

Author responses for “A new setup for simultaneous high precision measurements of CO₂, δ¹³C-CO₂ and δ¹⁸O-CO₂ on small ice core samples” by T. M. Jenk et al.

We thank both reviewers for the careful reading and the time and effort they put into improving the manuscript. We combined the comments of both reviewers in this document, responding individually to each of them. Since the line numbering they refer to is based on the version submitted for the initial 1st stage discussion forum of the interactive review process, we allowed us to add the numbering as shown in the online version in blue (brackets). Editorial (language, grammatical) revisions and minor changes were highly appreciated and were followed as suggested. Therefore they will only be listed if rephrasing of entire sentences was requested or in a very few cases where we disagreed with the suggestions because we think they would alter the initial statement. The reviewer comments are indicated by black text and our responses are in blue.

Anonymous Referee #1

Received and published: 7 March 2016

General:

This paper presents a method to precisely measure concentrations as well as stable carbon and oxygen isotope ratios of CO₂ in air extracted from ice core samples. A new approach is proposed for the correction of the procedural blank leading to more accurate results particularly for the measurements of small samples. Based on δ¹⁸O-CO₂ and δ¹⁸O-H₂O measurements, the authors introduce a method for analytical outlier detection. The use of isotope ratios for paleo-atmospheric records of carbon dioxide in ice cores provides important constraints on the natural variability of the carbon cycle.

The experimental work is of high quality and excepting some points, that need to be addressed, both description and discussion of measurements are well founded. The manuscript contributes to scientific progress within the scope of the journal, therefore it is suitable to be published in AMT.

Specific comments:

- Page9Lines268-276 (p9/line 31-p10/line7): The paragraph introducing the CO₂ mixing ratio and the delta notation requires total revision. The authors should consider using IUPAC recommendations (see e.g. Brandt et al., Pure Appl. Chem 2010).

The paragraph has been revised entirely. We did however not strictly follow the suggestion. Instead of considering Brandt et al. (Pure Appl. Chem, 2010) we followed the recommendations by Coplen (Coplen, TB; Guidelines and recommended terms for expression of stable isotope ratio and gas ratio measurement results. Rapid Commun Mass Spectrom 25: 2538–2560. doi:10.1002/rcm.5129, 2010), although in a slightly simplified form:

“CO₂ mixing ratios reported (in the literature also referred to as CO₂ concentrations) are defined as the dry air mole fraction expressed in parts per million by volume (ppm) and are linked to the World Meteorological Organization (WMO) mole fraction scale for CO₂ in air (Tans and Zhao, 2003; Zhao and Tans, 2006). Isotope ratios are reported relative to the international measurement standards (VPDB, VPDB-CO₂ and VSMOW for ¹³C-CO₂, ¹⁸O-CO₂ and ¹⁸O-H₂O, respectively) using the delta notation:

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1, \quad (1)$$

where R denotes the ratio of the heavy to light isotope in the sample and the standard, respectively.”

With this definition we believe it will be perfectly clear for all readers how the values are reported and to be interpreted. We hope the reviewer can agree with this new definition, otherwise we would be grateful for specific suggestions.

For better readability, very long phrases must be broken apart into shorter clearer sentences.

Examples:

Page3Lines63-67 (p3/line 21-25)

Rephrased to: “Further challenges arise from sorption and contamination effects at surfaces particularly in connection with mechanical friction between system components (e.g. Zumbunn et al., 1982), system leakage, outgassing materials and introduction of contaminants (e.g. drilling fluid).”

Page22Lines679-682 (p22/line 31-p23/line2)

Rephrased to: “However, such an approach requires the assumption that the extra CO₂ contribution of the procedural blank is variable in terms of amount (i.e. moles) in such a way, that regardless of the CO₂ mixing ratio of the sample and the amount of air extracted for the analysis the offset will result in a constant value of the mole fraction (i.e. the same value in terms of ppm).”

Page23Lines704-709 (p23/line 24-29)

Also the following part of this section was rephrased to: “For sample sizes 10 times bigger than the ones analyzed in this study (i.e. ~100 g ice), the scale compression bias resulting from the application of the conventional approach was calculated for an ice core record covering the Holocene (approximated range: 370 to 180 ppm in CO₂ and -6.6 to -6.3 ‰ in δ¹³C). For the δ¹³C of the blank, the determined low value of -27.6 ‰ was used. The procedural blanks for the conventional correction of CO₂ and δ¹³C were assumed to be 1 ppm and 0.1 ‰, respectively. These are typical literature values and small compared to the numbers determined in this study. Employing Eq. (2) for calculation, a potential additional effect arising from variations in the ice sample size used to obtain the record is not considered. Nevertheless, the expected scale

compression bias is calculated to be 0.06 % for the commonly applied procedural blank correction.”

The description of switching valves in the Section3 is very confusing. Add in the caption a description like ‘1’ for the depicted position and ‘2’ for the switched one...

We do believe this would be even more confusing. With all the helpful suggestions provided by both Reviewers also for this section we hope that it is not confusing anymore (though admittedly still complicated).

Anyhow, in order to immediately guide the reader to the setup scheme needed for orientation we added/rephrased the starting sentence of paragraph 2 in Section 3.1 and paragraph 4 in Section 3.2 to:

“The following detailed step by step description of the measurement procedure refers to part numbering and abbreviations shown in the setup scheme in Fig. 2.”

and

“The following step by step description of the measurement procedure refers to part numbering and abbreviations shown in the setup scheme in Fig. 2.”

Editorial revisions:

- Page6Lines169-170 (p6/line 28-29): reformulate the sentence

Reformulated to:

“Our NC design for ice samples with maximum dimensions of 2.3 x 2.5 x 2.5 cm³ and a typical mass of 8–13 g is shown in Fig. 1.”

- Page7Line209 (p8/line 2-4): replace ‘nitrogen above through the isolated tube to D2.’ by nitrogen upward through the isolated tube toward D2. “

The whole sentence does read: “Whenever heat is applied, LN evaporates around the heater and the evolving N₂ bubbles transport the still liquid nitrogen above through the isolated tube to D2.”

We think the suggested change would not result in exactly the same statement. We thus did change the sentence to:

“Whenever heat is applied, LN evaporates around the heater and the evolving N₂ bubbles transport the above, still liquid nitrogen through the isolated tube to D2.”

- Page8Line243 (p9/line 6): replace ‘a gas chromatography setup’ by ‘a separation section containing traps and GC units’

Changed to: “(i) a gas separation part which allows initial trapping of the transferred sample (T2), separation of CO₂ (and N₂O) from the major air components (T3) and subsequent partitioning of the two fractions to individual lines for either final detection (main air fraction) or further purification by gas chromatography (GC–1 and GC–2),”

- Page14Lines 439-441 (p15/line 13-15): rephrase

Reformulated to: “In every sequence, the first run which includes section A (run 6) is performed using an air standard of large size (aliquot expanded from the volume between the first and last valves of the gas manifold line).”

- Page15Lines 477-479 (p16/line 18-20): rephrase

Reformulated to: “However, it increases for runs requiring loading of a new ice sample (opening of the NC) and as a consequence the described evacuation and flushing steps (~50 min, e.g. runs 6, 11, 14 and 18 in Table 3).”

- Page18Line 547 (p18/line 26). I don't understand 'surplus signal'

Lines 23-31 were reformulated: “Because we have reasons to suspect small amounts of remnant gases being present in our BFI, we considered this latter value to be representative for the purely system related effects. Compared to other systems allowing analysis of similarly small sample sizes the here defined system offset is reduced (e.g. 4.9 ppm for the KUP NC; Bereiter et al., 2013b) and most likely a result of the combined positive effect of friction-reduced motion and lower operating temperature in our NC design. Anyhow, this CO₂ enrichment – expressed in ppm before – is observed in the raw data as an elevated signal in the IRMS CO₂ peak area. The size of this extra signal can therefore be directly estimated from procedural blank measurements using already crushed BFI (see Fig. S3). Advantageous, propagation of uncertainties associated with data post-processing can then be omitted.”

- Page19Lines584-586 (p19/line 31-p20/line2): rephrase

Reformulated to: “. To correct for blank contribution, the following equation which closely approximates the isotopic composition in a pool (δ_{Σ}) of isotopically different members (m_i with corresponding δ_i) was used:”

- Page20Lines607-609 (p20/line 23-25): rephrase

Reformulated to: “This is consistent with the idea that heavy isotopic fractionation occurs when CO₂ adsorbed on inner surfaces, trapping materials and GC columns is continuously released in tiny amounts.”

- Page21Lines656-658 (p22/line 8-10): rephrase

Reformulated to:

“This further validates our blank measurements performed on extremely small sample amounts, verifying their strongly depleted isotopic composition.”

- Page21Lines660-661 (p22/line 12-13): rephrase

Reformulated to: “All raw data were post-processed correcting for the effects characterized in the given order: ...”

- Page25Lines781-784 (p26/line 6-9): rephrase

Also considering the suggestions made by Reviewer 2, a larger section (lines 6-12) was reformulated to:

“Due to its strong seasonal cycle, $\delta^{18}\text{O}\text{-H}_2\text{O}$ can be expected to vary between adjacent samples even for the high CIC sampling resolution. Because of the oxygen exchange, this leads to an analytically independent variability also in replicates of $\delta^{18}\text{O}\text{-CO}_2$ measurements (see Sect. 4.3) although no seasonal cycle is initially retained in the gas (signal smoothing in the firm). This at least partly explains the two times higher variation measured for the DE08 replicates compared to the observed variability in the QCS (Sect. 4.2.1) as well as the deviation of inter-laboratory $\delta^{18}\text{O}\text{-CO}_2$ results considering the differences in sample size and resolution used at CSIRO and CIC. The main characteristics of the system described in this study are summarized in Table 1.”

- Page26Lines802-805 (p26/line 27-30): rephrase

Reformulated to:

“Parallel samples (same depth) were measured for $\delta^{18}\text{O}\text{-H}_2\text{O}$ in similar resolution if no data existed already.”

Anonymous Referee #2

Received and published: 24 February 2016

General comments:

T.M. Jenk and colleagues present a new method for measuring $\text{d}13\text{CO}_2$, $\text{d}18\text{O}(\text{CO}_2)$, and $[\text{CO}_2]$ on small ice samples. In addition to a thorough description of the setup and procedure, problems with the measurements (such as a non-zero blank measurement) are appropriately discussed. Furthermore, a technique for determining outliers based on $\text{d}18\text{O}(\text{CO}_2)$ values is presented. This paper is a good candidate for publication in AMT, as it is very appropriate to the content and aims of this journal.

Specific comments:

I would consider rephrasing statements about the “high precision” of this method, for example in line 37, to put this in perspective: yes, the precision is good, but it’s actually not as good as the published values of the Cheese Grater in Oregon (0.02 permil for $\text{d}13\text{C}$, Bauska et al., 2014) or the Sublimation system in Bern (0.07 permil). The precision for $[\text{CO}_2]$ is also not as good as other published methods, such as Bereiter et al. (2013).

We do agree that our precision is not as high as in some of the other systems. Nevertheless, the fact that other systems might be (even) higher in precision does not justify a change of wording since we never claim our precision is highest. After consideration we thus feel that “high precision” is appropriate here also because in the suggested new Table 1 where different systems

are compared (also including the one discussed), the numbers can be immediately put into perspective.

353 (p12/line 22): Please describe the advantage of having three sample aliquots.

The following description was added:

“Splitting the sample in aliquots allows for three IRMS measurements on the same sample theoretically improving the analytical precision. In practice, the therefore required quantitative splitting in three evenly-sized aliquots is difficult to achieve. For average values (weighted by mass, i.e. size) no increase or decrease in final precision compared to a single measurement was observed. However, the multiple measurements allowed statistical analysis of the results, e.g. to validate the robustness of the applied IRMS nonlinearity correction reducing the standard deviation over the three replicates (Sect. 4.1.2).”

Section 4.3: Note that the equilibration equations from Siegenthaler et al. (1988) do not seem to fit all datasets perfectly (e.g. Bauska et al., 2014). Using this relationship requires making an important assumption, which I think you should at least mention in the text.

We agree and (p26/line 27 – p27/line 4) was accordingly reformulated:

“Similar to the previous studies, high correlation between $\delta^{18}\text{O}-\text{CO}_2$ and $\delta^{18}\text{O}-\text{H}_2\text{O}$ was observed (see Fig. S5 showing measured $\delta^{18}\text{O}-\text{CO}_2$ and $\delta^{18}\text{O}-\text{H}_2\text{O}$ on their respective scales for one of the sections analyzed, Supplement). With this data set, the expected $\delta^{18}\text{O}-\text{CO}_2$ value in the following denoted as $\delta^{18}\text{O}-(\text{CO}_2\text{-ice})_{\text{eq}}$ could be calculated for each sample from its corresponding $\delta^{18}\text{O}-\text{H}_2\text{O}$ value considering oxygen exchange in thermodynamic equilibrium between gaseous CO_2 and the surrounding ice matrix. We thereby followed the approach by Siegenthaler et al. (1988) combining the thermodynamic equilibrium oxygen isotope fractionation factors α for ($\text{CO}_2-\text{H}_2\text{O}_{(\text{l})}$), ($\text{H}_2\text{O}_{(\text{l})}-\text{H}_2\text{O}_{(\text{g})}$) and ($\text{H}_2\text{O}_{(\text{g})}-\text{H}_2\text{O}_{(\text{s})}$) given therein. It should be noted that this approach might not be valid particularly for ice from very cold sites because it assumes that these values for α , experimentally determined at temperatures above the freezing point of water can be linearly extrapolated to temperatures below (< 273.15 K). Using the same approach for a site with annual mean temperatures of -26 °C (Berkner, Antarctica), comparable to the site temperatures at GRIP and NGRIP (around -30 °C), the time to reach 50 % of the thermodynamic equilibrium ($T_{1/2}$) was empirically determined to be 23 years (Assonov et al., 2005). Based on that, it is reasonable to assume that even the youngest samples analyzed in this study have reached complete equilibrium in the glacier.”

830 (p27/line 22): Is there corroborating evidence that these samples should indeed be discarded as outliers? Are there other samples that may also be outliers for [CO₂] and/or d13C? What is the probable cause of such outliers? Problems in ice? analytical system?

These are good questions pointing out the strength of this new approach overcoming the subjective questioning if some of the data points may or may not be outliers. We cannot give any objective answers but the text added hopefully provides further insight:

“For these samples, the CO₂ and δ¹³C measured values were rejected from the analyses. Unnoticed micro-cracks in the ice, formed during sample transport in the laboratory or at the time of sample placement in the extraction unit might be the most likely explanation for these outliers. Anyhow, in all cases the rejected samples showed suspicious values in both CO₂ and δ¹³C, but because no obvious reason such as issues with the analytical system was noticed (e.g. bad vacuum, trap temperatures being out of range), they could not have been consistently removed otherwise.”

Suggestions for minor changes/technical comments:

53-58 (p3/line 11): add Schmitt et al. (2011), Bauska et al. (2015)

Done (but Schmitt et al., 2012 which is the correct reference here, not 2011)

58-59 (p3/line 16-17): “constantly improving precision and accuracy” - I question the use of “accuracy” in this statement, as new results typically agree with previously published records

We followed the suggestion although “accuracy” was meant to be related to the improvement from a more standardized procedure for the use and distribution of standard gases and the increase in laboratory intercomparison studies performed.

68-69 (p3/line 26-27): maybe add references for examples of the different extraction methods (e.g., Schmitt et al, 2011, Bauska et al., 2014)?

Done. It now reads:

“In order to avoid the liquid phase of water, the air must either be extracted in a cooled vacuum chamber by dry mechanical techniques (e.g. Bauska et al., 2014) or by sublimation of the ice matrix (e.g. Schmitt et al., 2011).”

95-145 (p4/line 20 – p6/line 4): A table would be useful and could replace a lot of this text

Done. New Table 1 added and related changes in text made.

103 (p4/line 28): please reference the lowering of temperature statement (personal communication?)

Reference added:

“Leuenberger, D.: Highly resolved measurements of δ¹³C on CO₂ extracted from an EPICA Dome C ice core, Master Thesis, Division for Climate and Environmental Physics, Physics Institute and Oeschger Centre for Climate Change Research, University of Bern, 2009.”

135 (p5/line 27): not M. Rubino, pers. comm.?

Changed as suggested (now below Table 1).

150 (p6/line 9): compare “high precision” to Bauska et al. (2014)

See comment above.

170 (p6/line 29): I would recommend using SS for stainless steel, as this is a commonly used abbreviation, and SST is reserved throughout the literature for sea surface temperature

Changed as suggested.

176-8 (p7/line 4-6): consider rephrasing as: “resulting in an inner volume of half the size (110 cm³; 63 cm³ with the bellow compressed) ... reduced by about one-third” (or two-thirds?)

Changed as suggested to:

“Also, the bellow is mounted differently than in the design presented by Ahn et al. (2009) resulting in an inner volume of half the size (110 cm³; 63 cm³ with the bellow compressed) and an inner surface area reduced by about two-thirds.”

194-5 (p7/line 22-23): consider rephrasing to: “This sealing mechanism reduces the amount of time required to open and close the vessel compared to systems using bolts and nuts.”

Done

224 (p8/line 19): please clarify: “Compared to a common operating temperature of -30 C” - not all systems are operated at this temperature!

Paragraph re-written:

“Compared to other systems allowing analysis of similarly small sample sizes (e.g. other NC designs, CIM) the operating temperature of our extraction chamber is significantly lower (-45 °C compared to -35 / -27 °C). This is beneficiary because the resulting lower water partial pressure in the extraction chamber (about 5-fold) reduces the risk of in-situ CO₂ production by wet chemistry. This is supported by the findings of Bauska et al. (2014) which indicated that operating at low temperatures improves precision and decreases the blank of the method. For our design this is reflected in a reduced system offset compared to the KUP NC though most likely resulting from a combined positive effect of friction-reduced motion and lower operating temperature (see Sect. 4.1.1).”

251 (p9/line 14): amount of what? Please clarify

Rephrased to:

“...to quantify amount and isotopic ratios of the CO₂ fraction.”

273 (p10/line 5): no “m,” as the ratio is defined as rare-to-abundant; include the permit conversion in the equation

Definition and Equation have been changed entirely (see related comment to Reviewer 1). The permit conversion (x 1000) is although commonly used incorrect and thus not recommended (see reference given further up: Coplen, 2011).

294 (p10/line 25): reference for laser spectrometer?

Added: “The other tanks have then been calibrated against these three standards at CIC both with the setup described in this study and directly from the tanks using a Wavelength Scanned-Cavity Ring Down Spectrometer (WS-CRDS; CFADS36 CO₂/CH₄/H₂O analyzer, Picarro Inc., USA).”

318 (p11/line 19): what temperature?

At LN temperature. Sentence re-written to clarify:

“T2 together with trap T3 connected in series (empty 1/16 inch SS Swagelok tube) has been previously cooled by being immersed into liquid nitrogen (V1 still in the depicted position).”

350 (p12/line 20): exclusively (hopefully not present in your standard!)

Yes, exclusively. “primarily” intended to refer to water deleted as it is redundant (see next comment).

352 (p12/line 22): “In parallel. . . one after the other” This is confusing; are they are lifted at the same time? What do you mean by “in parallel?”

Rephrased to clarify: “To vent remaining H₂O and potential contaminants from drilling fluid (for ice samples) V3 is switched before signal detection in the PDD (~70 s after the maximum in the CO₂ peak) and the GC column is then conditioned for the next sample by heating to 150 °C. In the separated part of the line, the three CF capillaries are meanwhile lifted one after the other out of the LN, subsequently releasing the sample – now split in three aliquots – for further transport in a reduced He flow of 1.5 ml min⁻¹.”

356-7 (p12/line 27): Please be consistent with the dimensions of the columns (length x ID as in line 355)

Done.

359 (p12/line 29): Briefly explain what on/off peaks are

Changed to “reference peaks” as suggested by Reviewer 1 and rephrased to:

“Finally, the sample gases are introduced to the IRMS via the open-split of the GC interface. Before the three CO₂ sample peaks elute, the reference gas (CO₂-WS, here the same as the sample gas) is injected several times (reference port) in order to reach stable IRMS-source conditions (Fig. S1).”

407 (p14/line 14): “time the NC is opened,” Can you be sure that no carrier N₂ is present in the samples? Tests, maybe by analyzing d15N?

It has been tested by procedural blank measurements. The N₂ is first separated from CO₂ in T2. Whereas N₂ is then routed in one line to the TCD detector, CO₂ is further purified in a second

line (among other gases also from the remnant N₂), see inset in the lower panel of Fig. S2 (Supplement). Only after N₂ (and O₂) is detected in the PDD and background has been reached V3 is switched from the “vent” to the CF (20 s after the N₂ peak is detected). N₂ is therefore completely removed through the vent and cannot be detected in the IRMS even for samples with much higher N₂ content (see Fig. 3). For procedural blanks also no signal is detected in the TCD were by far the largest fraction of the N₂ is routed through.

415 (p14/line 23): What is the high vacuum pressure in the NC?

Described in lines 433-436 (i.e. on p15/line 7-10).

449 (p15/line 23): This is confusing; do you mean “expanded into the NC, which has been disconnected from the vacuum?” I would delete the latter clause, as you’ve already stated that.

Yes. Done as suggested.

449-50 (p14/line 23-24): air sample or standard gas?

Standard gas. Changed accordingly.

473 (p16/line 14): In what case are additional steps necessary?

No additional steps to the ones described are needed. Rephrased to: “Including section A of the system with the additional steps required does not add much to the total measurement time given in Sect. 3.1.”

Figure 4B: Perhaps also show the typical sample size in this plot as a gray region?

This is not possible because neither axis indicates the sample size (y-axis: CO₂ mixing ratios of the standards, x-axis: TCD / pressure ratio). If anything, the graph would become entirely gray.

671 (p22/line 22): Maybe indicate briefly why this is crucial?

As this entire Sect. 4.1.3 is giving detailed explanation why this is crucial we believe this would be redundant. Anyhow, the paragraph now reads:

“For any analytical application, a thorough assessment and quantification of the blank is crucial. Whereas, the system blank can usually be considered for the analysis of standards ultimately used for calibration of the results, the procedural blank – here related to the measurement of ice core samples – can include additional contribution from processes not covered by the system blank (e.g. sample preparation or mechanical movement in the NC).”

749 (p25/line 7): perhaps “Note that DE08 was dry-drilled”

Added.

781-784 (p26/line 6-9): I don’t think you’ll be able to measure any seasonal cycle, as the CO₂ has already had time to equilibrate with the ice

Yes, we do (see Fig. S5 in Supplement) and Sect. 4.3.

We tried to clarify by reformulating to:

“Due to its strong seasonal cycle, $\delta^{18}\text{O}\text{-H}_2\text{O}$ can be expected to vary between adjacent samples even for the high CIC sampling resolution. Because of the oxygen exchange, this leads to an analytically independent variability also in replicates of $\delta^{18}\text{O}\text{-CO}_2$ measurements (see Sect. 4.3) as $\delta^{18}\text{O}\text{-CO}_2$ does pick up the seasonal $\delta^{18}\text{O}$ cycle present in the ice although no seasonality is initially retained in the gas (signal smoothing in the firn). This at least partly explains the two times higher variation measured for the DE08 replicates compared to the observed variability in the QCS (Sect. 4.2.1) as well as the deviation of inter-laboratory $\delta^{18}\text{O}\text{-CO}_2$ results considering the differences in sample size and resolution used at CSIRO and CIC.”

In addition, the following changes were made to the Figures:

Fig. 2: Added number for Valve (15) to allow simplification in the text describing the procedure.

Fig. 3: Changed “drilling liquid” to “drilling fluid” to be consistent with the text

Fig. 4 (panel B): changed x-axis title from “pCO₂ ...” to “CO₂ ...” consistent with the rest of the manuscript.