**Dear reviewers**,

5

We thank all four reviewers for their careful review of our paper, and their positive evaluation of the work. We appreciate their useful comments and believe their input has improved the paper. Below, we address the comments in blue and the revised texts in the manuscript in green.

All the best, on behalf of all co-authors, Jinhwa Shin

## 10 Anonymous Referee #1

Received and published: 17 January 2020

Review of manuscript cp-2019-142:

#### **General Comments:**

The manuscript by Shin and others presents new, high-resolution measurements of CO2, CH4, and δ15N in EDC
ice core samples spanning the glacial period, MIS 6. The new data resolve millennial-scale variations in CO2 and CH4. The authors independently identified MIS 6 stadial durations in tree pollen % and planktonic δ18O in the Iberian Margin marine sediment core MD01-2444. The authors also revised the MIS 6 gas age chronology of the EDC ice core (previously AICC 2012) using new estimates of Δdepth from the δ15N data. The revised EDC age scale, along with the timing of climate variations observed in the sediment core, provides the authors with a temporal framework for understanding millennial-scale CO2 variations during the penultimate glacial period.

The authors specifically analyze the timing of the CO2 changes relative to changes in CH4, considered here a proxy for NH warming, identifying leads/ lags between the two records. They also discuss differences between the CO2 features in MIS 6 and analogous features that occurred in MIS 3. The authors also observe differences in the magnitudes of CO2 maxima during MIS 6. They identify a relationship between the amplitude of CO2

- 25 change and the duration of the preceding stadial event, offering the hypothesis that the amplitude of CO2 variations depends on the duration of AMOC perturbations. They also identify a shift in the lag of CO2 maxima from MIS 6e to MIS 6d and suggest that this may be due to a change in the organization of AMOC. This manuscript is well written, organized, and clearly presented, the science is in my opinion sound, and the new datasets represent important contributions that will be of interest to others in the field. The work is appropriate for
- 30 the journal Climate of the Past, and I recommend this paper for publication after minor revisions. Below I list specific comments that, if addressed, will aid in the clarity of the paper and hopefully strengthen the analyses therein. I also list technical corrections below.

35

## **Specific Comments:**

## INTRODUCTION

- P3L9 - Can you provide a reference for the longer duration of stadials in early MIS 6?

Accepted. A reference (Margari et al., 2010) added in the text.

5 – P3L15 – There are more pre-existing CO2 measurements from late MIS 6 besides those from Vostok (Lourantou et al., 2010; Schneider et al., 2013).

References added in P3L15.

## METHODS

- P3L31 - Did the measured CO2 concentration depend on the amount of air injected?

**10** The CO<sub>2</sub> concentrations of 5 measurements were constant. The amount of air injected did not impact the CO<sub>2</sub> concentration.

(Presumably, the pressure in the sample loop depleted across the 5 individual injections. Was there a linearity effect?)

The  $CO_2$  concentrations do not depend on the sample size, and for the 5 consecutive injections on the same sample

we obtained a linear relationship between pressure and partial pressure of CO<sub>2</sub>, i.e., concentrations did not change
 P4L18-19 – Was the amount of contamination in each chamber consistent from day to day?

Each chamber shows different contamination levels. We could measure 3-4 samples a day and blank tests were conducted every 10 measurements of natural ice. The amount of contamination in each chamber varied within  $\sim$ 0.5-2 ppm, averaging 1 ppm during the measurement, and no drifts were observed during the 2 months.

20 Did it depend on the length/ amount of crushing?

To avoid any effect of the duration/ amount of crushing and  $CO_2$  contamination caused by crushing process on the measured CO2 concentration we kept the same length/ amount of crushing process both for real samples and standards over ice.

## - Did you run replicate CO2 measurements on ice samples from the same depths?

25 In this study, large sample sizes (40g) were used, and because limited ice samples were available, we could not make replicates. To ensure precise data, we controlled the precision of the system to around 1 ppm using gas standards over gas-free synthetic ice measurements and assume their variability to be the same as for true ice. In my opinion, this would be a better estimate of the true system precision.

Replicates additionally account for any differences between two ice samples, making a better estimate of standard
 deviation of the final measurement but not necessarily of system precision itself. For example, Lüthi et al. (2010) show that there exists true small scale variability in CO<sub>2</sub> concentrations in the ice below the Bubble Clathrate Transition Zone. Due to the diffusion effect, this small variation of atmospheric CO<sub>2</sub> is smoothed to some degree. In our study, large sample sizes (40g) of the ball mill system were used to reconstruct atmospheric CO<sub>2</sub>, so a lownoise signal from the ice core is extracted (the smaller measurements used in other systems would be noisier in

35 theory). The standard deviation of the measurement is estimated from the 5 injections, but system precision, which is added to the uncertainty of the measurements, was calculated from the blank measurement, accounting for the possible sources of  $CO_2$  contamination with our analytical procedure.

This is added to new section 3.2 Data verification

- P4L25 - Can you state briefly how the new, corrected CO2 record compares to the preexisting CO2 data?

The new  $CO_2$  data from EDC are corrected for gravitational fractionation and contamination caused by the analytical process. The previous  $CO_2$  measurements from Vostok ice core by ball mill system (Petit et al., 1999) from EDC measured by ball mill (Lourantou et al., 2010) were corrected for gravitational fractionation effect but not corrected the  $CO_2$  contamination effect (Figure 4 in the manuscript). Additionally, the Vostok data use a less

## 5 precise age scale.

We have included a discussion of the  $CO_2$  offset between the new data set and existing data sets in detail in section 3.1.

P4L32 – Can you state the precision of the CH4 measurements?
 This is now included. The precision of the system was estimated at ~11 ppb on average.

10 – P5L3 – What do you think are possible reasons for the systematic offset? Please describe briefly.

A systematic offset of 6 ppb between IGE and CEP was observed (Loulergue et al., 2008). The offsets are due to differences in corrections for contamination caused by the analytical procedure, a systematic offset of 6 ppb between IGE and CEP was observed (Loulergue et al., 2008).

Revised to: The previous CH4 dataset (Loulergue et al., 2008) from EDC was produced at both IGE and Climate
and Environmental Physics (CEP), Physics Institute, University of Bern, Switzerland. CH4 measured at CEP is systematically higher than CH4 measured at IGE by 6 ppb (Loulergue et al., 2008). The offsets are due to differences in corrections for contamination caused by the analytical procedure between the datasets. In order to produce a coherent dataset, 6 ppb were added to the data obtained at IGE (Loulergue et al., 2008).

– P6L20 – Figure S4 in the SI does not have a label to distinguish blue from red.

20 Revised

- P6L22 - I do not follow how Figure 2 supports the claim that the previous method was "relatively unbiased but not entirely exact."

## Sorry, this was the wrong figure number. That was explained in Figure S3. Figure number revised to Figure S3.

- P6L13 In Figure 3 it appears that the midpoints in the transitions are somewhat ambiguously defined.
  Sometimes they fall between a local max and min for d18O, sometimes for pollen %. The markers are chosen as midpoints between local maxima/minima, but sometimes it is unclear where those max/ min data points are. 6d.2, for example, could easily be shorter (i.e., it looks like the end marker at 174.2 ka could be defined at an older age).
  6c.2 is a particularly ambiguously defined stadial I do not see which maximum and minimum pair defines the older marker. Could you define the stadial durations more objectively? The ambiguity and subjectivity in picking
- 30 the stadial transitions lead me to believe that they were defined while also considering the ice core data. That's not necessarily a bad thing, but perhaps you should just be forthright and show the gas data in Figure 3 along with the sediment core data.

In our study, the durations of the six NA stadials were originally defined as the interval between the midpoints of the stadial transition of both  $\delta^{18}$ O of planktonic foraminifera and tree pollen in MD01–2444 (C and D in figure 3)

35 which was suggested by Margari et al. (2010). With this data we observed that the magnitude of atmospheric CO<sub>2</sub> change is generally correlated with the NA stadial duration (r=0.7, n=6) during the early MIS 6 period.

As the reviewer mentioned, not all of the stadial durations during MIS 6 are entirely clear using this method. As suggested by the reviewer, a synthetic Greenland  $\delta^{18}O_{ice}$  record (Barker et al., 2011) and  $\delta D$  variations in Antarctic ice core are plotted in Figure 3 as references(AICC2012 age scale). The interval between the maximum and the preceding minimum of  $\delta D$  in the EDC record can also be used to estimate the duration of the stadial transitions

5

(Gottschalk et al., 2020; Margari et al., 2010). In most cases, the synthetic Greenland  $\delta^{18}O_{ice}$  record and the interval between the maximum and the preceding minimum of  $\delta D$  in the EDC record confirm the definition of NA stadials selected by  $\delta^{18}O$  of planktonic foraminifera in MD01–2444 and tree pollen in MD01–2444. However, the duration of the NA stadial in MIS 6d.2 is not clearly confirmed by Greenland  $\delta^{18}O_{ice}$  and  $\delta D$  in the EDC (Figure 3).



10

15

**Figure 3 (in the manuscript):** The durations of the six NA stadials during MIS 6 defined by Margari et al. (2010). A:  $\delta D$  composition of the EDC ice core (Jouzel et al., 2007). B: Greenland synthetic  $\delta^{18}O$  composition of ice (Barker et al., 2011). C: Tree pollen percentage in the MD01-2444 (Margari et al., 2010) D:  $\delta^{18}O$  of planktonic foraminifera in the MD01-2444 (Margari et al., 2010). Proxy data shown here are given on the AICC2012 age scale. Red lines indicate the midpoint between the midpoints of the stadial transition of both  $\delta^{18}O$  of planktonic foraminifera and tree pollen in MD01–2444. Light green bars indicate the uncertainty of the duration of each stadial estimated as half of the temporal difference between maxima and minima of  $\delta^{18}O$  of planktonic foraminifera. Red dots indicate minima and maxima of  $\delta D$  composition of the EDC ice core selected in this study. The event numbers are written at the top.

20

We recalculated the durations of the six NA stadials using the interval between the stadial transitions as recorded in the EDC  $\delta$ D record (Gottschalk et al., 2020; Kawamura et al., 2017; Margari et al., 2010). Minima and maxima were selected by finding zero values in the second Savitsky–Golay filtered derivative of the data (the same method we used to pick minima and maxima of atmospheric CO<sub>2</sub>; P9 in SI and Figure 1 in this text).

25 The red dots and error bars on  $\delta D$  in the EDC record in Figure 3 of the main text show the estimated minima and maxima of temperature corresponding to stadial transitions using this method, along with their uncertainties.

However, using this tool, durations of 6e.1 and 6e.2 are apparently overestimated due to ambiguity concerning the maximum in 6e.1 and minimum in 6e.2. Neither our method nor that of Margari et al. (2010) can be considered absolutely correct. To account for the differences between the two methods, we took the stadial duration to be the mean of the duration estimated by both  $\delta^{18}$ O of planktonic foraminifera and tree pollen in MD01–2444 and dD definitions. The correlation coefficient between the magnitude of atmospheric CO<sub>2</sub> change and the NA stadial duration remains high (r=0.93, n=6) during the early MIS 6 period.

5

This new calculation was added in section 2.6



**Figure 1:** Temperature records from EDC during MIS 6. The black curve in both panels shows the Savitsky-Golay filtered  $\delta D$  series, and the blue curve shows the original data. (A) Red vertical lines mark inflection points. (B) Blue vertical lines show the minima and maxima, the blue shading illustrates the estimated uncertainties of their timing. The event numbers are written at the top.

## 2.6 Definition of NA stadial duration is revised to:

10

Due to the absence of a Greenland temperature record for MIS 6, the durations of the six NA stadials were defined using  $\delta^{18}$ O of planktonic foraminifera and tree pollen in MD01–2444, which reflect temperature variability in the NH (Margari et al., 2010). The midpoint of the stadial transitions in both  $\delta^{18}$ O of planktonic foraminifera and tree pollen in MD01–2444 were used to identify the NH stadial stadial transitions. The time interval between two stadial transition points were defined as the NA stadial duration. In this approach, small variations of the two records may bias the calculation of the duration of short stadials in the NH. However, the average age difference

- 15 between the durations identified using the two methods is only 205 years, which is less than the sampling resolution of MD01–2444 during MIS 6. The stadials identified for MIS 6 are shown in Figure 3. The uncertainty of the duration of each stadial was estimated as half of the temporal difference between maxima and minima of  $\delta^{18}$ O of planktonic foraminifera. However, not all of the the stadial durations during MIS 6 are entirely clear using this method. Figure 3 shows synthetic Greenland  $\delta^{18}$ O<sub>ice</sub> record (Barker et al., 2011) and Antarctic ( $\delta$ D) variations
- 20 in Antarctic ice core on the AICC2012 age scale. The interval between the maximum and the preceding minimum of  $\delta D$  in the EDC record can also be used to estimate the duration of the stadial transitions (Gottschalk et al., 2020; Margari et al., 2010). In most cases, the synthetic Greenland  $\delta^{18}O_{ice}$  record and the interval between the maximum

and the preceding minimum of  $\delta D$  in the EDC record confirm the definition of NA stadials selected by  $\delta^{18}O$  of planktonic foraminifera in MD01–2444 and tree pollen in MD01–2444. However, the duration of the NA stadial in MIS 6d.2 is not clearly confirmed by Greenland  $\delta^{18}O_{ice}$  and  $\delta D$  in the EDC. We recalculated the durations of the six NA stadials identified during the MIS 6 period were previously defined by Margari et al. (2010). Between

- 5 the maximum and the preceding minimum of δD in the EDC record is defined as the stadial durations (Gottschalk et al., 2020; Kawamura et al., 2017; Margari et al., 2010). Minima and maxima were selected by finding zero values in the second Savitsky–Golay filtered derivative of the data (the same method we used to pick minima and maxima of atmospheric CO<sub>2</sub>; Figure S11 in SI). The red dots and error bars on δD in the EDC record in Figure 3 show the estimated minima and maxima of temperature corresponding to stadial transitions using this method,
- 10 along with their uncertainties. However, using this tool, durations of 6e.1 and 6e.2 are apparently overestimated due to ambiguity concerning of maximum in 6e.1 and minimum in 6e.2. Neither our method nor that of Margari et al. (2010) can be considered absolutely correct. To account for the differences between the two methods, we took the stadial duration to be the mean of the duration estimated by both  $\delta^{18}$ O of planktonic foraminifera and tree pollen in MD01–2444 and dD definitions (Table 2).
- 15

## RESULTS

- P8L3 - You should mention the known phenomenon of CO2 offsets between different ice cores (e.g. WAIS versus Law Dome). The co-author Christoph could certainly comment on this.

- When the air is extracted from an ice core sample where bubble and clathrates co-exist, different dry extraction methods with different extraction efficiencies on bubbly and clathrate ice may lead to biased CO<sub>2</sub> concentrations (Lüthi et al., 2010; Schaefer et al., 2011). During clathrate formation, the gas is partitioned into clathrates due to the different gas diffusivities and solubilities (Salamatin et al., 2001). CO<sub>2</sub> has consistently been observed to be depleted in bubbles and enriched in clathrates (Schaefer et al., 2011). Degassing from clathrates during extraction takes much longer than air release from bubbles; thus, if air from the clathrate ice is not extracted entirely, CO<sub>2</sub>
- 25 measurement will be lower than the true value.

The ball mill shows extraction efficiencies of ~62% for bubbles and ~52% for clathrates on average (Schaefer et al., 2011). If the ball mill is used to reconstruct  $CO_2$  in Bubble–Clathrate Transformation Zone (BTCZ),  $CO_2$  concentrations can be biased.

- CO<sub>2</sub> concentrations from EDC were reconstructed from 150 depth intervals that cover 2036.7 to 1787.5 m along
   the EDC ice core, which consist of clathrate ice. There exists true small scale variability in CO<sub>2</sub> concentrations in the ice below the Clathrate Zone (Lüthi et al., 2010). Due to the diffusion effect, this small variation of atmospheric CO<sub>2</sub> is smoothed. Thus, CO<sub>2</sub> concentrations in these depth intervals might represent the initial mean atmospheric concentration. However, the EDC ice core for MIS 6 was drilled in 1999 and, the ice core has been stored for ~20 years in cold rooms at -22.5 ± 2.5°C before the gas is analysed. More than 50% of the initial hydrates present in
- 35 the freshly drilled ice may have been decomposed and transformed into secondary bubbles, or gas cavities (Lipenkov, *Pers. Comm.*). We expect the same fractionation as during the clathrate formation process, hence bubbles would be depleted in CO<sub>2</sub>. Thus, CO<sub>2</sub> concentrations from EDC may be lower. The portion of the Vostok ice core covering MIS 6 is also clathrate ice, but it was drilled in 1998 and measured immediately (Petit et al., 1999), and less clathrates may have transformed into secondary bubbles. Thus CO<sub>2</sub> concentrations from Vostok

during MIS 6 may be higher and potentially reflect the true atmospheric concentration more closely. In our study we concentrate on the relative millennial changes of  $CO_2$  around the mean glacial concentration, which are the same in all the  $CO_2$  records available so far, Thus, our conclusion in this paper are independent of which absolute mean  $CO_2$  level is correct. As the new data in this study are currently the best quality data in terms of repeatability, we use our new data as the reference record and correct for any inter-core offsets. We, however, state explicitly

5

10

## This is written to Section 3.1 The new high-resolution and high precision CO<sub>2</sub> record during MIS 6

in the text that the absolute mean  $CO_2$  level during MIS6 is not known better than 5 ppm.

P25 Fig5 – It is unclear how the blue CDM events were defined. Do they relate somehow to the stadial duration markers you defined previously? If not, please clarify how you identified them (or provide proper reference to SI).
 Revised. It is explained in Table S1 and Figure S10. These references were added in Section 3.3.

P26Fig6 – Shading or vertical lines would help to delineate the CDM's in Figure 6. Right now the text floats at the bottom and is unclear exactly what the labels refer to.





15

– One result that strikes me as interesting, and not discussed in the paper, is that the lowest CO2 and Antarctic temperature values occur in the early/ middle part of MIS 6, not the latest part (as in MIS 2). CH4, on the other hand, reaches the lowest values during late MIS 6, right before the termination, as does peak glaciation as inferred from the benthic d18O. This is unlike MIS 2, which is characterized by low CO2, low Antarctic temperature, low CH4, and peak glaciation occurring simultaneously. Can you speculate why CO2 is higher in late MIS 6 relative

20

25

to earlier in MIS 6, despite full glacial extent? A saturation index indicating variations in respired carbon content in the deep sub-Antarctic Atlantic (MD07-

3077) and atmospheric  $CO_2$  have been shown to be closely anti-correlated (Gottschalk et al., 2020). This observation indicates that the regulation of global atmospheric  $CO_2$  variations on millennial time scales is highly influenced by the marine carbon cycle in the Southern Ocean (Fischer et al., 2010) during MIS 6.

As shown in this figure, atmospheric CO<sub>2</sub> from EDC is highly co-related with dust flux in EDC (Lambert et al., 2012),  $\delta D$  in EDC (Jouzel et al., 2007) and summer sea surface temperature in the deep sub-Antarctic Atlantic (MD07-3077) (Gottschalk et al., 2020). Iron Fertilization and temperature in the Southern Ocean can affect CO<sub>2</sub> variations on millennial time scales. However, the main difference of climate between late MIS 6 and early MIS

5 6 is temperature in the Southern Ocean. Colder conditions are observed in the Southern Ocean in early MIS 6 than in late MIS 6. Colder conditions in early MIS 6 would allow for more carbon uptake in the southern Ocean. Thus, the CO<sub>2</sub> level during the early MIS 6 might be slightly lower than the late MIS 6 due to colder ocean conditions during the early MIS 6. In contrast, CH<sub>4</sub> is reflecting primarily climate/hydrological conditions on land in the tropics and to a much smaller extent in high northern latitudes. Thus, a decoupling of the two parameters suggests different glacial climate evolution in high southern latitudes and the tropics.

10

(P8L1-P8L10 is written in the Section 3.2. the Section name is revised to "Relationship between the temperature in the Southern Ocean and atmospheric CO<sub>2</sub>")



15 Figure 2: Climate proxies during MIS 6. Vertical blue dotted lines indicate the six CDM events that we identify during the early MIS 6. A: Dust flux in EDC (Lambert et al., 2012). B: EDC water isotopic record (Jouzel et al., 2007). C: Sea summer surface temperature in the deep sub-Antarctic Atlantic (MD07-3077) (Gottschalk et al., 2020). D: Saturation Index in the deep sub-Antarctic Atlantic (MD07-3077) (Gottschalk et al., 2020). E: Atmospheric CO<sub>2</sub> from EDC (this study). The red line indicates Savitsky Golay filtering curve made with a ~150

20 yr cut-off period (red dotted line).

> - P28Fig8 - The authors compare the timing of CO2 maxima relative to the onset of NH warming. The CO2 measurements come from different ice cores with different age scales (to my knowledge at least, Byrd is not synchronized to the AICC 2012 as EDML, EDC, and TALDICE are). What is the bias or uncertainty in the analysis due to age offsets? Why not exclusively use the EPICA cores on a unified age scale for this analysis?

25 To calculate leads and lags between  $CO_2$  and the abrupt warming in NH, we calculated the time lag for each CDM following abrupt warming events in the NH. In this study, given the fact that when temperature increases rapidly in Greenland, CH<sub>4</sub> increases rapidly within 50 yrs (Baumgartner et al., 2014; Rosen et al., 2014), we used CH<sub>4</sub> as a time marker of rapid warming in the NH.

 $CH_4$  and  $CO_2$  signals are both reconstructed from the air bubbles in the same ice, and as such there is no chronological uncertainty with respect to individual timings. The Byrd core was synchronized to the EDML core in the gas phase by Bereiter et al. (2012), and thus can be synchronized to the AICC2012 chronology as well. Without synchronization, there can be significant differences in event duration between two cores. However, with

5 the synchronization between Byrd and EDML, these inconsistencies should be minimized. The measurements for each period are chosen to maximize resolution and minimize uncertainty related to gas trapping. –The estimation of the exact timing of CDM from the EDC ice core might be less accurate compared to that from the TALDICE ice core, for example, due to the narrower gas age distribution of TALDICE (Bereiter et al., 2012). The remaining uncertainty is related to analytical uncertainties and to the temporal resolution of the two records.

## 10 DISCUSSION

30

- P11L26&31 - When you say that the terrestrial biosphere can "compensate" for the slow response of the deep ocean, do you mean in terms of its timing or in terms of the direction of CO2 change? The direction of CO<sub>2</sub> change.

This paragraph was revised to: As mentioned above, atmospheric CO<sub>2</sub> on millennial timescales can be controlled
by CO<sub>2</sub> exchange between the ocean and the atmosphere, as well as changes of terrestrial carbon stocks. Coupled climate carbon cycle models reported that the variations of atmospheric CO<sub>2</sub> concentration on millennial timescales are mainly dominated by deep ocean inventory, requiring a few millennia to react to climate change (Schmittner and Galbraith, 2008). On the other hand, the response of the terrestrial biosphere is fast (centennial timescale) (Bouttes et al., 2012; Menviel et al., 2014; Schmittner and Galbraith, 2008). Although different models

- 20 differ significantly in the CO<sub>2</sub> response to AMOC changes, the initial CO<sub>2</sub> evolution of the terrestrial biosphere and deep ocean to AMOC perturbations tends to be opposite in model simulations (Gottschalk et al., 2019). Thus, due to the opposite direction of CO<sub>2</sub> change of ocean and terrestrial reservoirs, atmospheric CO<sub>2</sub> variations might be muted if the stadial in the NA is short (Bouttes et al., 2012; Menviel et al., 2014; Schmittner and Galbraith, 2008). There is, on the other hand, evidence that not all of the processes of CO<sub>2</sub> exchange follows these general
- 25 trends. For example, atmospheric CO2 might be changed on centennial timescales by carbon exchange between the deep and surface ocean (Rae et al., 2018) or atmospheric CO2 might be influenced slowly by soil decomposition (Köhler et al., 2005).

Please clarify. "Compensate" may not be the best word to use in case it is confused with carbonate compensation. Revised. Compensate was mentioned twice in the text at P11L27 and P11L32. The first one was changed to "muted" and the second one was changed to "be offset by"

P13 – After the discussion of AMOC and deep ocean ventilation, I realized there was no discussion entertaining productivity fluctuations as a possible mechanism for millennial-scale CO2 variability (Ziegler et al., 2013; Gottschalk et al., 2016; Anderson et al., 2014; Martinez-Garcia et al., 2014).

The dust flux in EDC clearly shows millennial variations during MIS 6. The anti-correlation between atmospheric
CO<sub>2</sub> and dust fluxes in EDC during the MIS 6 implies millennial-scale CO<sub>2</sub> variations might be influenced by iron fertilization in the Southern Ocean during the MIS 6 (Ziegler et al., 2013; Gottschalk et al., 2016; Anderson et al., 2014; Martinez-Garcia et al., 2014). In today's Southern Ocean, biological productivity is limited, reflected in a relatively low chlorophyll content. This indicates that the phytoplankton in the Southern Ocean have limited access to essential micronutrients such as iron. Aeolian dust input into the Southern Ocean can modulate iron

deposition. If the amount of aeolian dust input in the Southern Ocean increases, the productivity of phytoplankton in the Southern Ocean increases and carbon fixation in the Southern Ocean biosphere is thus enhanced. Organic detritus sinks into the deep ocean reservoir (Marinov et al., 2008), and atmospheric  $CO_2$  can thus be drawn down by what is known as the biological carbon pump (Martin, 1990).

5

20

This is also written in the revised manuscript in new section 3.3 Relationship between the dust flux in EDC and atmospheric  $CO_2$ 

- P13L13-18 - Need more references in this paragraph. Bereiter et al. (2012) added

- P14 After reading this section it strikes me that there is a large amount of discussion about AMOC changes without actually showing any AMOC data. The discussion is very "AMOC-centric." Indeed, we believe that AMOC changes are probably key to explaining the MIS 3 CO2 changes, but to assume the same mechanism operates in MIS 6 without data to suggest so, and then to make assertions about the AMOC based on the CO2 trends at least requires some qualification in my mind. It is okay to speculate, but please say explicitly that you are doing so and that it is based on extrapolation of the relationships observed in MIS 3.
  - Due to the lack of existing proxy data with high temporal resolution and high precision and modelling studies,

explanations of carbon cycle mechanisms during MIS 6 are limited. However, hypotheses of these mechanisms have been presented by previous studies, and the continued discussion of these hypotheses and how our new observations may redirect the discussion, even if the very limited amount of data means that this discussion is speculative in nature, is important. We hope that this discussion will be helpful for future studies, and have made sure, as suggested by the reviewer, to clearly label any speculative discussion in the text.

Some paragraphs in Section 4.1 and 4.2 were removed and re-written, please see below.

- P11L12- P12L16 in the manuscript revised to: As mentioned above, atmospheric CO<sub>2</sub> on millennial timescales
  can be controlled by CO<sub>2</sub> exchange between the ocean and the atmosphere, as well as changes of terrestrial carbon stocks. Coupled climate carbon cycle models reported that the variations of atmospheric CO<sub>2</sub> concentration on millennial timescales are mainly dominated by deep ocean inventory, requiring a few millennia to react to climate change (Schmittner and Galbraith, 2008). On the other hand, the response of the terrestrial biosphere is fast (centennial timescale) (Bouttes et al., 2012; Menviel et al., 2014; Schmittner and Galbraith, 2008). Although different models differ significantly in the CO<sub>2</sub> response to AMOC changes, the initial CO<sub>2</sub> evolution of the terrestrial biosphere and deep ocean to AMOC perturbations are opposite in model simulations (Gottschalk et al., 2019). Thus, due to the opposite direction of CO<sub>2</sub> change of ocean and terrestrial reservoirs, atmospheric CO<sub>2</sub> variations might be muted if the NH duration is short (Bouttes et al., 2012; Menviel et al., 2012; Menviel et al., 2012; Menviel et al., 2014; Schmittner and Galbraith, 2008). There is, on the other hand, evidence that not all of the processes of CO<sub>2</sub> exchange follow these
- 35 general trends--for example, atmospheric  $CO_2$  might be changed on centennial timescales by carbon exchange between the deep and surface ocean (Rae et al., 2018) or atmospheric  $CO_2$  might be influenced slowly by soil

decomposition (Köhler et al., 2005); and it is important to note that modeling studies are limited by the available proxy data during MIS 6.

Another possible reason for the difference between CO<sub>2</sub> changes during short and long stadials may be related to a stronger reduction of the NADW during long stadials (Henry et al., 2016; Margari et al., 2010), which would

- 5 cause a stronger upwelling of deep water in the Southern Ocean (Menviel et al., 2008; Schmittner et al., 2007). These events may reduce stratification in the Southern Ocean due to an increase in salinity of the surface waters and a relative freshening of the deep water (Schmittner et al., 2007). As a result, atmospheric CO<sub>2</sub> can be increased due to upwelling and outgassing of CO<sub>2</sub> in the Southern Ocean (Schmittner et al., 2007). The co-occurring upwelling in the SO during AIMs for the last termination has been examined (Anderson et al., 2009) but, due to
- 10

the lack of proxy data with precise age scale for upwelling in the Southern Ocean, this hypothesis cannot be confirmed during MIS 6.

P13L5-P13L12 in the manuscript revised to: Two different lags of CO<sub>2</sub> variations with respect to NH warming are present in the MIS 6 period (Figure 8). CDM 6e.2 is nearly synchronous with the abrupt warming in the NH (no significant lag of 200±360 yrs), while the lags for CDM 6d.2 (1,300±450 yrs) and CDM 6d.1 (1,500±280 yrs)

15 are much longer. Two modes of CO<sub>2</sub> variations are also observed during the last glacial period. As the last glaciation progressed from MIS 5 to MIS 3 (Figure 8), the lag of CO<sub>2</sub> maxima with respect to NH millennial-scale warming significantly increased. This observation may be explained by the different AMOC settings in MIS 5 and MIS 3 (Bereiter et al., 2012). We speculate that, as observed during the last glacial period, the configuration of oceanic circulation during MIS 6d might be also the cause of the change in the time lags between NH abrupt 20 warming events and CO<sub>2</sub> variations during the early MIS 6.

P13L30- P14L12 in the manuscript revised to: In spite of the inconclusive modeling studies, limited proxy evidence does not exclude the possibility that the configuration of AMOC and its changes over MIS 6 may explain the presence of two different CDM lags. We find this hypothesis to be worth at least a speculative discussion. According to the  $\delta^{13}C_{\text{benthic}}$  record in the MD01-2444 core (Margari et al., 2010), the value of  $\delta^{13}C_{\text{benthic}}$  during

- 25 during 180-168 kyr BP was lower than during MIS3, which indicates that the North Atlantic overturning cell during MIS 6 was likely even shallower than that during MIS 3 (Margari et al., 2010). This implies southernsourced water masses were more expanded to the north, and the density difference between the northern-sourced water masses and southern-sourced water masses increased. This shallower oceanic circulation during MIS 6 (Margari et al., 2010) may have caused the millennial-scale delays with respect to abrupt NH warming events
- 30 during MIS 6. It seems pertinent to investigate whether the slightly different ocean settings during MIS 3 and 6 (Margari et al., 2010) can also explain the longer lag between the abrupt warming in NH and CDMs during MIS 6d (1,400±375 yrs on average) when compared to the lags of CDMs (770±180 years on average) during MIS 3. However, our study has lower temporal resolution compared to the CO<sub>2</sub> data set during MIS 3. In addition, because of the low accumulation at EDC, the estimation of the exact timing of CDM from the EDC ice core might be less
- 35 accurate compared to that from the TALDICE ice core, for example, due to the narrower gas age distribution of TALDICE (Bereiter et al., 2012). The remaining uncertainty is related to analytical uncertainties and to the temporal resolution of the two records. To further investigate the exact relationship between CDM and abrupt warming in the NH, additional CO<sub>2</sub> measurements from a higher accumulation site could be helpful.

## CONCLUSIONS

- P14L22 - "Unprecedented" strikes me as too strong of a word.

Revised to "with high temporal resolution and improved analytical precision"

- I think the conclusion section should contain less about the AMOC. The primary contributions of the paper (in my mind) are the new data, the revisions to the EDC gas age scale, and perhaps the observations of leads/ lags relative to abrupt CH4 changes. The differences in the organization of AMOC between and within MIS 6 and MIS 3, as well as the relationships between stadial length and AMOC perturbation should be left out here. They are interesting hypotheses, but they are not supported by data. See also my note above about rewording the discussion to be more explicitly speculative.
- 10 Two sentences removed from the text: "probably because the duration of upwelling in the Southern Ocean was not sufficient to impact atmospheric CO<sub>2</sub>, in line with Ahn and Brook (2014)" "The change in lag time might be related to a change in the organization of the AMOC from MIS 6e to MIS 6d."

## **Technical Corrections:**

- Section 2.4 is titled "Ice age revision: : :" but the gas chronology, not the ice chronology, is what is actually revised. It might be confusing, so consider titling this section "Gas age revision: : :"

#### Revised

15

– In Figure 8 the authors show various CO2 maxima plotted against the lead/lag with respect to the onset of Northern Hemisphere warming. It would be helpful to clarify, for example, "CDM 12" corresponds to DO 12, etc. A sentence added to the caption: During the last glacial period, the AIM number corresponds to the DO number

20 for corresponding DO and AIM events.

- P2L10 - Capitalize "Hemisphere" in "Northern and Southern hemisphere, respectively."

Revised

- P2L15 - "opposite"

Revised

25 – P2L17 – I suggest leaving out "In response to the millennial temperature perturbations,"

## Removed

- P2L32-33 - No need to repeat "MIS 3" and "MIS 6" in parentheses. Just state the age ranges.

This sentence summarizes the research purpose in this study. We prefer re-introducing the target period specifically here. In addition, the age of both MIS 3 and MIS 6 were not mentioned before that sentence. Thus, in

30 our opinion, it is appropriate to mention both stage name and age range in this sentence.

– P2L32 – Why just "early MIS 6?" The data also span some of late MIS 6, younger than 160 kyr.

New data covers the entire MIS 6 but we focused on the interpretation of prominent  $CO_2$  variations, which occur in early MIS 6.

– P3L10 – I think the sentence about a shallower AMOC cell can be combined with the preceding discussion about weaker AMOC.

Accepted, rewritten.

35

40

- P12L8-9 - You already said this in the previous sentence (NADW can be slowed down after freshwater forcing). I think it can be omitted.

The sentence "When large amounts of low-density fresh water are released into the NA, NADW formation can be slowed down." removed

- P25Fig5 - There is a typo in the legend. "Uncertainties of calculated from savitsky golay filtering." I am not certain exactly what it is supposed to say.

Revised to "Uncertainties of Savitsky Golay filtering."

- SI P7FigS7 - The caption says "Two boxes: : :" but there are five.

5 Revised

> Anderson, R. F., Barker, S., Fleisher, M., Gersonde, R., Goldstein, S. L., Kuhn, G., Mortyn, P. G., Pahnke, K., and Sachs, J. P.: Biological response to millennial variability of dust and nutrient supply in the Subantarctic South Atlantic Ocean, Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences, 372, 17, 10.1098/rsta.2013.0054, 2014.

10

Gottschalk, J., Skinner, L. C., Lippold, J., Vogel, H., Frank, N., Jaccard, S. L., and Waelbroeck, C.: Biological and physical controls in the Southern Ocean on past millennialscale atmospheric CO2 changes, Nat. Commun., 7, 11, 10.1038/ncomms11539, 2016.

15

Lourantou, A., Chappellaz, J., Barnola, J. M., Masson-Delmotte, V., and Raynaud, D.: Changes in atmospheric CO2 and its carbon isotopic ratio during the penultimate deglaciation, Quat. Sci. Rev., 29, 1983-1992, 10.1016/j.quascirev.2010.05.002, 2010.

- 20 Martinez-Garcia, A., Sigman, D. M., Ren, H. J., Anderson, R. F., Straub, M., Hodell, D. A., Jaccard, S. L., Eglinton, T. I., and Haug, G. H.: Iron Fertilization of the Subantarctic Ocean During the Last Ice Age, Science, 343, 1347-1350, 10.1126/science.1246848, 2014.
- Schneider, R., Schmitt, J., Kohler, P., Joos, F., and Fischer, H.: A reconstruction of atmospheric carbon dioxide 25 and its stable carbon isotopic composition from the penultimate glacial maximum to the last glacial inception, Climate of the Past, 9, 2507-2523, 10.5194/cp-9-2507-2013, 2013.

Ziegler, M., Diz, P., Hall, I. R., and Zahn, R.: Millennial-scale changes in atmospheric CO2 levels linked to the Southern Ocean carbon isotope gradient and dust flux, Nature Geoscience, 6, 457-461, 10.1038/ngeo1782, 2013.

30

## **References**

Ahn, J. and Brook, E. J.: Siple Dome ice reveals two modes of millennial CO<sub>2</sub> change during the last ice age, Nat. Commun., 5, 3723, 2014.

Baumgartner, M., Kindler, P., Eicher, O., Floch, G., Schilt, A., Schwander, J., Spahni, R., Capron, E., Chappellaz, 35 J., and Leuenberger, M.: NGRIP CH<sub>4</sub> concentration from 120 to 10 kyr before present and its relation to a  $\delta^{15}$ N temperature reconstruction from the same ice core, Clim. Past, 10, 903-920, 2014.

Bouttes, N., Roche, D., and Paillard, D.: Systematic study of the fresh water fluxes impact on the carbon cycle, Clim. Past, 7, 2012.

Fischer, H., Schmitt, J., Lüthi, D., Stocker, T. F., Tschumi, T., Parekh, P., Joos, F., Köhler, P., Völker, C., and Gersonde, R.: The role of Southern Ocean processes in orbital and millennial CO<sub>2</sub> variations–A synthesis, Quaternary Sci. Rev., 29, 193-205, 2010.

Gottschalk, J., Skinner, L. C., Jaccard, S. L., Menviel, L., Nehrbass-Ahles, C., and Waelbroeck, C.: Southern

- Ocean link between changes in atmospheric CO<sub>2</sub> levels and northern-hemisphere climate anomalies during the last two glacial periods, Quaternary Sci. Rev., 230, 106067, 2020.
   Lambert, F., Bigler, M., Steffensen, J. P., Hutterli, M., and Fischer, H.: Centennial mineral dust variability in high-resolution ice core data from Dome C, Antarctica, Climate of the Past, 8, 609-623, 2012.
   Lüthi, D., Bereiter, B., Stauffer, B., Winkler, R., Schwander, J., Kindler, P., Leuenberger, M., Kipfstuhl, S.,
- Capron, E., and Landais, A.: CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> variations in and just below the bubble–clathrate transformation zone of Antarctic ice cores, Earth and planetary science letters, 297, 226-233, 2010.
   Menviel, L., England, M. H., Meissner, K., Mouchet, A., and Yu, J.: Atlantic-Pacific seesaw and its role in outgassing CO<sub>2</sub> during Heinrich events, Paleoceanography, 29, 58-70, 2014.
   Petit, J.-R., Jouzel, J., Raynaud, D., Barkov, N. I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Davis,
- M., and Delaygue, G.: Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, Nature, 399, 429, 1999.
   Rosen, J. L., Brook, E. J., Severinghaus, J. P., Blunier, T., Mitchell, L. E., Lee, J. E., Edwards, J. S., and Gkinis,

V.: An ice core record of near-synchronous global climate changes at the Bølling transition, Nat. Geosci., 7, 459, 2014.

- Salamatin, A. N., Lipenkov, V. Y., Ikeda-Fukazawa, T., and Hondoh, T.: Kinetics of air–hydrate nucleation in polar ice sheets, Journal of crystal growth, 223, 285-305, 2001.
   Schaefer, H., Lourantou, A., Chappellaz, J., Lüthi, D., Bereiter, B., and Barnola, J.-M.: On the suitability of partially clathrated ice for analysis of concentration and δ<sup>13</sup>C of palaeo-atmospheric CO<sub>2</sub>, Earth Planet. Sci. Lett., 307, 334-340, 2011a.
- Schaefer, H., Lourantou, A., Chappellaz, J., Lüthi, D., Bereiter, B., and Barnola, J.-M.: On the suitability of partially clathrated ice for analysis of concentration and δ 13C of palaeo-atmospheric CO<sub>2</sub>, Earth and Planetary Science Letters, 307, 334-340, 2011b.
   Schmittner, A. and Galbraith, E. D.: Glacial greenhouse-gas fluctuations controlled by ocean circulation changes,
- 30 Bereiter, B., Lüthi, D., Siegrist, M., Schüpbach, S., Stocker, T. F., and Fischer, H.: Mode change of millennial CO<sub>2</sub> variability during the last glacial cycle associated with a bipolar marine carbon seesaw, Proc. Natl. Acad. Sci., 109, 9755-9760, 2012.

Lourantou, A., Chappellaz, J., Barnola, J.-M., Masson-Delmotte, V., and Raynaud, D.: Changes in atmospheric CO<sub>2</sub> and its carbon isotopic ratio during the penultimate deglaciation, Quaternary Sci. Rev., 29, 1983-1992, 2010.

- Lüthi, D., Bereiter, B., Stauffer, B., Winkler, R., Schwander, J., Kindler, P., Leuenberger, M., Kipfstuhl, S., Capron, E., and Landais, A.: CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> variations in and just below the bubble–clathrate transformation zone of Antarctic ice cores, Earth and planetary science letters, 297, 226-233, 2010.
   Petit, J.-R., Jouzel, J., Raynaud, D., Barkov, N. I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Davis, M., and Delaygue, G.: Climate and atmospheric history of the past 420,000 years from the Vostok ice core,
- 40 Antarctica, Nature, 399, 429, 1999.

Nature, 456, 373, 2008.

Anderson, R., Ali, S., Bradtmiller, L., Nielsen, S., Fleisher, M., Anderson, B., and Burckle, L.: Wind-driven upwelling in the Southern Ocean and the deglacial rise in atmospheric CO<sub>2</sub>, science, 323, 1443-1448, 2009.

Bereiter, B., Lüthi, D., Siegrist, M., Schüpbach, S., Stocker, T. F., and Fischer, H.: Mode change of millennial CO<sub>2</sub> variability during the last glacial cycle associated with a bipolar marine carbon seesaw, Proc. Natl. Acad.

# Sci., 109, 9755-9760, 2012. Bouttes, N., Roche, D., and Paillard, D.: Systematic study of the fresh water fluxes impact on the carbon cycle, Clim. Past, 7, 2012.

Gottschalk, J., Battaglia, G., Fischer, H., Frölicher, T. L., Jaccard, S. L., Jeltsch-Thömmes, A., Joos, F., Köhler, P., Meissner, K. J., and Menviel, L.: Mechanisms of millennial-scale atmospheric CO<sub>2</sub> change in numerical model

- simulations, Quaternary Sci. Rev., 220, 30-74, 2019.
   Gottschalk, J., Skinner, L. C., Jaccard, S. L., Menviel, L., Nehrbass-Ahles, C., and Waelbroeck, C.: Southern Ocean link between changes in atmospheric CO<sub>2</sub> levels and northern-hemisphere climate anomalies during the last two glacial periods, Quaternary Sci. Rev., 230, 106067, 2020.
   Henry, L., McManus, J. F., Curry, W. B., Roberts, N. L., Piotrowski, A. M., and Keigwin, L. D.: North Atlantic
- 15 ocean circulation and abrupt climate change during the last glaciation, Science, 353, 470-474, 2016. Lüthi, D., Bereiter, B., Stauffer, B., Winkler, R., Schwander, J., Kindler, P., Leuenberger, M., Kipfstuhl, S., Capron, E., and Landais, A.: CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> variations in and just below the bubble–clathrate transformation zone of Antarctic ice cores, Earth and planetary science letters, 297, 226-233, 2010. Margari, V., Skinner, L., Tzedakis, P., Ganopolski, A., Vautravers, M., and Shackleton, N.: The nature of
- millennial-scale climate variability during the past two glacial periods, Nat. Geosci., 3, 127, 2010.
   Menviel, L., England, M. H., Meissner, K., Mouchet, A., and Yu, J.: Atlantic-Pacific seesaw and its role in outgassing CO<sub>2</sub> during Heinrich events, Paleoceanography, 29, 58-70, 2014.
   Menviel, L., Timmermann, A., Mouchet, A., and Timm, O.: Meridional reorganizations of marine and terrestrial productivity during Heinrich events, Paleoceanography, 23, PA1203, 2008.
- 25 Schaefer, H., Lourantou, A., Chappellaz, J., Lüthi, D., Bereiter, B., and Barnola, J.-M.: On the suitability of partially clathrated ice for analysis of concentration and  $\delta^{13}$ C of palaeo-atmospheric CO<sub>2</sub>, Earth Planet. Sci. Lett., 307, 334-340, 2011.

Schmittner, A., Brook, E. J., and Ahn, J.: Impact of the ocean's overturning circulation on atmospheric CO<sub>2</sub>. In: Ocean Circulation: Mechanisms and Impacts, AGU Geophysical Monograph Series, 173, American Geophysical

 Union, Washington DC, 315–334, 2007.
 Schmittner, A. and Galbraith, E. D.: Glacial greenhouse-gas fluctuations controlled by ocean circulation changes, Nature, 456, 373, 2008.