Dear reviewers,

We are grateful for the detailed suggestions, and we believe that these suggestions will considerably improve our study. 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

**Anonymous Referee #4**

Received and published: 3 April 2020

Jinhwa Shin and colleagues present new measurements of CO2 trapped in bubbles of ice at the EPICA Dome C (EDC) site in Antarctica during the penultimate glaciation. They reconstruct a high-resolution record of atmospheric CO2 changes and compare its variations to climatic signals from Antarctica and the North Atlantic region. For the early part of their glacial record, atmospheric CO2 and CH4 display contrasting lags, shifting from hundreds to more than one thousand years. The authors interpret this shift in terms of a reorganization of the Atlantic meridional overturning circulation, and also conclude that the amplitude of CO2 variations may be influenced by the duration of AMOC perturbations.

The new data are welcome, nearly tripling the existing CO2 record from Vostok and nearly doubling the existing CH4 record from EDC, and the resulting discussions are worthwhile. This is a potentially valuable new contribution and can be considered for publication following revision that should include addressing the following points.

1) The new CO2 data are offset to lower values from previous data, and are not replicated. Is there an explanation for the first point and a justification for the latter?

**$CO_2$ offsets:** The ball mill system has a different extraction efficiency depending on the presence of bubbles and/or clathrates in the ice sample, which may cause an accuracy for reconstructing absolute mean $CO_2$ level. 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 $CO_2$ 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). $CO_2$ 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, $CO_2$ 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. $CO_2$ 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 $CO_2$ concentrations in the ice below the Clathrate Zone (Lüthi et al., 2010). Due to the diffusion effect, this small variation of atmospheric $CO_2$ is smoothed. Thus, $CO_2$ 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 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 $CO_2$. Thus, $CO_2$ 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 $CO_2$ 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 in the text that the absolute mean $CO_2$ level during MIS6 is not known better than 5 ppm.

This offset does appear to evolve over time, changing during late MIS 6. Additionally, uncertainties in the alignment of the Vostok and EDC age scales over MIS 6 make it unclear if the variations in the two data series are indeed contemporaneous.

This is written to Section 3.1 The new high-resolution and high precision $CO_2$ record during MIS 6.

**Data verification:** Replicates account for differences between two ice samples at the same depth, 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 $CO_2$ concentrations in the ice below the Bubble Clathrate Transition Zone, which could be accounted for by using replicates, especially for small sample sizes. Due to the diffusion effect, this small variation of atmospheric $CO_2$ is smoothed to some degree. In our study, large sample sizes (40g) of the ball mill system were used to reconstruct atmospheric $CO_2$, so a low-noise signal from the ice core is extracted (the smaller measurements used in other systems would be noisier in theory). The standard deviation of the measurement is estimated from the 5 injections, but system precision was calculated from blank measurements, which were performed after every 10 measurements accounting for the possible sources of $CO_2$ contamination with our analytical procedure.
To verify our new dataset, we made a composite data set using by aligning previous sets of measurements made over the MIS 6 period on the EDC ice core to our dataset. First, we compared to two existing $CO_2$ data sets and two new $CO_2$ data sets from EDC (Figure 1 and Table 1). There are two published $CO_2$ datasets for EDC during MIS6—the first measured by the ball mill system at IGE (Lourantou et al., 2010) and the second by the sublimation system at CEP (Schneider et al., 2013). We also compared unpublished atmospheric $CO_2$ measurements from EDC by a novel centrifugal ice microtome (CIM) system, a needle cracker and a ring mill system (Shin, 2019). All records are on the AICC2012 air age scale (Bazin et al., 2013). All data sets is corrected for the gravitational fractionation effect using the new $\delta^{15}N$ data in our study.

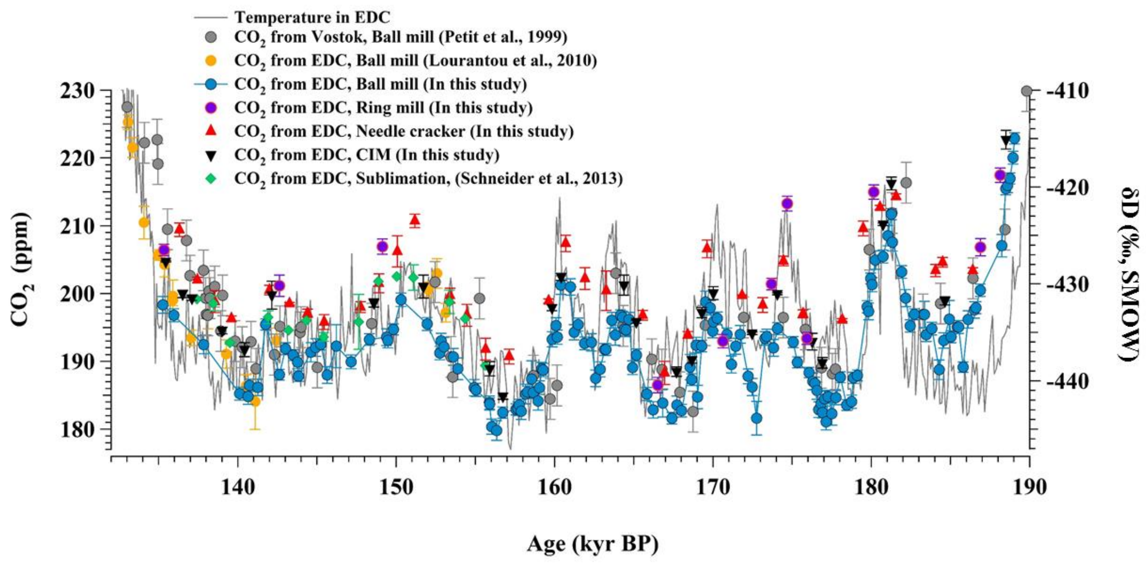


**Figure 1:** Atmospheric $CO_2$ from EDC and Vostok ice cores, compared to the δD of water at EDC (temperature proxy) during 190—135 kyr BP. Blue dots: Atmospheric $CO_2$ from EDC by ball mill system (this study). Yellow dots: Atmospheric $CO_2$ from EDC by ball mill system (Lourantou et al., 2010). Purple dots: Atmospheric $CO_2$ from EDC by ring mill system. Red equilateral triangles: Atmospheric $CO_2$ from EDC by needle cracker. Black inverted triangles: Atmospheric $CO_2$ from EDC by CIM. Green rhombuses: Atmospheric $CO_2$ from EDC by sublimation. Grey dots: Atmospheric $CO_2$ from the Vostok ice core (Petit et al., 1999). Grey line: δD of water at EDC (Jouzel et al., 2007).

Because of the limited amount of samples available, the data reconstructed by both ball mill and ring mill methods are single measurements from the depth interval. $CO_2$ records by CIM, needle cracker and the sublimation methods were reconstructed from 2–5 replicates from individual depth intervals. The error bars of data without replicate indicate that the standard deviation of five consecutive injections of the gas extracted from each sample into the gas chromatography (Lourantou et al., 2010; Petit et al., 1999). The error bars of data with replicate indicate the standard deviation of the mean of replicates from the same depth interval (Schneider et al., 2013). Figure 1 shows $CO_2$ concentrations measured by the ball mill system, the ring system, the sublimation, the CIM and the needle cracker. These $CO_2$ concentrations by the ball mill system (Lourantou et al., 2010), the ring system, the sublimation (Schneider et al., 2013), the CIM and the needle cracker are systematically higher than $CO_2$ concentrations measured by the ball mill system in our study (Table 1 and Figure 1). Atmospheric $CO_2$ during the MIS 6 period shows an offset between $CO_2$ data in this study and other $CO_2$ sets, which might be related with different analytical methods.

Where the additional datasets have enough resolution, the millennial-scale variations shown in our MIS 6 dataset are reproduced. Nevertheless, the measurements in the different datasets cannot be immediately aggregated because of offsets between their absolute $CO_2$ values. Offset residuals show that these offsets do not present any significant temporal evolution over MIS 6, but rather appear to be constant. In order to estimate these offsets while accurately accounting for both measurement uncertainty and uncertainty in the offsets themselves, we rely on a Monte Carlo procedure, which is run for 1000 iterations. At each iteration, the data from all datasets is resampled within its measurement uncertainty. Then, a Savitsky-Golay filter with an approximate cutoff period of 150 years (using a 7-point sliding window and cubic fit, sampled at 250-year resolution) is applied to the new EDC data from this study. The offsets between each additional dataset and our data are calculated. At the end of the stochastic procedure, mean and standard deviations of each offset are calculated, and used to adjust each dataset to create the composite.

In order to test the sensitivity of the stack to the interpolation methods, Monte Carlo procedures were also run using linear interpolation, cubic spline filtering, and enting spline filtering in place of the Savitsky-Golay filter. The mean calculated offsets did not vary by more than 0.2 ppm depending on the method, well within the uncertainty ranges calculated for the offsets themselves.

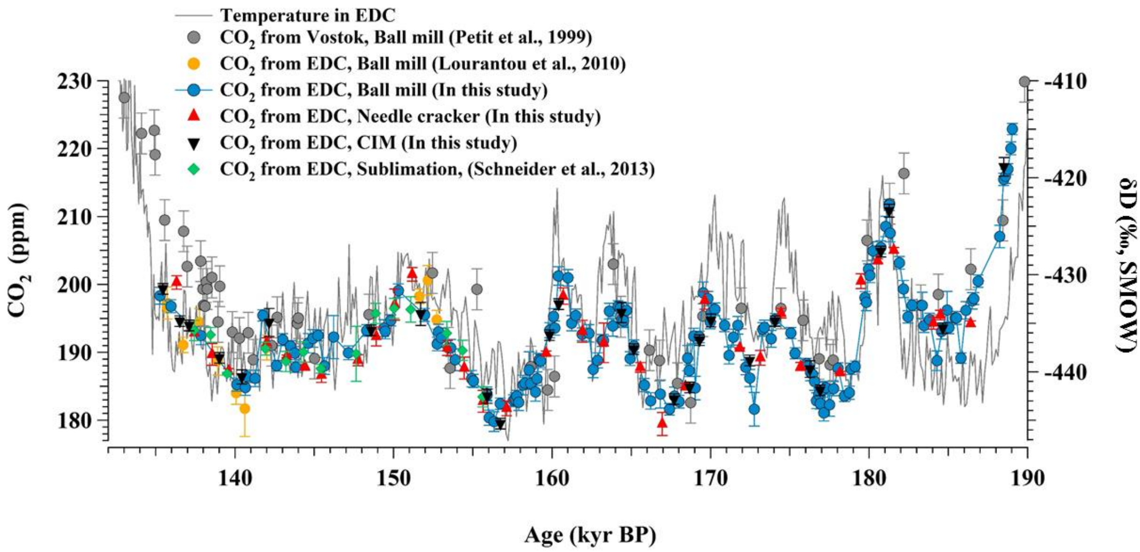


**Figure 2:** Atmospheric $CO_2$ from EDC and Vostok ice cores, compared to the δD of water at EDC (temperature proxy) during 190—135 kyr BP. Blue dots: Atmospheric $CO_2$ from EDC by ball mill system (this study). Yellow dots: Atmospheric $CO_2$ from EDC by ball mill system (Lourantou et al., 2010). Purple dots: Atmospheric $CO_2$ from EDC by ring mill system. Red equilateral triangles: Atmospheric $CO_2$ from EDC by needle cracker. Black inverted triangles: Atmospheric $CO_2$ from EDC by CIM. Green rhombuses: Atmospheric $CO_2$ from EDC by sublimation. Grey dots: Atmospheric $CO_2$ from the Vostok ice core (Petit et al., 1999). Grey line: δD of water at EDC (Jouzel et al., 2007).

There are two main sources of uncertainty in the composite dataset--the measurement uncertainty of the data, and the uncertainty of the offset itself. The offset uncertainty is not independent for each point, but should rather have very high covariance, which we cannot account for exactly since there are no exact replicates, and we are limited to estimating a mean offset for each data set. Therefore, these two sources of uncertainty are presented separately, and not aggregated.

We also use this procedure to estimate an offset between our data and the data measured on the Vostok ice core. However, this offset does appear to evolve over time, changing during late MIS 6. Additionally, uncertainties in the alignment of the Vostok and EDC age scales over MIS 6 make it unclear if the variations in the two data series are indeed contemporaneous. We therefore do not include the Vostok data in the composite.

The composite dataset confirms the millenial-scale variations shown in the data from this study (Figure 2). Although none of the individual additional datasets is of high enough resolution to show millenial-scale variations with accuracy, when aligned to our data the new data follow the millenial-scale variations with very few outliers.

Finally, the uncertainty with respect to the absolute $CO_2$ value should be noted. The offsets between the multiple datasets are in large part likely due to differences in extraction efficiency between the measurement methods. The sublimation and ring mill systems have high extraction efficiency on clathrates, and should therefore present more unbiased baseline $CO_2$ values. However, since these datasets are as of now incomplete, we have aligned all datasets to the baseline absolute value of our ball mill dataset, and the absolute $CO_2$ values are reported within an uncertainty of ~5 ppm. We emphasize that the conclusions in this paper are only made with respect to relative values, and absolute values are only considered within their uncertainties.

**Table 1:** Existing $CO_2$ data sets from EDC and Vostok ice core and new $CO_2$ data from EDC during MIS 6.

| Ice core | Method (Reference) | $CO_2$ difference with $CO_2$ from EDC by ball mill in this study (ppm) | Contamination correction | Number of replicates | Number of sample |
|---|---|---|---|---|---|
| EDC | Sublimation at CEP Schneider et al. (2013) | 4.7± 1.7 (1σ) | O | 2–5 | 14 |
| | Ball mill at IGE Lourantou et al. (2010) | 2.4±2.1 (1σ) | X | 1 | 11 |
| | Ring mill at IGE (In this study) | 8.2±1.1 (1σ) | O | 1 | 11 |
| | Needle cracker at CEP (In this study) | 7.8± 1.1 (1σ) | O | 2–4 | 35 |
| | CIM at CEP (In this study) | 5.4± 1.0 (1σ) | O | 2–4 | 26 |
| Vostok | Ball mill at CEP Petit et al. (1999) | 4.6± 3.0 (1σ) | X | 1 | 49 |

This is written to new section 3.2 Data verification.

2) The authors state that they "make use of contrasting boundary conditions during the last two glacial periods to gain insight into the co-occurring carbon cycle changes." They then note that those boundary conditions are only "slightly different", and in the end, never explain what those differences are or why they might be expected to matter. This undermines the rationale for proceeding with this study and should be much better explained in a revised manuscript.

P3L1-P3L11 revised to: Comparing $CO_2$ changes on millennial time scales during the past two glacial periods, MIS 3 (MIS 3, 60–27 kyr BP) and early MIS 6 (early MIS 6, 185–160 kyr BP) can provide us with a better understanding of the carbon mechanisms at work, due to the similarities but also differences of climate conditions and events during the last two glacial periods (see Figure S1 in SI (Supplement Information)). Proxy evidence indicates that the states of several important components of the climate-carbon cycle were not entirely analogous in MIS 3 and MIS 6. Sea ice cover in the South Atlantic was more extensive during MIS 6, and sea surface temperature in the South Atlantic is thought to have been lower (Gottschalk et al., 2020). The bipolar see-saw phenomenon also has been observed to be active during the early MIS 6 period (Cheng et al., 2016; Jouzel et al., 2007; Margari et al., 2010). For example, the bipolar see-saw events during MIS 6 are longer than MIS 3. Events of iceberg discharge into the NA, which are thought to have driven millennial-scale changes in the meridional overturning circulation during MIS 3 (de Abreu et al., 2003; McManus et al., 1999) appear to be much more frequent during MIS 3 than during MIS 6. During the early MIS 6, iceberg discharge was muted (de Abreu et al., 2003; McManus et al., 1999). During the time period around 175 kyr BP, summer insolation levels in the Northern Hemisphere approached interglacial values (Berger, 1978). Due to the stronger Northern Hemisphere insolation, the intertropical convergence zone (ITCZ) is thought to have shifted northward, intensifying monsoon systems in low latitude regions, such as in Asia, the Appenine Peninsula and the Levant (Ayalon et al., 2002; Bard et al., 2002; Cheng et al., 2016). This may have led to a weaker overturning circulation due to the reduction of the density of the North Atlantic surface water, making the AMOC cell shallower during MIS 6 than during MIS 3 (Margari et al., 2010). Thus, this intensified hydrological cycle may help explain a shallower AMOC cell with a limited iceberg discharge in NA and the prolonged bipolar see-saw events during the early MIS 6 (Gottschalk et al., 2020; Margari et al., 2010).

3) It appears that a potentially significant conclusion of the manuscript derives from the observations associated with a single small millennial event. This hardly seems justified and should be bolstered either by theoretical arguments or indications of similar behavior in existing data from another time interval.

Many similar events are present in MIS3 (see Figure 7 in the main text), bolstering our conclusion.

Revised to: We measured 150 samples of the EDC ice core to reconstruct atmospheric $CO_2$ during the MIS 6 period (189–135 kyr BP), with a high time resolution and an improved analytical precision. In this study, we investigate how different climate background conditions during the last two glacial periods impact atmospheric $CO_2$. Millennial-scale atmospheric $CO_2$ changes are found during both last two glacial periods, with amplitudes ranging between 15 to 25 ppm, mimicking similar trends in Antarctic δD variations (Ahn and Brook, 2014; Bereiter et al., 2012). On the other hand, during short NA stadials which last less than 1,500 yrs, atmospheric $CO_2$ variations are negligible and decoupled with δD in EDC. This finding suggest that during the last two glacial periods, the amplitude of $CO_2$ is highly determined by the NA stadial duration (r=0.83, n=20).

The division and labeling of sub-events is neither referenced nor adequately described, much less explained. Such division is understandable and can be helpful, but only if clearly delineated and consistently applied. Are the divisions related to marine oxygen isotopes, and should they be, or to something else? What is the justification for 6c, 6d, and 6e, when there is no 6a or 6b?

Carbon Dioxide Maxima (CDM) are named according to the MIS timescale developed by Railsback et al. (2015). Figure 1 in the main text revised.

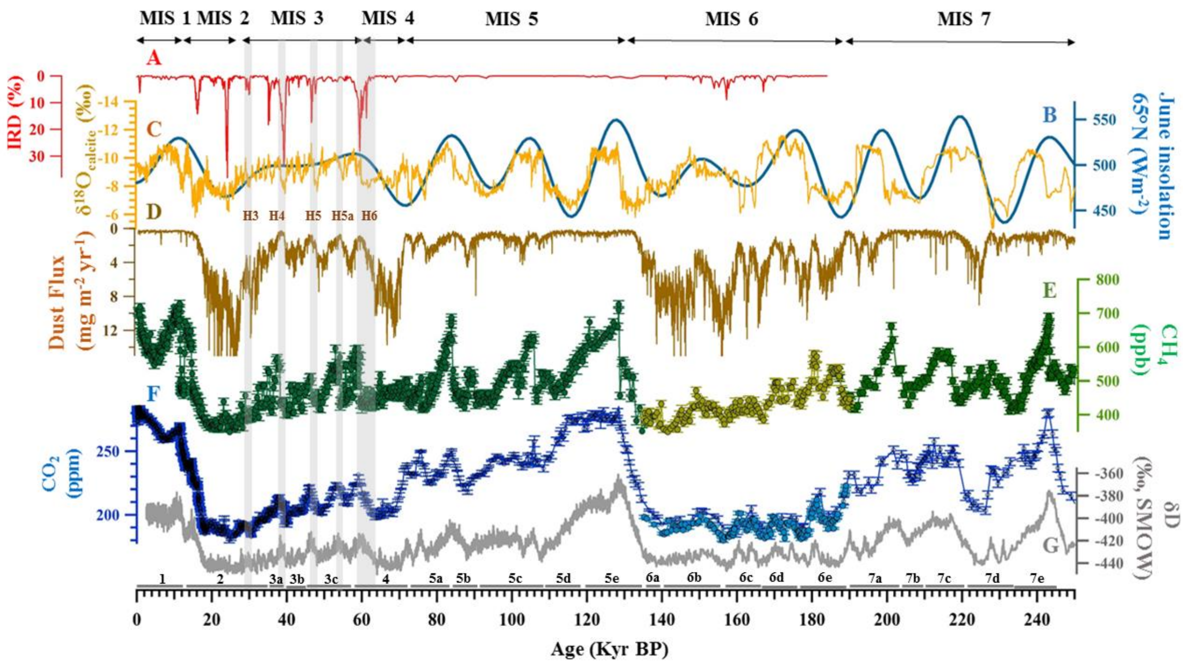


**Figure 1:** Proxy data during 250 kyr BP. A: Ice-rafted debris (IRD) input in the Iberian margin core MD95–2040 (de Abreu et al., 2003). B: 21 June insolation for 65°N (Berger, 1978). C: $\delta^{18}O_{calcite}$ from Sanbao cave, corresponding with the strength of the East Asian monsoon (Cheng et al., 2016). D: Dust flux in EDC (Lambert et al., 2012). E: Atmospheric $CH_4$ in EDC (green dots) (Loulergue et al., 2008) and Atmospheric $CH_4$ in EDC in this study (light yellow dots). F: Atmospheric $CO_2$ from EDC in this study (light blue dots) and composite $CO_2$ from Antarctic ice cores (dark blue dots) (Bereiter et al., 2015). G: δD composition in EDC, Antarctica (Jouzel et al., 2007). Vertical grey bars indicate the timing of Heinrich events. The sub-stage numbers are written at the bottom (Railsback et al., 2015).

Smaller points to be considered and addressed:

Page 2 line 15 – "opposite behaviour"

Revised

Page 2 line 17 – Do the authors really infer that CO2 changes are "in response" to temperature?

Removed

Page 7 line 8 - The half cycle between minimum and maximum values is not the definition of an inflection point, nor is it any point at all.

Revised to: "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."

Page 14-15 – Data do appear to be limited, although Helmke, 2003, Kandiano, 2003, Obrochta 2014, Mokkeddem 2016, and Barker 2015 come to mind.

These datasets, while valuable for discussing MIS6, are too scattered to observe exact variations on millennial time scales and have larger age uncertainties with respect to EDC, making it complicated to use them to comment on the relationship between climate and prominent $CO_2$ variation during the early MIS 6 on millennial time scales.

Page 15, line 16 – "available"

Revised

Figure 3 – What are the "Six variations on millennial time scales: : :"?

Revised to: The durations of the six NA stadials during MIS 6 defined by Margari et al. (2010). Tree pollen percentage (top) and $\delta^{18}O$ of planktonic foraminifera (bottom) in the MD01-2444 (Margari et al., 2010). Red lines indicate the midpoint between the maximum and the preceding minimum of both $\delta^{18}O$ of planktonic foraminifera and tree pollen in MD01–2444. Blue bars indicate the range between the maximum and the preceding minimum.

Figure 5 – Golay should be capitalized in the legend.

Revised

## References


Ahn, J. and Brook, E. J.: Siple Dome ice reveals two modes of millennial $CO_2$ change during the last ice age, Nat. Commun., 5, 3723, 2014.

Ayalon, A., Bar-Matthews, M., and Kaufman, A.: Climatic conditions during marine oxygen isotope stage 6 in the eastern Mediterranean region from the isotopic composition of speleothems of Soreq Cave, Israel, Geology, 30, 303-306, 2002.

Bard, E., Antonioli, F., and Silenzi, S.: Sea-level during the penultimate interglacial period based on a submerged stalagmite from Argentarola Cave (Italy), Earth Planet. Sci. Lett., 196, 135-146, 2002.

Bereiter, B., Lüthi, D., Siegrist, M., Schüpbach, S., Stocker, T. F., and Fischer, H.: Mode change of millennial $CO_2$ variability during the last glacial cycle associated with a bipolar marine carbon seesaw, Proc. Natl. Acad. Sci., 109, 9755-9760, 2012.

Berger, A. L.: Long-Term Variations of Caloric Insolation Resulting from the Earth's Orbital Elements 1, Quat. Res., 9, 139-167, 1978.

Cheng, H., Edwards, R. L., Sinha, A., Spötl, C., Yi, L., Chen, S., Kelly, M., Kathayat, G., Wang, X., and Li, X.: The Asian monsoon over the past 640,000 years and ice age terminations, Nature, 534, 640, 2016.

de Abreu, L., Shackleton, N. J., Schönfeld, J., Hall, M., and Chapman, M.: Millennial-scale oceanic climate variability off the Western Iberian margin during the last two glacial periods, Mar. Geol., 196, 1-20, 2003.

Gottschalk, J., Skinner, L. C., Jaccard, S. L., Menviel, L., Nehrbass-Ahles, C., and Waelbroeck, C.: Southern Ocean link between changes in atmospheric $CO_2$ levels and northern-hemisphere climate anomalies during the last two glacial periods, Quaternary Sci. Rev., 230, 106067, 2020.

Jouzel, J., Masson-Delmotte, V., Cattani, O., Dreyfus, G., Falourd, S., Hoffmann, G., Minster, B., Nouet, J., Barnola, J.-M., and Chappellaz, J.: Orbital and millennial Antarctic climate variability over the past 800,000 years, Science, 317, 793-796, 2007.

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.

McManus, J. F., Oppo, D. W., and Cullen, J. L.: A 0.5-million-year record of millennial-scale climate variability in the North Atlantic, science, 283, 971-975, 1999.

Railsback, L. B., Gibbard, P. L., Head, M. J., Voarintsoa, N. R. G., and Toucanne, S.: An optimized scheme of lettered marine isotope substages for the last 1.0 million years, and the climatostratigraphic nature of isotope stages and substages, Quaternary Science Reviews, 111, 94-106, 2015.

Lüthi, D., Bereiter, B., Stauffer, B., Winkler, R., Schwander, J., Kindler, P., Leuenberger, M., Kipfstuhl, S., Capron, E., and Landais, A.: $CO_2$ and $O_2/N_2$ variations in and just below the bubble–clathrate transformation zone of Antarctic ice cores, Earth and planetary science letters, 297, 226-233, 2010.

Railsback, L. B., Gibbard, P. L., Head, M. J., Voarintsoa, N. R. G., and Toucanne, S.: An optimized scheme of lettered marine isotope substages for the last 1.0 million years, and the climatostratigraphic nature of isotope stages and substages, Quaternary Science Reviews, 111, 94-106, 2015.

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 $CO_2$, Earth Planet. Sci. Lett., 307, 334-340, 2011.