

Dear reviewers,

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

Anonymous Referee #3

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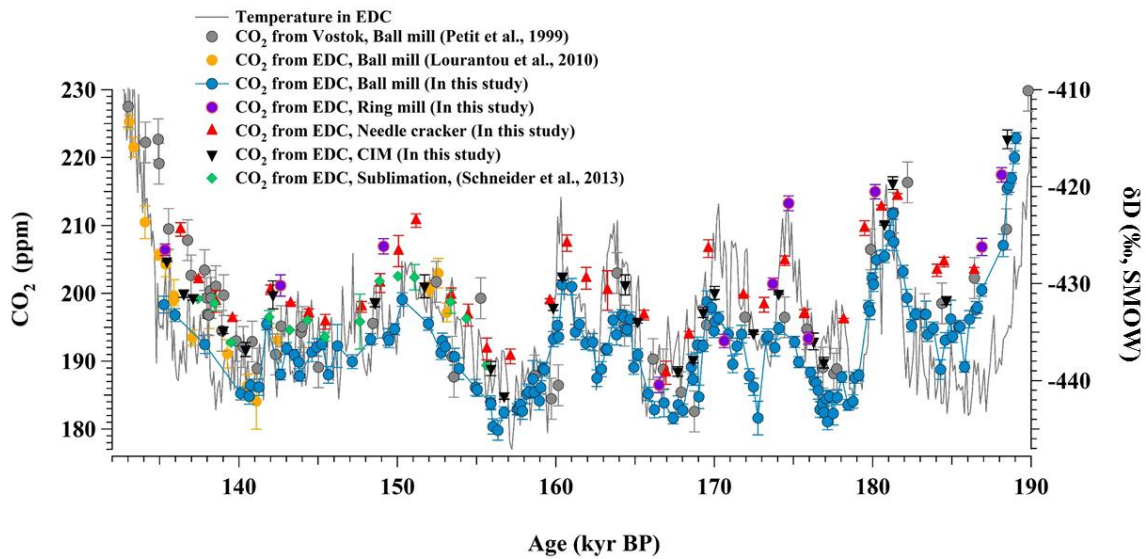
This manuscript presents new and important atmospheric CO₂ concentration data from the penultimate glacial period, also known as MIS6. The data concern so-called millennial-scale climate change, which has been well documented from Greenland ice cores. Because the Greenland ice cores do not extend back into MIS6, the natural archive in which to study millennial-scale climate for this period is Antarctic ice. The data appear to be of high quality and the discussion is appropriately oriented to the question of the temporal lag of peak CO₂ behind millennial-scale warm intervals. The lag is found to be larger in the colder intervals than in the warmer intervals, much as was previously found for the more recent period of MIS 3 to MIS 5.

The one major thing I find lacking in this paper is replication of CO₂ data points from the same depth in the ice core. Replication of gas measurements in ice cores is fundamental in order to have confidence in the accuracy of the data. Furthermore, the authors should calculate a pooled standard deviation from the means of replicates cut from the same depth in the ice core. This is widely viewed in the field as the most reliable indicator of the overall precision of the measurement, including potential issues arising from the ice itself (such as in-situ CO₂ production).

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 CO₂ 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 CO₂ is smoothed to some degree. In our study, large sample sizes (40g) of the ball mill system were used to reconstruct atmospheric CO₂, 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 CO₂ 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 CO₂ data sets and two new CO₂ data sets from EDC (Figure 1 and Table 1). There are two published CO₂ 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 CO₂

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 $\delta^{15}\text{N}$ data in our study.



5 **Figure 1:** Atmospheric CO₂ from EDC and Vostok ice cores, compared to the δD of water at EDC (temperature proxy) during 190—135 kyr BP. Blue dots: Atmospheric CO₂ from EDC by ball mill system (this study). Yellow dots: Atmospheric CO₂ from EDC by ball mill system (Lourantou et al., 2010). Purple dots: Atmospheric CO₂ from EDC by ring mill system. Red equilateral triangles: Atmospheric CO₂ from EDC by needle cracker. Black inverted triangles: Atmospheric CO₂ from EDC by CIM. Green rhombuses: Atmospheric CO₂ from EDC by sublimation. Grey dots: Atmospheric CO₂ 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. CO₂ 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 CO₂ concentrations measured by the ball mill system, the ring system, the sublimation, the CIM and the needle cracker. These CO₂ 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 CO₂ concentrations measured by the ball mill system in our study (Table 1 and Figure 1). Atmospheric CO₂ during the MIS 6 period shows an offset between CO₂ data in this study and other CO₂ sets, which might be related with different analytical methods.

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 CO₂ 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). CO₂ 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, CO₂ 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 CO₂ in Bubble–Clathrate Transformation Zone (BTCZ), CO₂ concentrations can be biased.

Table 1: Existing CO₂ data sets from EDC and Vostok ice core and new CO₂ 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

CO₂ 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 CO₂ concentrations in the ice below the Clathrate Zone (Lüthi et al., 2010). Due to the diffusion effect, this small variation of atmospheric CO₂ is smoothed. Thus, CO₂ 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 bubble would be depleted in CO₂. Thus, CO₂ concentrations from EDC may be lower. In addition, different analytical methods can cause CO₂ offsets.

In our study, we concentrate on the relative millennial changes of CO₂, which are confirmed by all of the EDC CO₂ records available so far. Thus, our conclusion in this paper are independent which absolute mean CO₂ 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 reference record and correct for any inter-core offsets (see Figure 2 and Figure 3). We, however, state explicitly in the text that the absolute mean CO₂ level during MIS6 is not known better than 5 ppm.

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.

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. 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.

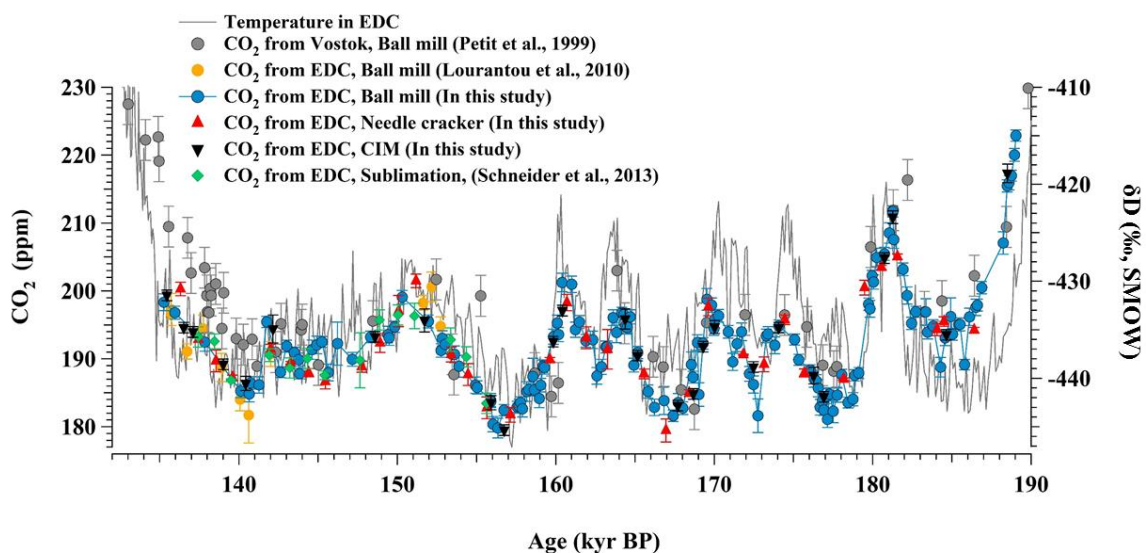


Figure 2: Atmospheric CO₂ from EDC and Vostok ice cores, compared to the δD of water at EDC (temperature proxy) during 190—135 kyr BP. Blue dots: Atmospheric CO₂ from EDC by ball mill system (this study). Yellow dots: Atmospheric CO₂ from EDC by ball mill system (Laurantou et al., 2010). Purple dots: Atmospheric CO₂ from EDC by ring mill system. Red equilateral triangles: Atmospheric CO₂ from EDC by needle cracker. Black inverted triangles: Atmospheric CO₂ from EDC by CIM. Green rhombuses: Atmospheric CO₂ from EDC by sublimation. Grey dots: Atmospheric CO₂ 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—rather, since the offsets

appear to be approximately constant, the offset uncertainty should apply to all points together (or at least present very high covariance). 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.

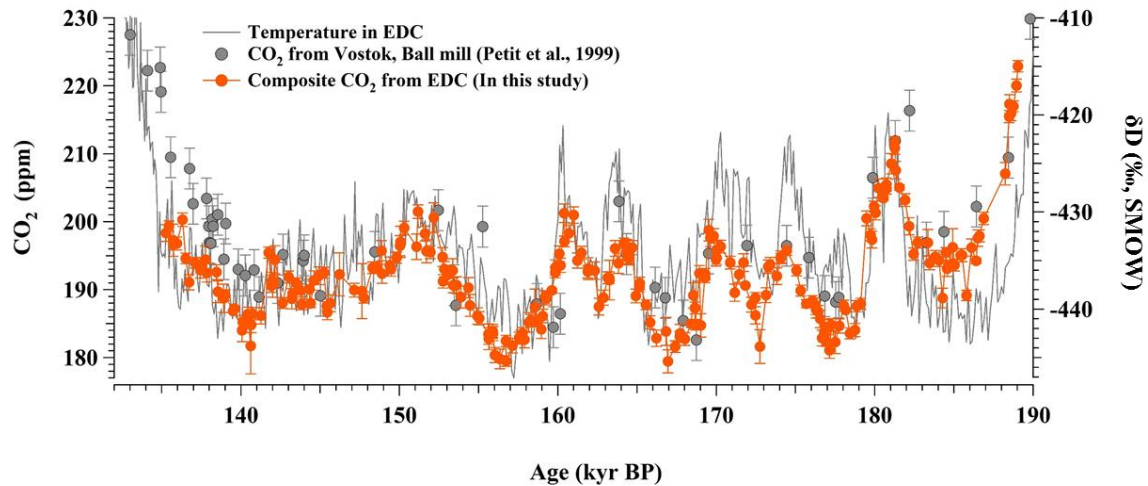


Figure 3: A composite CO₂ from EDC and Vostok ice cores, compared to the δD of water at EDC (temperature proxy) during 190—135 kyr BP.

The composite dataset confirms the millennial-scale variations shown in the data from this study (Figure 2 and Figure 3). Although none of the individual additional datasets is of high enough resolution to show millennial-scale variations with accuracy, when aligned to our data the new data follow the millennial-scale variations with very few outliers.

Finally, the uncertainty with respect to the absolute CO₂ 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 CO₂ 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 CO₂ 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.

As the new data set measured in this study provides the best record in terms of repeatability of the CO₂ measurements for the time interval of MIS 6, we use it as reference data set to homogenize all the individual CO₂ reconstructions from different cores. To this end we used a low-pass filtered version of new data from this study and calculated the residuals of each individual other CO₂ data set to this spline. To correct that data set, we used a constant offset that minimizes the root mean square error relative to this spline. Note that while this methods

finds an optimum homogenization of the data sets given their scatter and potential cross-dating issues, it does not make a statement of the correct absolute level of the homogenized data set, as all data sets are equally likely to be correct in their absolute level. As we are only interested in the relative variations over MIS 6 in our study, this has no impact on our conclusions.

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P2L24–P3L19 written to the revised manuscript in Section 3.1 The new high-resolution and high precision CO₂ record during MIS 6.

P1L23–P2L23 and P3L20–P6L4 written to the revised manuscript in new section 3.2 Data verification.

10 It is now well known that bacteria living in the ice can and do produce CO₂. The only question is, how much? So it is absolutely essential to replicate CO₂ analyses on pieces of ice cut from the same depth (and therefore presumably the same age, and having been exposed to the same atmospheric gas concentrations).

15 CO₂ records can be contaminated by the in-situ production of CO₂ caused by carbonate-acid reactions and oxidation of organic molecules, which are mostly observed in Greenland ice cores. This is because of higher values of impurities such as Ca²⁺, hydrogen peroxide H₂O₂ and formaldehyde HCHO in Greenland ice cores. These impurities can cause carbonate-acid reactions and the oxidation of organic carbon, leading to large scattering of atmospheric CO₂ data.

20 Thus to obtain less in situ CO₂ production in ice, a low carbonate concentration and H₂O₂ in an ice core are important. Luckily, Antarctic ice cores have relatively low concentrations of H₂O₂ and carbonates and have low temperature compared to Greenlandic ice cores, which reduces the risk of CO₂ contamination (Tschumi and Stauffer, 2000). It is estimated that the in-situ production of CO₂ for Antarctic ice cores is smaller than 1.5 ppm (Bereiter et al., 2009). Thus, in-situ production of CO₂ cannot be ruled out but the effect should not greatly impact our main observations. In contrast, the observed offsets (see comments above) can be explained by the combination of clathratization/relaxation processes and incomplete extraction efficiencies of the various methods used. Accordingly, we refrain from discussing a potential in situ production issue in our manuscript.

25 Therefore the authors must return to the laboratory and measure essentially another 150 pieces of ice, before this manuscript can be published in CP. The authors must also quote their value they have found for the pooled standard deviation.

30 I also did not notice any mention of the number of samples that were rejected (but perhaps I just missed it). The authors must mention this number clearly in the main text (not in the Supplement).

2 data points were identified for which experimental error could not be ruled out, so we did not include these 2 points in this study. Except for these two points, data was not rejected.

Another problem with the manuscript as it stands is the large amount of speculation in the discussion. This doesn't add to the value of the paper and can be mostly cut out, or clearly labelled as speculation in the text.

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.

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