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Interactive comment on "A high resolution record of atmospheric carbon dioxide and its stable carbon isotopic composition from the penultimate glacial maximum to the glacial inception" *by* R. Schneider et al.

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Anonymous Referee #2 Received and published: 18 June 2013 Review of Schneider et al. CPD 9, 2015-2057, 2013

The structure and length of the paper are appropriate and the figures are for the most part clear, though I had trouble reading Figure 2 (perhaps not a problem for an online journal though). I did not see any mention of archiving the data once published, though this group has a great track record of doing that.

Figure 2 was actually intended for a single column figure over the entire length of a A4 page. This has been obviously scaled down for the web publication in CPD. For the final publication, we request that it will be a full length figure in CP.

Similar to the procedure of Schmitt et.al (2012), data will be archived at NOAA and PANGEA once published.

2016, line 8. It would be helpful to say in the abstract which direction the 0.4 permil offset goes – that is, which period is heavier?

We changed “offset” to “shift to heavier values”

2017, line 9. It is not clear to me what “rate of damping” means.

This accounts for the damping strength, meaning that the amplitudes of natural changes in CO2 or δ13Catm are reduced in ice cores to e.g. 50% or 20% depending temperature and accumulation rates at the specific site. This is now clarified in the text.

2017, line 10-11. I agree that precision better than 0.1 per mil is needed. But, what does “significantly better” than 0.1 per mil mean? I think this is a little vague.

We deleted “significantly”.

2018, line 25. It is not clear to me what “mean reproducibility of the respective core” means. Can you clarify?

Here, the mean reproducibility is defined as the average of the one σ standard deviation values of depths where replicate measurements were performed. This has now been stated explicitly in the manuscript.

2019, line 2. The title of the paper includes the words “high resolution” but the mean sample resolution is 600 years. Is this high resolution? There is no standard that I know of for when to use this term, but one might think it relates somehow to the ratio of the data resolution to the shortest possible variations recorded in the archive.

CPD
9, C1390–C1399, 2013

By that standard I would not say that the data are high resolution. One might also say that its use related to how difficult the measurements are or what has been done previously.Sorry, this is a minor point, but perhaps the issue is whether more data would potentially reveal more about the system or not. The authors might want to address this, though I leave that decision to the editor.

We changed the title to a less subjective measure of resolution:

“Centennial record of atmospheric carbon dioxide and its stable carbon isotopic composition from the penultimate glacial maximum to the glacial inception”

2020, line 14-17. This sentence below does not make sense to me and does not seem to convey any information. Can you elaborate?

This sentence suffers from some disarrangement. We changed it to: For this time interval, this offset between the Schmitt et al.(2012) and the Lourantou et al.(2010a) EDC bubble ice data was systematic and was attributed to any method specific systematic fractionation.

2020, line 26. One of the 13C should be a 12C. We changed the first of the 13C to 12C.

2021, line 1-2. Delta 15N can be affected by temperature change and that, and why it is probably not important in this context, should be mentioned here.

We added: “Note, that due to thermo-diffusion effects in the firn column 15N can also be affected by temperature changes, which however is of negligible importance for the EDC and Talos Dome sites, where temperature changes are reported to be slow (Jouzel et al., 2007; Stenni et al., 2011).”

2021, line7. I might have just missed it but I don’t think I saw a source for the Talos Dome delta 15N data.

This is unpublished data measured by the group of A. Landais. In the acknowledgments section, we thank A. Landais and co workers for making the data available. The data itself will be published elsewhere.

2021, line 13. Although it is true that the uncertainty in the 15N correction does not affect the single point precision of any one delta 13C measurement it surely affects comparing the atmospheric signal of one single point to another single point unless they are from the same depth. So I am not sure why it is important to raise this issue of the precision of a single point.

You are right. There is no need to draw this connection. We deleted the part "...but not single point precision."

2021, line 19. Why choose cutoff of 375 yr? What happens if you choose a different number?

Choosing a different number would result in MCAs with more or less wiggles. The cutoff of 375 years accounts for the signal damping rate in the EDC ice core at that time (described in detail in Schmitt et al. (2012)). Due to the gas enclosure process, faster amplitudes than 375 years cannot be resolved in measurements. Thus, with choosing 375 years as cutoff, we perform a maximum possible spline calculation. Note however, that the true atmospheric evolution is not represented by the spline itself; this gives just a guide to the eye. The true centennial atmospheric evolution follows a temporal evolution that stays within the error-range of the MCA. We clarify this now in the manuscript.

2022, line 27. I think it would be clearer if there were a comma after "0.2."

We added the comma.

2023, line 5. Figure 3 is referred to here and I do not think I saw a reference to figure 2 before this. Are they out of order?

On page 2022, line 16, we first refer to Figure 2.

2024, line 9-12. What is the evidence for no carbonate reactions in Talos Dome? The current statement is a bit vague. Also on these lines, the statement about the gravitational correction is unclear. Does it mean that when that correction is made the difference between the cores in CO2 concentration increases?

Talos Dome shows very low dust level concentrations. Furthermore, Talos Dome replicates of same depth intervals show the best quality in δ13CO2, meaning error bars are smallest compared to e.g. very scattered EDML data, where we know that a very small contribution of in situ production of CO2 occurs. Hence, we do not have a hint for disturbed δ13CO2 and CO2 data from Talos Dome, however, we cannot completely rule out in situ effect even smaller than for EDML. We added this to the text. Furthermore, it is correct, that the offset between the cores in CO2 will slightly increase when both cores are corrected for their individual gravitational settling, meaning that this effect cannot explain the observed difference but does make things worse. We clarified that in the text.

2024, line 15-21. The discussion about damping of the signal explaining part of the offset between the cores does not completely convince me. I think the mean value for both cores over the period of interest should be the same, one should just be more smoothed than another. I would like to see a model of the process if the authors believe it is the correct explanation. Otherwise I would suggest reconsidering the possibility of in situ production or at least giving it a little more credibility. Note that a millennial excursion is noted in the EDC record on lines 28-29, so these can be preserved. Also in this section, the authors should refer to the CO2 data from the Dome Fuji ice core from Kawamura et al. (2007, Nature, dry and wet extraction) for Termination II, both in terms of timing and absolute values.

We agree that in situ production cannot be completely ruled out. However, neither can be the signal damping. The CO2 data sets of Talos Dome and EDC tend to overlap after 126'000 years BP. The CO2 peak around 128'000 years BP just might be more pronounced in Talos Dome as accumulation rates were higher. Furthermore, the Talos

CPD
9, C1390–C1399, 2013

Dome evolution is potentially stretched due to erroneous dating in that time interval. The used Talos Dome age scale is one of the first versions and not completely aligned to other cores, via matching using e.g. methane data. This is a crucial point questioning the overall possibility to accurately compare the Talos Dome and EDC CO2 data around that time interval. We believe that the CO2 data measured on Dome Fuji by Kawamura et al. (2007) do not draw a consistent picture. Wet and dry extraction data neither completely agree with each other nor with established data by e.g. Petit et al. (1999). Especially for MIS5.5 the wet extraction CO2 data is significantly higher than the dry extracted CO2 data, which resembles the atmospheric value more closely. Accordingly, the wet extraction data do not help to assess the early CO2 peak in MIS5.5. Unfortunately, there exist no dry extraction CO2 data from Dome Fuji for the onset of MIS5.5 in the paper by Kawamura. Accordingly also, dry extraction data do not help to assess the early CO2 peak. Because of this and to avoid confusion and a discussion concerning accuracy and precision of data sets measured with different techniques at different laboratories on different ice cores, we focused on the comparison of our data sets, measured with the same technique, by the same person at the same spot. However, we now mention and cite the Kawamura data in the paper and clarify that this data set does not help to assess the early CO2 peak in MIS5.5

2024, line 19-28. The change in d13CO2 in interval 2 becomes important later in the paper because an analogy is drawn to the large decrease during the early part termination 1. Here though the paper is a bit vague about how much d13C of CO2 really changes during that interval. A figure of about 0.2 per mil is quoted, but the data are pretty scattered. Because it becomes important later I think more attention should be given to how much the data really constrain trends during this interval.

It is true, that the decrease in the δ 13Catm data in interval II is less sharp and clear in Termination II as during Termination I. However, the spline as well as the uncertainty range clearly decreases by about 0.2 permil between 14’500 and 13’000 years BP. We agree that the data resolution is not very high in that time frame and future studies

CPD
9, C1390–C1399, 2013

might clarify this issue. For the time being the statistical analysis of the MCA is the best way to assess the d13Catm dip and this qualitatively points to a δ 13Catm drop at the beginning of both Termination 1 and 2, within the error limits. We discuss this now in some more detail in the manuscript.

2026, line 14. I suggest changing "we briefly report on" to something like "it is useful to consider."

We changed that.

2027, lines 5-15. It would be helpful to state the isotopic composition of the carbon source in the scenarios discussed here. What about methane hydrates, could they be involved in this putative oscillation?

For detailed calculations and discussions of the scenario we refer to Köhler et al. (2011). Here we want to state that an even lighter isotopic signature of CO2 produced from oxidation of hydrate released CH4 in the water column could be envisaged to create a fast drop in d13Catm but cannot explain the even faster re-increase in d13Catm after the event, as we think a rapid clathrate formation event is essentially impossible. Moreover, even so the coeval CO2 increase due to such a hydrate related CO2 release would be most likely 50-70% smaller than for terrestrial carbon, we should still be able to resolve such a CO2 increase in our concentration record. Accordingly, we think clathrates cannot explain the fast events in the Lourantou data and some analytical problem appears more likely, as we do not see such d13Catm excursion in our data set.

2027, line 19-24. It appears to me that the authors feel that the oscillation reported by Lourantou et al. are some kind of analytical artifact but the text does not quite state that clearly. The use of the terms "rather must consider" is vague. I suggest some clarification here.

It is neither in the scope of the paper nor in the abilities of the authors to judge the correctness of data measured by others. We only can have an objective look on published data in the context of natural possibilities and limitations, which in this specific case favour analytical artifacts being the most likely explanation for the oscillation reported by Lourantou et al.

2028, line 12. The word "incline" is confusing here.

We changed "incline" to "decline".

2028, line 25-26. Here the decrease during interval II is described as a maximum of 0.2 per mil. Referring to my earlier comment, I am just not sure how robust this change is in the data. I am concerned that the authors are trying to tell a simple story, that the terminations I and II are similar, but it is not clear to me that the data are really good enough. As mentioned above I think this deserves some more attention.

See above.

2029, line 25. It is not clear what "our record" refers to here. T1 data or T2?

It is Termination I. We added that to the text.

2030, line 24-28. This paragraph needs a citation.

We added the citation: Menviel, L., Joos, F., and Ritz, S. P.: Simulating atmospheric CO2, 13C and the marine carbon cycle during the Last Glacial/Interglacial cycle: possible role for a deepening of the mean remineralization depth and an increase in the oceanic nutrient inventory, Quat Sci Rev, 56, 46-68, 10.1016/j.quascirev.2012.09.012, 2012.

2033, line 14-16. As mentioned above I am concerned about how well constrained a decrease in d13C is during the beginning of TII, which is the feature that I assume leads to the conclusion that upwelling of isotopically light water and/or decrease in iron fertilization happened at this time. At least it would be good for the authors to comment (as requested above) on how well the data really constrain the d13C change.

See above.

2035. General comment on section 4.4 : I find the question this section addresses very interesting. I wonder if changes in the amount of carbon in the methane hydrate reservoir would have any leverage on the difference between the two glacial periods. Could this be addressed?

We are grateful to the reviewer for pointing out the potential influence of a changing methane hydrate reservoir size on the carbon cycle evolution. To assess this potential influence, the overall methane hydrate reservoir size is an important point. Current estimates are 500 to 2500 GtC (Milkov, 2004). Redoing the same mass balance calculation as done in section 4.4 of the manuscript at an assumed signal preservation of 50% but an isotopic signature of -60 permil (representative for methane hydrates) instead of -28 permil, reveals a necessary hydrate buildup of about 500 GtC to account for the 0.4 permil shift between PGM and LGM. In the frame of the estimates by Milkov (2004), this number would require that of 20-100 % of the carbon stored in hydrates would have been built up during the last 100,000 years, which appears to be unrealistically large. However, we acknowledge that using older, larger estimates of the hydrate reservoir would make this scenario more likely. Moreover, Fenn et al. (2000) report that today's methane hydrates were formed million of years before than the time interval discussed in this paper. This would also be at odds with relatively young hydrate accumulated during the last 100,000 years. As sea level and temperature conditions during the PGM and the LGM were not too different, it appears also unlikely that there was a major change between these two time intervals in the stability conditions for marine hydrates and, thus, their reservoir size. Hence, methane hydrates represent a further possibility to account for the measured δ 13C offset, and our data per se cannot rule out such a scenario, however, in the bigger picture of hydrate amount and age, a major influence is rather unlikely. We added a respective paragraph to the text.

2035, line 7-9. Not clear what the word “favourable” refers to.

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We deleted “favourable”.

2037, line 18. I think a flux is being discussed so a time unit is needed (Gt C/yr?).

corrected.

2039, line 26. “Both time intervals are about 120,000 yr apart” does not quite work – the intervals are 120,000 years apart from each other. Rewording (replace “both time”with “the”) is needed.

corrected

2040, line 8. It would be best to use a different term than “isotopic dilution process” since isotope dilution has a specific meaning in analytical geochemistry.

We changed it to ”isotopic attenuation process”

2040, line 16. Misspelling – “preservation” should be preservation.

corrected

Figure 1. Typo in caption (scalqe instead of scale).

corrected

Figure 3. The caption says that d13C is plotted but only CO2 is plotted.

We deleted δ 13Catm.

Interactive comment on Clim. Past Discuss., 9, 2015, 2013.