

Author comments and responses to T. Röckmann (Referee)

First of all, the authors would like to thank T. Röckmann for his insightful comments on this draft, which definitely improve the quality of this paper. Based on the interactive comments by T. Röckmann, the authors have carefully revised the paper. Below are the authors' responses to the specific question or comment.

1) The description of blanks, the discussion of the relevant data in the tables and the correction for blanks in the derivation of the final concentration and isotope values.

Answer: There are two different blanks addressed in the paper: Schütze blank and ice blank. The Schütze blank arises from the cryogenic vacuum extraction system itself. While the origin of the Schütze blank is not clear, it is likely impurities from the ingredients used to make the reagent are responsible for the majority. Another possibility is outgassing from the viton o-rings, however after three years' use the blank has not changed appreciably. All viton o-rings were originally baked out at 130°C for 24 hrs after which the blank was unchanged. The ice blank arises from the cleaning process of ice and wet extraction process. To derive the final CO concentration or isotopic ratios for ice core samples, the signal from these two blanks is subtracted from the sample signal with a mass balance calculation. Therefore, characterization for blanks is very crucial for our results. The Schütze blank signal (table 3) is believed to be proportional to the collection time rather than the sample amount. First, the CO concentration of the zero air used to determine Schütze blank is estimated to be less than 1 ppbv based on the conventional extraction method by processing hundreds of liters of sample. Second, with the same collection time, doubling the flow rate from 50 mL/min to 100 mL/min only increases the Schütze blank by 10%, indicating the Schütze blank is not sensitive to sample volume at all.

2) Don't you want to say at least a few sentences about the scientific significance of the ice air results? I do not suggest a full interpretation, but at least some remarks on what you see there. For example: How do the isotope values in the ice compare to the annual average in Antarctica? Heavier or lighter? Does it go in the same direction as expected from the gravitational signal, or opposite? How large is the shift compared e.g. to the $\delta^{15}\text{N}$ of N_2 , which should be a good proxy for the gravitational effect in $\delta^{13}\text{C}$ of CO , since it has the same masses. A few words would make this paper much more interesting than just presenting reproducibility.

Answer: A paragraph has been added in the revised draft to address the questions the referee mentioned.

3) There are (too) many spelling and language errors throughout the manuscript, at least from page 2692 on, which the authors should correct. I note several of them below, but I strongly recommend the authors to perform a thorough language check!

Answer: The paper has been checked thoroughly by a native English speaker.

Ad 1) Please describe in detail what the different blanks are the “analytical blank”, the “system blank”, the Schütze blank” and the “ice blank” page 2694, 15 ff: Please describe the data in table 3 in more detail. What is the average isotopic composition? How is this used to correct samples? What about the dependence on the gas amount (or extraction time)? It would have been useful to perform one test with 100 ml only but extended time to be able to differentiate between sample amount and extraction time. If you have data, please show them.

Answer: Please see answer above on the system blank.

page 2694, 115 ff: please specify: after the ice was flushed with zero air for a few times??? What is really done? Can the blank be decreased even further? Discuss the data in table 4, including the isotope data. How is this blank taken into account in the calculation of the final delta value? And variations of this blank (factor 2 in table 4)?

Answer: Please refer to the revised draft. High ice blank of 140 pmol CO was found resulting from CO adsorption on the ice surface, which decreased significantly to a level of 20 pmol CO after the ice and container was repeatedly evacuated and flushed with zero air three times. This ice blank could not be reduced more with further flushing by zero air.

Why is the d18O value from the "dark" experiment significantly lighter than the rest (but the amount and d13C) are not significantly higher? What would you actually expect from photochemical production? Please discuss the table better!

Answer: Please refer to the revised draft. In situ photochemical production CO gives lighter $\delta^{13}\text{C}$ since $\delta^{13}\text{C}$ of CO from oxidation processes is much lighter (Stevens and Wagner, 1989) than the -15‰ observed in this study.

page 2697, section 3.3: Please show how the blank contamination is accounted for in the calculation of the ice core data. there may be two different blanks here, the ice blank and the Schütze blank. How sensitive are the results to these blanks?

Answer: Please see answer above on the system blank.

I suggest that the tables are listed in the order they are used in the text, and I think this is 3-4-1-2 ad 3)
It has been changed.

All comments listed on the grammar mistakes have been taken and they have been corrected in the revised paper.

114 FF: write down the average and standard deviation for the dual inlet and con flow results, either in the text or in table 1. Please also report the usually assigned error for a "full" dual inlet measurement, not only the MS error, this is comparing apples and pears. Also mention that the sample from Mauna Loa can be used to assess the linearity of the system, since this sample is isotopically far away from the others.

Answer: the standard deviation for full dual inlet measurement has been reported in the revised draft and the linearity problem has also been addressed based on the Mauna Loa sample.