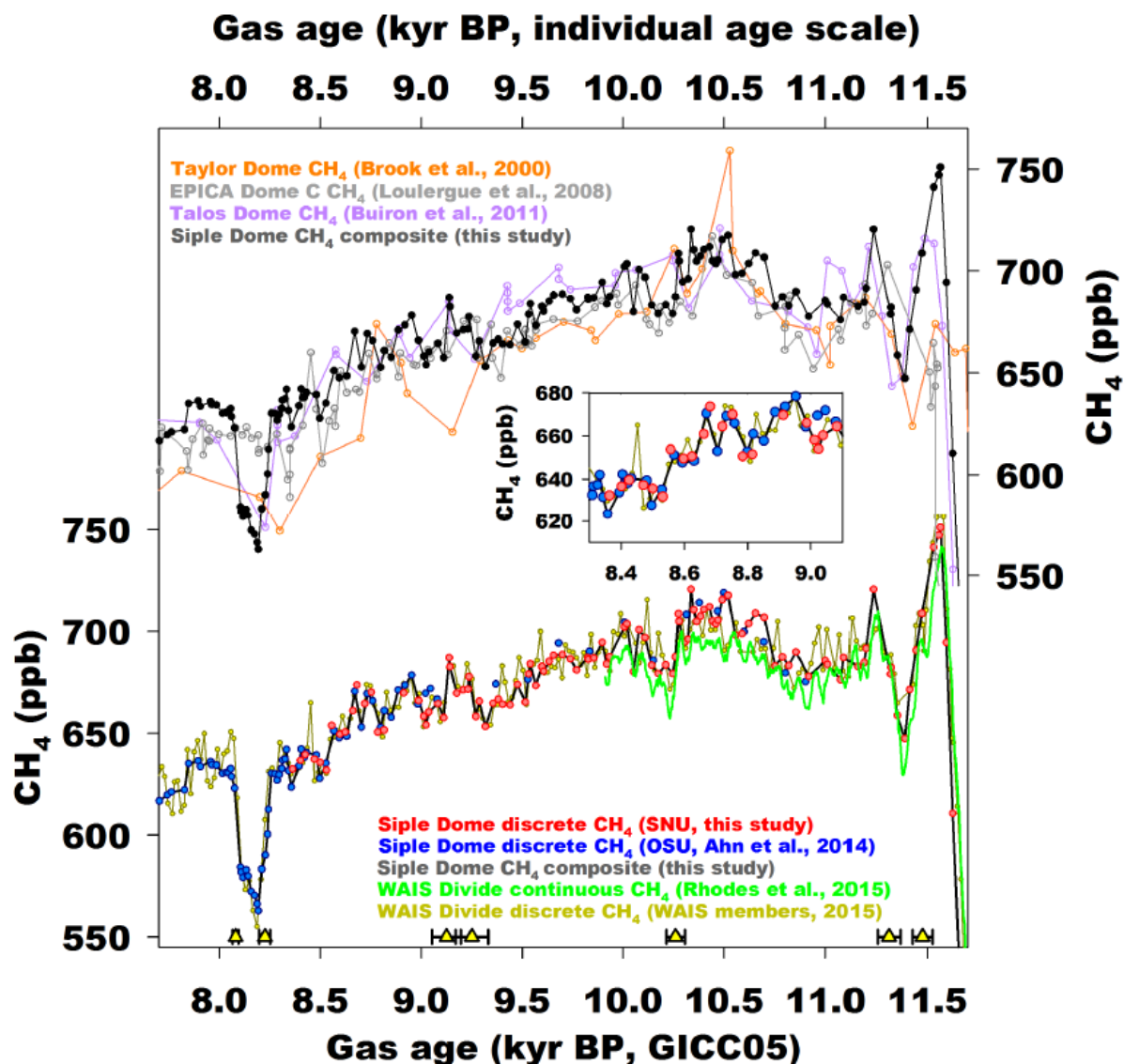
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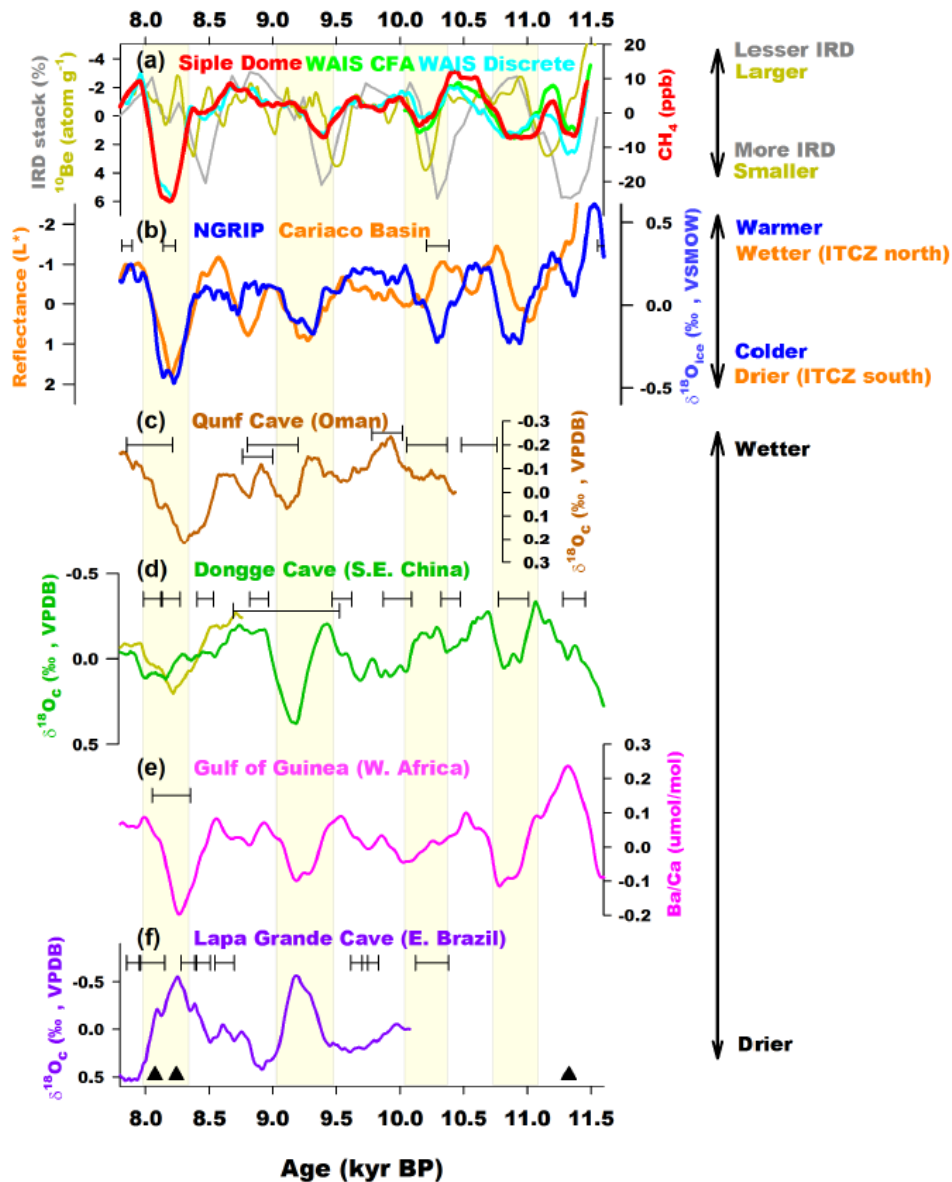
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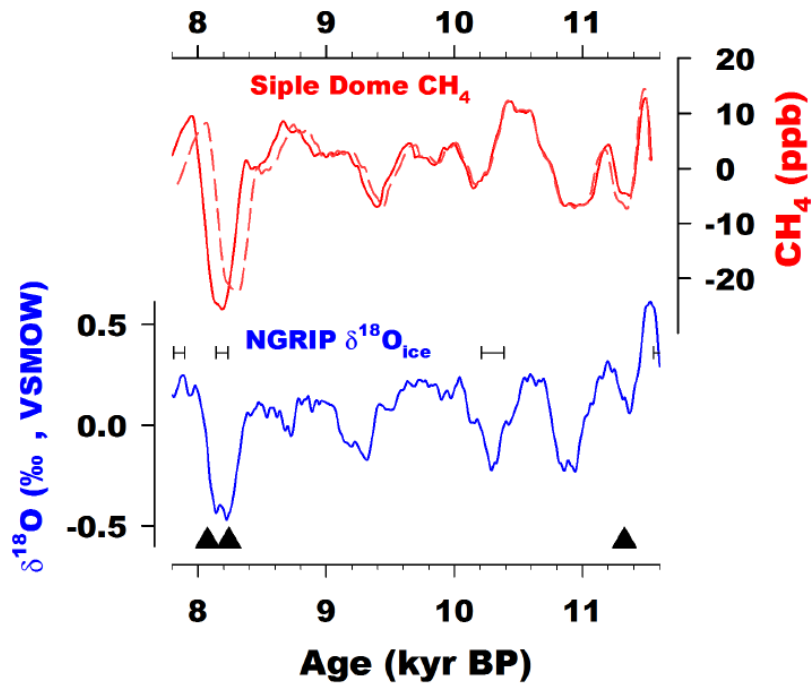
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1
2 Figure 1. Atmospheric CH₄ concentration reconstructions during the early Holocene. Top: new high-
3 resolution Siple Dome composite (black, this study and Ahn et al., 2014) compared with previous records
4 from Taylor Dome (orange, Brook et al., 2000), EPICA Dome C (grey, Loulergue et al., 2008), and Talos
5 Dome (purple, Buiron et al., 2011²). Bottom: Siple Dome CH₄ records measured at OSU (blue, Ahn et al.,
6 2014) and SNU (red, this study). Siple Dome composite (black line) is plotted with WAIS Divide discrete
7 (dark yellow, WAIS Divide project members, 2015) and continuous measurement records (green, Rhodes
8 et al., 2015). Inset: Enlarged plot showing overlapped interval between OSU and SNU Siple Dome data.
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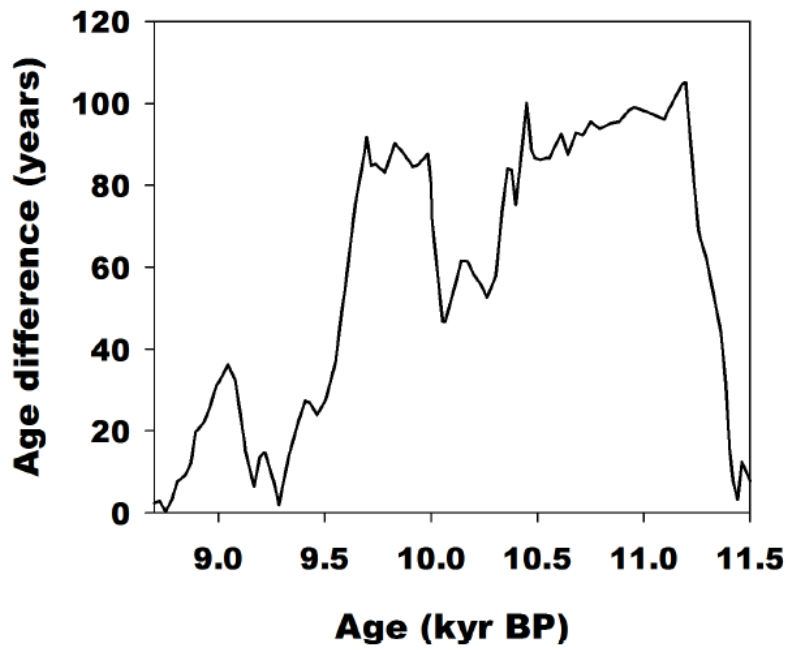


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2 **Figure 2. Millennial scale climate variability.** All proxies presented here were smoothed by 250-year
3 running average and detrended by high-pass filter with 1/1800-year window. (a) Siple Dome CH₄ (red,
4 this study), Greenland ¹⁰Be (dark yellow, Finkel and Nishizumii, 1997), North Atlantic IRD stack (grey,
5 Bond et al., 2001). Also shown are WAIS Divide CH₄ data by discrete (cyan, denoted “WAIS Discrete”,
6 WAIS Divide project members, 2015) and continuous (yellow green, denoted “WAIS CFA”, Rhodes et al.,
7 2015) technique. (b) NGRIP stable water isotope ratio (blue, Rasmussen et al., 2006) and Cariaco Basin
8 reflectance (orange, Deplazes et al., 2013). (c) Qunf Cave speleothem oxygen isotope (Fleitmann et al.,
9 2007). (d) Dongge Cave speleothem oxygen isotope (green, Dykoski et al., 2005; dark yellow, Wang et al.,
10 2005). (e) Gulf of Guinea planktonic Ba/Ca ratio (Weldeab et al., 2007). (f) Lapa Grande Cave speleothem
11 oxygen isotope (purple, Strikis et al., 2011). Black solid triangles are age tie-points used to adjust Siple
12 Dome and WAIS Divide CH₄ data to GICC05 scale.



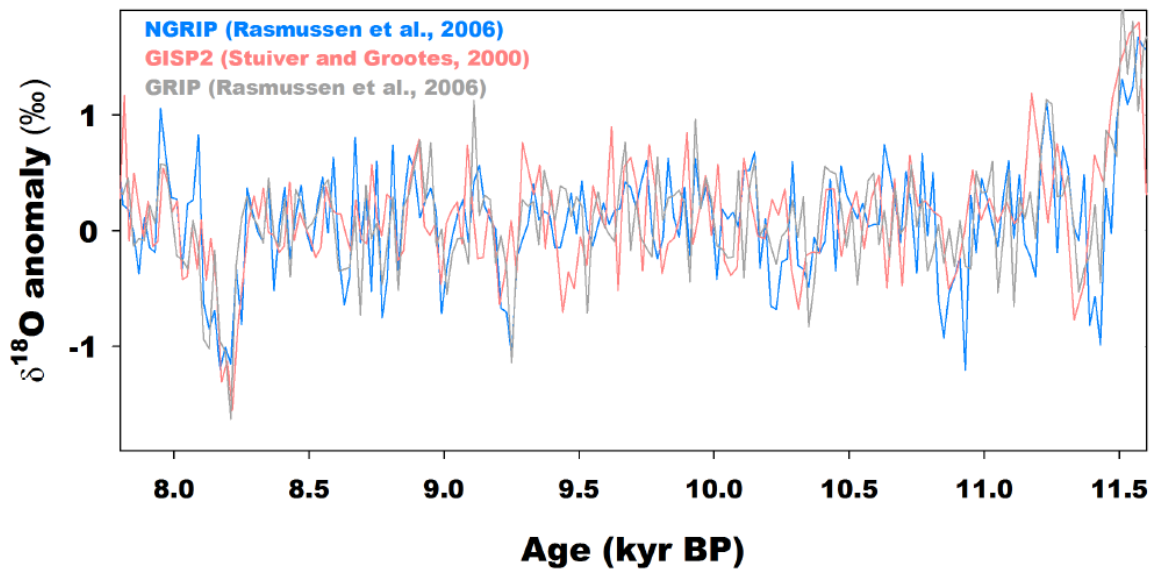
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Figure 3. Upper: Comparison between Siple Dome CH₄ anomalies plotted with gas age adjusted to GICC05 (red, solid) and previous gas age (red, dashed; Brook et al., 2005). Lower: NGRIP δ¹⁸O anomaly in GICC05 scale. The horizontal error bars denote the age uncertainty of GICC05 chronology (Rasmussen et al., 2006), and the black triangles are age tie points used to adjusting the Siple Dome age scale to GICC05 scale.

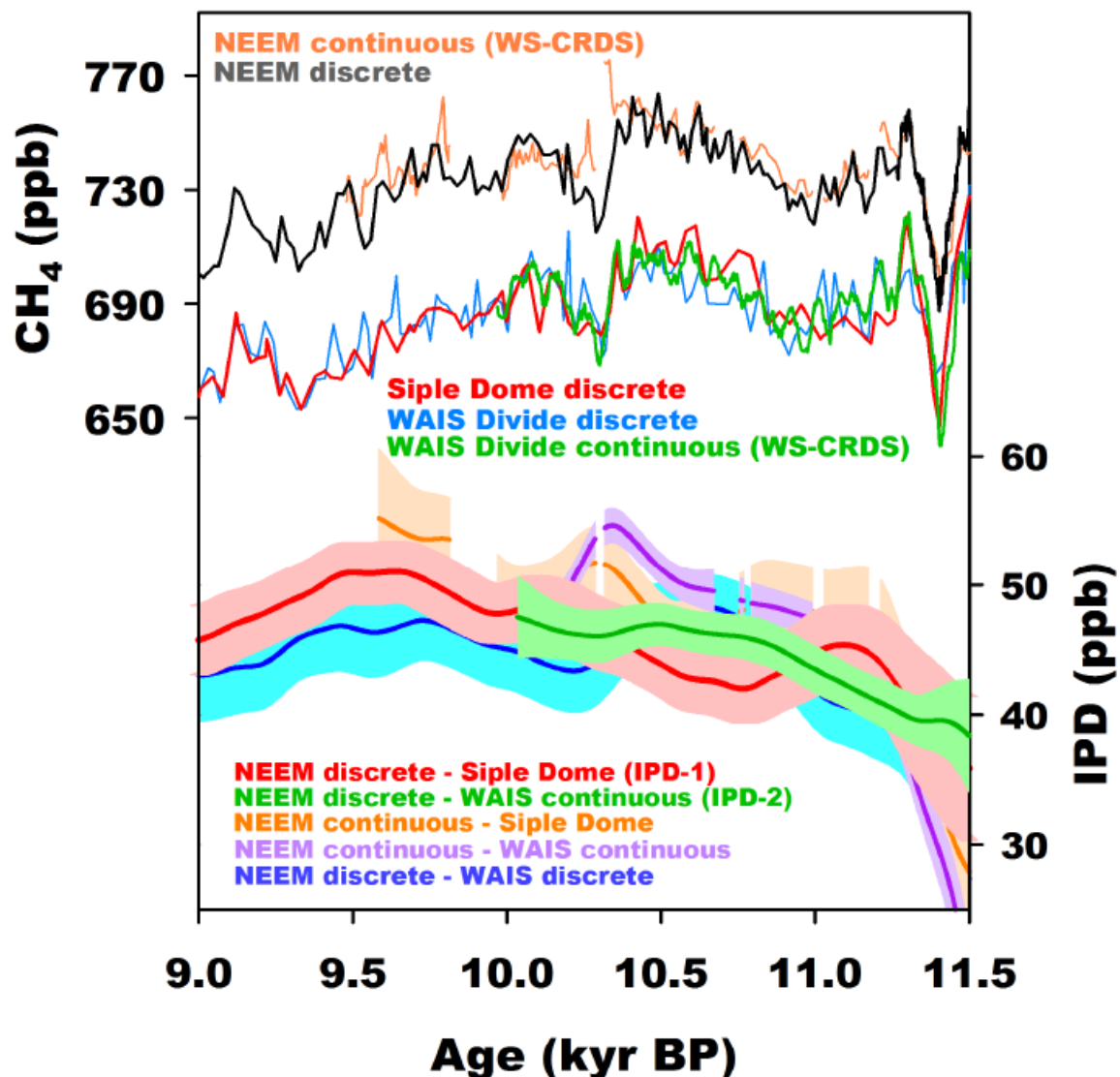


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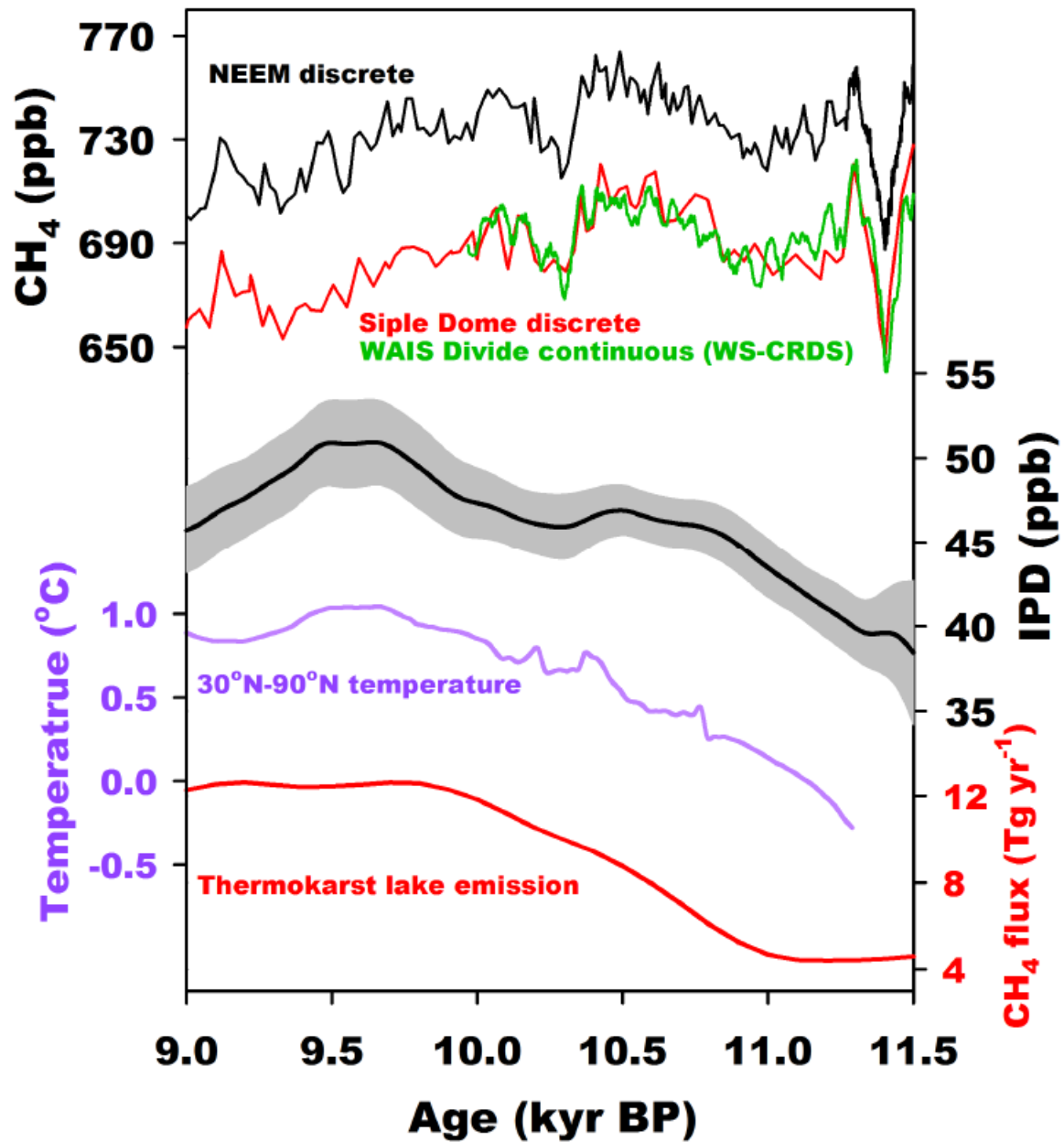
2 **Figure 4. Age difference between the new gas age scale adjusted to GICC05 by Monte Carlo matching**
3 **with NEEM discrete CH₄ (Chappellaz et al., 2013) and the original gas age based on CH₄ and $\delta^{18}\text{O}_{\text{atm}}$**
4 **correlation (Severinghaus et al., 2009).**



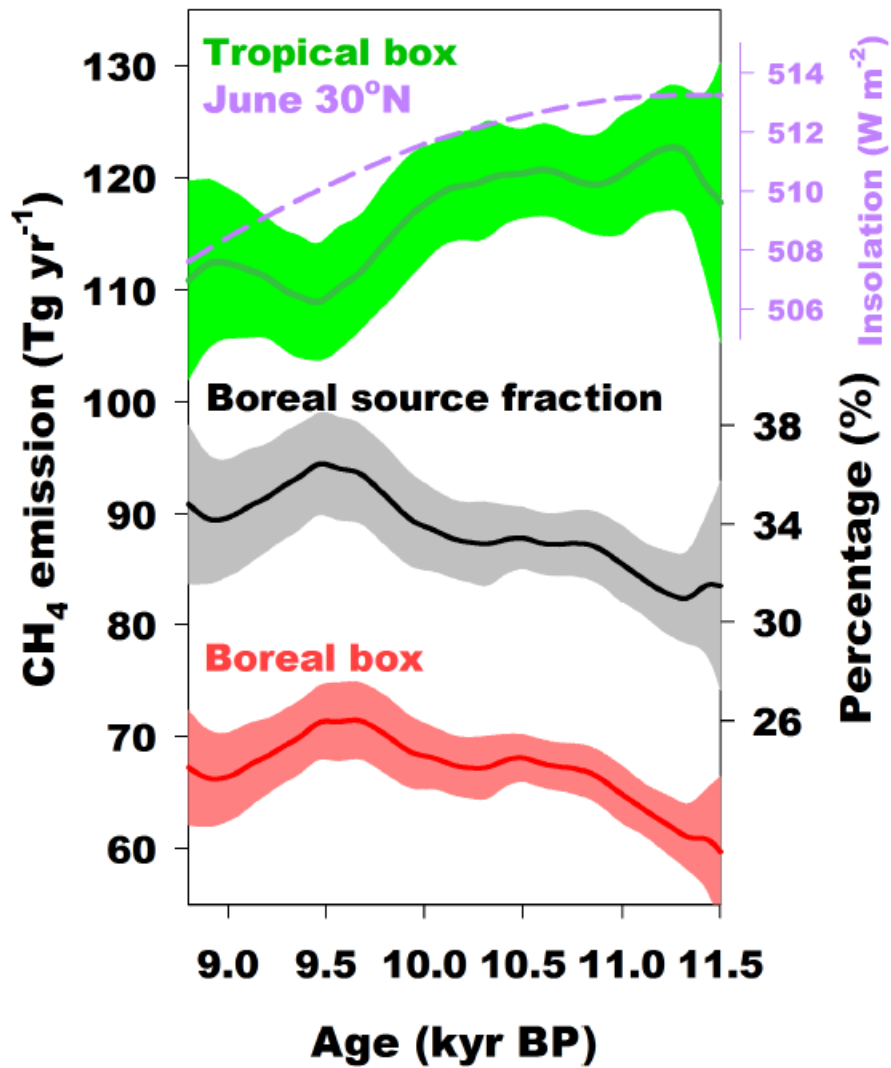
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 2 Figure 5. Comparison of Greenland oxygen isotope ratios from NGRIP (blue, Rasmussen et al., 200
 3 6), GISP2 (red, Stuiver and Grootes, 2000). All time series
 4 were high-pass filtered with 1/1800-year window. Note that the cooling amplitude at 10.3 ka is sma
 5 ller than 8.2 and 9.3 ka events in NGRIP records, but this is not clear in GRIP and GISP2 ice cor
 6 es.
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2 Figure 6. CH₄ inter-polar difference (IPD) and high latitude CH₄ sources. Top: High-resolution CH₄
3 discrete measurements from NEEM discrete (black, Chappellaz et al., 2013), NEEM continuous (orange,
4 Chappellaz et al., 2013), WAIS Divide discrete (light blue, WAIS Divide project members, 2015), WAIS
5 Divide continuous (green, Rhodes et al., 2015), and Siple Dome (red, this study) ice core records. Bottom:
6 1000-year low-pass filtered IPD reconstructions by using various pairs of Greenland- and Antarctic
7 records, in which the IPD-1 and IPD-2 are shown in red and green, respectively. The shaded area
8 indicate 95% significance interval.



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 2 **Figure 7. CH₄ inter-polar difference (IPD) and high latitude CH₄ sources. Top: High-resolution CH₄**
 3 **discrete measurements from NEEM discrete (black, Chappellaz et al., 2013), WAIS Divide continuous**
 4 **(green, Rhodes et al., 2015), and Siple Dome (red, this study) ice core records. Middle: 1000-year low-pass**
 5 **filtered combined IPD with 95% significance interval (shaded). Bottom: Previous estimates are marked in**
 6 **green and orange (Brook et al., 2000; Chappellaz et al., 2013). Proxy-based temperature reconstruction**
 7 **for 30°N-90°N (purple, Marcott et al., 2013). CH₄ flux estimate from Siberian- and Alaskan thermokarst**
 8 **lakes (red, Walter-Anthony et al., 2014).**
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Figure 8. 3-box source distribution model results of tropical (green) and boreal (red) boxes. Black line shows the boreal to total source fraction (see text). Purple dashed line plotted with tropical emission is summer insolation in 30°N (Berger and Loutre, 1991).

1 **Table 1. Summary of results of replicate analysis from 8 depth intervals. The rightmost two columns show**
 2 **the difference between the means of the first- and the second measurements.** The depth difference
 3 **between the first- and second replicate samples is 10 cm.**

Depth	1 st measurement				2 nd measurement				Difference in means <u>1st - 2nd</u>
	Dup.1	Dup.2	Mean <u>± 1σ</u>	Date	Dup.1	Dup.2	Mean <u>± 1σ</u>	Date	
(m)	(ppb)	(ppb)	(ppb)	(dd/mm/yy)	(ppb)	(ppb)	(ppb)	(dd/mm/yy)	(ppb)
523.150	634.8	634.7	634.7- <u>± 0.1</u>	27-01-14	637.5	634.3	635.9- <u>± 0.1</u>	24-02-14	-1.2
530.950	669.0	665.8	667.4- <u>± 1.6</u>	03-02-14	669.4	670.7	670.0- <u>± 0.1</u>	24-02-14	-2.6
558.295	682.5	678.2	680.3- <u>± 2.2</u>	14-03-14	687.5	678.3	682.9- <u>± 0.1</u>	02-04-14	-2.6
559.850	689.8	680.3	685.0- <u>± 4.7</u>	03-02-14	683.8	690.0	686.9- <u>± 0.1</u>	26-03-14	-1.9
561.150	687.8	689.2	688.5- <u>± 0.7</u>	14-03-14	684.0	690.4	687.2- <u>± 0.1</u>	02-04-14	1.3
562.407	687.2	685.5	686.4- <u>± 0.8</u>	26-03-14	689.4	686.4	687.9- <u>± 0.1</u>	02-04-14	-1.5
575.913	679.2	679.2	679.2- <u>± 0.0</u>	07-02-14	686.7	678.9	682.8- <u>± 0.1</u>	28-03-14	-3.6
<u>578.150</u>	<u>675.6</u>	<u>685.1</u>	<u>680.4</u> <u>± 4.7</u>	<u>04-02-14</u>	<u>676.0</u>	<u>680.7</u>	<u>678.3</u> <u>± 0.1</u>	<u>24-04-14</u>	<u>2.0</u>

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1 **Table 2. Results of the 3-box source distribution model from the combined IPD showing emissions of**
2 **tropical (green, T) and boreal (red, N) boxes and boreal source fraction (N/(T+N+S)) at specific time slices.**
3 **Also shown are previous estimates for comparison. Errors denote 95% confidence interval. The**
4 **uncertainty for 9.5 – 11.5 ka period is the average of 95% confidence interval of the low-pass filtered**
5 **reconstruction of each box emission.**
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Ref.	N box	T box	Boreal source fraction N/(N+T+S)
(ka)	(Tg yr ⁻¹)		(%)
Brook et al., 2000 (9.5-11.5 ka)	64 ± 5	123 ± 8	32 ± 3
Chappellaz et al., 1997 (9.5-11.5 ka)	66 ± 8	120 ± 9	33 ± 3
This study (9.5 – 11.5 ka)	67 ± 3	118 ± 5	33 ± 2
This study (11.5 ka)	60 ± 7	118 ± 12	31 ± 4
This study (9.5 ka)	71 ± 3	109 ± 5	36 ± 2
This study (9.0 ka)	66 ± 4	112 ± 7	34 ± 2

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