

Interactive comment on “A sublimation technique for high-precision measurements of $\delta^{13}\text{CO}_2$ and mixing ratios of CO_2 and N_2O from air trapped in ice cores” by J. Schmitt et al.

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Review of J. Schmitt et al.: “A sublimation technique for high-precision measurements of $\delta^{13}\text{CO}_2$ and mixing ratios of CO_2 and N_2O from air trapped in ice cores”

The authors present a new technique for extracting gases from ice samples using sublimation and subsequent measurement of CO_2 and N_2O mixing ratios as well as $\delta^{13}\text{CO}_2$, the latter as the main focus of the work. This serves to reconstruct palaeo-atmospheric changes in $\delta^{13}\text{CO}_2$, which may be used to constrain past changes in the carbon cycle. The presented method presents the new state of the art. It is well designed in all aspects and details. The description and documentation for the purpose

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of this paper is excellent. The only point where I see room for improvement is the calibration procedure (discussed below). I recommend the manuscript for publication in Atmospheric Measurement Techniques. I think that several points listed below should be discussed before publication in order to improve the manuscript.

General comments:

The figure numbering and their mentioning in the text are erroneous. My best guess is that the source for the confusion stems from two photo figures, i.e. current Fig. 2 and an apparently removed Fig. 3. All figure numbers in text and captions should be updated.

At several incidences the authors stress the ability of the presented method to extract gas at close to 100% efficiency, as well as the importance of this to make the method superior to mechanical extraction techniques. However, at no point do they present evidence of their actual extraction efficiency. The latter could theoretically be reduced due to, e.g., absorption on surfaces or in the deposited ice in the primary (internal) water trap, or being retained in subsequent traps. This is not to be critical of the method, which demonstrably produces excellent results, but if such importance is placed on quantitative extraction the point should be proven and discussed.

Single point calibrations as they are used here introduce uncertainty because there may be a slope to the instruments response, even if the latter is linear. The uncertainty could be avoided by moving from a single point calibration system to one where reference gases or internal standards bracket the expected ranges of palaeo-values. This could easily be done with the presented set-up. All that is required are internal standards with appropriate isotopic composition (mixing ratios are already covered by the existing standards) and a processing procedure for the results that makes use of both sets of standard runs. I recommend including a discussion of this point, if only as an outline for future measurements.

Detailed comments:

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Page 1855, lines 20-23: This statement implies that dry extraction techniques are not suitable for $\delta^{13}\text{CO}_2$ reconstructions. I feel that this is an overstatement given that no problems with dry extraction techniques have yet been reported. The theoretical limitations are well stated in the preceding lines, but unless it is proven that these have practical implications dry extraction cannot be dismissed for $\delta^{13}\text{CO}_2$ analyses. In fact, a recent study that the authors cannot be aware of suggests that a dry extraction technique can yield reliable $\delta^{13}\text{CO}_2$ from fully clathrated ice (Schaefer et al., in press at EPSL). Having said that, the presented sublimation technique certainly deserves to be portrayed as the method of choice and as being subject to lower uncertainty.

1856, lines 8-10: this sentence could be tightened up.

1857, Line 4: the following paragraph may be easier to follow if the two systems would be named here, e.g., "sublimation system" and "inlet system".

line 5: Fig 3 is mentioned in the text before Fig. 2.

1858, line 9: a) this is the first mention of Fig. 2 in the text (after mentioning Figs. 3 and 4); b) Fig. 3 shows a schematic of the inlet system.

Lines 21-23: this sentence is not clear: what conductance and what cross section is referred to?

1859, line 18: Does the term "re-sublimation" refer to the reverse process of sublimation? If so, it seems that "deposition" would be the appropriate term.

Page 1860, line 10: it would avoid confusion if the "internal water trap" would be introduced by that name where it is first mentioned (page 1858, line 18 and 19; I assume) and where it is described in detail (page 1859 lines 3-19).

Page 1861, lines 6-8: this sentence should be reworded so that temperature and saturation pressure are not treated as equivalent.

Page 1861, line 16: U-shaped?

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Page 1862, lines 18-22: The range in $\delta^{13}\text{CO}_2$ provided by the two reference air tanks and the ones observed during the last two glacial terminations do not overlap (although they are close) (Lourantou et al., 2010a and b). This should be mentioned and could be followed by demonstrating the linearity of the IRMS with regards to $\delta^{13}\text{CO}_2$ (not linearity vs peak area) over the expected palaeo-range to preempt skepticism on the part of the reader. As mentioned above, the real solution for this problem is to move to a dual point calibration with appropriate internal standards.

Page 1864, line 13: disentangle?

Lines 13-14: may I suggest "...diffusion processes in the transformation zone between... and below..." in order to avoid a confusing mix of references to process and location.

Line 23: acts as a cold finger?

Lines 25-27 does the transfer last for the mentioned 60 s of warming the trap or longer? Is there a way of monitoring whether transfer is complete, e.g. via a P-sensor?

Page 1866, lines 10-22: what is the $\delta^{13}\text{CO}_2$ value of the CO_2 in the pulses?

Page 1871, lines 11-13: the fractionation observed by Luethi et al. (2010) is specific to the bubble-clathrate transformation zone (BCTZ), it is neither observed in pure bubble ice or pure clathrate ice. It stems from the preferential release of air from bubbles where those co-exist with clathrates (the latter enrich CO_2 relative to N_2 and O_2). It is correct that longer equilibration times lead to a less fractionated sample. Moreover, it is also true that a remainder of sample in the sublimation chamber is no deterrent for gas sampling efficiencies. However, the representation of the findings by Luethi et al. should be corrected to avoid confusion.

1872, lines 15-16: this is not clear; do you mean that linearity peaks contain either 1, 2 or 3 loop fillings at 8 nmol each, which then get accumulated in the cryofocussing step? If I understand correctly that each filling/flushing of the sample loop adds to the

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total sample measured, then what is the amount added per injection? Table 1 suggests that it is 8 nmol, whereas page 1873, lines 3-4 seems to say that three flushings sum to 8 nmol.

1874, lines 1-5: what about other CO₂ isotopologues that are trapped? Given the different elution times one would expect ¹³CO₂ to be enriched in the peak tail and this enrichment would be added to the measured peak. If all peaks (EQ, L, and SA) are close enough in their isotopic ratios the effect would likely cancel out (i.e., each peak would be added a similar “tail” as it loses itself). In addition, the effect may be negligible. Nevertheless, the problem is worth a short discussion.

1874, line 17: what is the isotopic composition of the monitoring gas? Is it traced back to primary standards?

1875, lines 5-10: are the peak heights for CO₂ calculated also by a one point calibration? There is no further description, yet it seems that both Boulder 1 and 2 with their mixing ratios that bracket glacial-interglacial atmospheric values should be used.

1875, lines 12-13 and 21-23: I assume this means that all values are shifted by the difference between mean of the day’s air references and assigned tank value. However, the step is mentioned twice; at the beginning and end of this paragraph. Is this correction applied before or after the other corrections?

1876, section 5.1: there is no discussion of differences between sample sets with different characteristics, i.e., bubble, clathrate, or transformation ice.

1876, lines 11-13: it would be helpful to say explicitly that precision on the Boulder tanks applies to standard gas transfers during sublimation, as opposed to direct GC-IRMS measurements of these tanks.

1877, line 2: “. . .in contrast to other ice cores.”?

1878, lines 10-13: This sentence implies that for mechanical extraction the accuracy of CO₂ concentration analyses depends on extraction efficiency. This is incorrect,

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as long as there is no fractionation between extracted and remaining gas. Given the importance of CO₂ reconstructions and the fact that mixing ratios derived with dry extraction from clathrated ice (e.g., Luethi et al., 2008) are generally regarded as true palaeo-atmospheric values, it would be quite important to test sublimation versus dry extraction on clathrated ice. Seen that data from clathrated EDC are listed in table 1, why not compare those to data published by Luethi et al. (2008)?

1878, lines 25-27: repeating the observed offsets and pooled standard deviations between Francey et al. and the new sublimation technique would be convenient for the reader, even if they have been published by Elsig et al. (2009).

1879, line 2: precision on both sets of EDC samples is lower than 0.05%.

Fig 1: graphically connecting the fore vacuum pump to the line at V(PV2) would make the graph more intuitive to read. Also, the function of the He purge with valve S1c is clear from the text, but not from the schematic.

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