

Author responses for MS No.: amt-2014-103, Bauska et al., High precision dual-inlet IRMS measurements of the stable isotopes of CO₂ and the N₂O/CO₂ ratio from polar ice core samples

We thank both reviewers for the time and effort they put into improving the manuscript. We hope we have provided sufficient changes. In the case of reviewer #1, we extracted all the comments embedded in the PDF and responded to them in this document (with the exception of grammatical fixes). The reviewer comments are indicated by black text and our responses are in blue.

Anonymous Referee #2

Received and published: 25 August 2014

Review of "High precision dual-inlet IRMS measurements of the stable isotopes of CO₂ and the N₂O/CO₂ ratio from polar ice core samples" by Bauska et al. AMTD, 7, 6529-6564, 2014

General: The manuscript describes an improved dual-inlet IRMS method for carbon stable isotopes on CO₂ combined with N₂O/CO₂ ratios in polar ice cores. The paper is well structured and well written. Despite the fact that the method is not new the improvement in accuracy and precision in both the carbon isotope analysis and the N₂O/CO₂ ratios determination strongly supports its publication, in particular in view of the still sparsely available carbon stable isotope measurements on polar ice cores.

There are a couple of points that should be improved before publication that includes:

- 1) The reproducibility is estimated to be 0.02 ‰ for δ¹³C-CO₂ cannot directly be compared to the uncertainty given in other publication listed in the manuscript since the authors do not include effects like the gravitational enrichment, thermal diffusion or bubble enclosure on δ¹³C-CO₂ in their estimate. Therefore, their statement should be adapted slightly.

We have amended our paragraph on the precisions reported in previous studies to conclude (pg. 3) "Note that the precisions we quote are not all directly comparable as there is currently no standard for estimating error. In addition to the reproducibility of the δ¹³C-CO₂ measurement (which we focus on in this study) the reported error can include uncertainty introduced from corrections external to the *in situ* ice core δ¹³C-CO₂ measurement including gravitational enrichment in the firn (in the case of Friedli and Stauffer, 1986; Leuenberger et al., 1992; Indermuhle et al., 1999; Smith et al., 1999) and diffusive fractionation during intervals of rapid atmospheric CO₂ change (in the case of Rubino et al., 2013)."

Our understanding is that corrections for thermal diffusion have been discussed but assumed to be negligible for the δ¹³C-CO₂ (e.g. Lourantou et al., 2010; Rubino et al., 2013) and thus not treated explicitly. Similarly, other processes involved in "bubble enclosure" such as molecular size dependent fractionation have been described for other gases (Huber

et al., 2006; Severinghaus and Battle, 2006) but not treated in ice core records of $\delta^{13}\text{C}-\text{CO}_2$. Possibly, we are missing are reference or require further information about the “bubble enclosure” processes referred to by the reviewer.

2) There are only a few publications that used the same principle to determine N_2O via the $\text{N}_2\text{O}/\text{CO}_2$ ratio. Therefore, it would be adequate to list them, but in particular Leuenberger and Siegenthaler, Nature 1992.

We now include this reference (Leuenberger and Siegenthaler, 1992) in our description of previous mass spectrometry methods for measuring N_2O . (pg. 12, line 26)

3) The discussion of the oxygen stable isotopes of water is rather lengthy and not convincing since the general message is that, even after combining the presented data with previous published data of Siegenthaler et al., 1988, the relationship between the measured oxygen isotope difference of CO_2 and surrounding H_2O with temperature is unconstrained. However, I agree with their statement that additional data, in particular at sites with very cold temperatures are required but in addition a thorough history of temperature exposure of the ice samples.

We have included a short description of the temperature history of the samples in this study.

Pg.5 Line 3 “The Taylor Glacier samples were cored in 2010/2011 austral summer, stored at $\sim 25^\circ\text{C}$ with the exception of $\sim 1\text{hr}$ transport from the field, and analyzed in January 2012 . WDC05A was cored in 2005/2006, stored largely at $\sim 25^\circ\text{C}$ before analysis in December 2011. The WDC06A section was cored in 2007/2008, stored in the field at $< 20^\circ\text{C}$, archived at $\sim 36^\circ\text{C}$ before transport to OSU for analysis in February of 2012. “

Detailed comments: P6537, l.14: attached→attached

P6539, l. 14:

...it does suggest that...

...

P6541, l. 13: add Leuenberger and Siegenthaler, Nature 1992

P6542, l. 23:

...spaced 20 cm apart...

Thank you, we made these changes.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 6529, 2014

Anonymous Referee #1

Received and published: 18 July 2014

The manuscript describes high precision measurements of $\delta^{13}\text{C-CO}_2$, $\delta^{18}\text{O-CO}_2$ and $\text{N}_2\text{O/CO}_2$ ratio of gases extracted from ice cores. High precision measurements of isotopic ratios of CO_2 in ice core have been proven to be difficult to attain. Bauska et al. show a reproducibility of less than 0.02 per mil and a total uncertainty of 0.04 per mil. The study is an interesting piece of experimental work. The results are well described and significant. I suggest a number of minor changes reported as comments in the attached pdf file.

Pg. 1, Line 17: "Exceptional" does not sound very scientific. Consider replacing with "very high"

We have changed the wording to "very high"

Pg.1, Line 21: "Why don't you also mention the accuracy (which I would rather call "total uncertainty") you get here?"

Please see the discussion below. As the reviewer fairly points out, and we briefly discuss in this paper, referring to the accuracy of ice core measurements is not straightforward. Instead of refereeing to accuracy, we shall include an estimate of the procedural blank offset in the abstract.

Pg 1, line 23 of the abstract now reads "Our experiments show that minimizing water vapor pressure in the extraction vessel by housing the grating apparatus in a ultra-low temperature freezer (-60°C) improves the precision and decreases the experimental blank of the method to $-0.07 \pm 0.04\text{‰}$."

Pg. 2, Line. 11: "Why don't you put some references here? It does not really matter if you will mention them again later on."

We prefer the flow paragraph as is.

Pg. 2, Line 12, "Why is the range dynamics?"

We use the term "dynamic range" because we refer not simply to the glacial-interglacial difference in $\delta^{13}\text{C-CO}_2$ (which is quite small), but also the range of previously observed variability that can occur within, for instance, a glacial-interglacial transition. We have changed the wording to read: "This limits interpretation of mechanisms because the uncertainty is about 1/3 of the full range of variability currently observed on glacial-interglacial timescales..."

Pg. 2, Line 16 "This number actually depends on the timescale you are considering, as explained in Trudinger et al. (2002). Are you sure that decadal and centennial terrestrial biosphere carbon fluxes are expected to give the same change? Please, consider giving a range instead."

The 0.03‰ per ppm CO_2 is intended as a back-of-the-envelope approximation to give the measurement precision in context. We have also amended the parenthetical statement that

follows to point of this relationship “(though this relationship changes with time due to exchange with the oceanic reservoir)”

Pg. 3, Line 6 “Because d13C measurements are always relative to standards, it could be misleading to talk about accuracy. Consider replacing "accuracy" with "blank correction””

We have changed to “accuracy” to “ procedural blank correction”.

Pg. 4 line 11-12 “As far as I can see, you have not detected any contamination with your detectors, have you? it seems to me that you have just used "additional cleaning steps" to get rid of contamination from drilling fluid. If that is the case, I don't see why you write: "We observe that drilling fluid contamination can be monitored using higher-mass detectors””

We mention the higher mass “clumped isotope” detectors as a potentially interesting aside that might be useful as clumped isotope equipped instruments become more prevalent. But it was perhaps not clear how they were employed. We amended the sentence to read “We used higher-mass detectors of high sensitivity (m/z 47,48 and 49) to monitor for drilling fluid contamination independently from the CO₂ isotope measurement, with anomalous enrichments indicating the presence of drilling fluid.”

Pg. 6, Line 1, “My experience with ice from Greenland is that one cannot get rid of the contamination by removing the exterior. The NGRIP ice core has been drilled with the same drilling fluid (HCFC-141B) as WDC06A. We found contamination in the mass spec even when the exterior part of the ice sample was removed. I am surprised to see that you can get rid of the contamination. The only difference I can think about is that NGRIP had been drilled many years before we tried to analyze the CO₂ and d13C-CO₂, and the drilling fluid had had more time to diffuse to the inner part of the ice core.”

This is interesting. We only have a little experience with very poor quality Taylor Dome ice where drilling fluid (n-butyl acetate) was also very problematic. My guess is that the excellent core quality of WAIS Divide at the depths we have studied is the reason that drilling fluid can be minimized by simply removing the outer portions of the core.

Pg 6, Line 26 “It would be good to have some references here to know which studies you are comparing to”

We have added: “This is on the low end of typical dry extraction methods, with other methods reporting the percentage of ice grated at 73-84% (Rubino et al., 2013) to 99% (Sapart et al., 2011) and an area for future improvement.”

Pg 7 Line 3 “For clarity, explain here what this small aliquot is used for.”

We have added “...for use as a CO₂ concentration measurement”

Pg 7, Line 7-8, "From Fig. 1, I would guess the air is injected into the GC on-line through valve 13. If so, can you specify this here?"

We amended the sentence to read "This air sample is warmed to room temperature and stored for a few hours before being expanded via valve 13 into a sample loop and analyzed with an Agilent 7890A GC to determine the CO₂ mixing ratio"

Pg 7, Line 30 "This effect is described in Bertolini et al. (2005), Journal of Mass Spectrometry. Consider citing that paper here."

Excellent reference. We will include it (Bertolini et al., 2005).

Pg 8 Line 2, "This sentence does not read well. Maybe, replace the "and" with a comma

Yes, this was a typo.

Pg 9 Line12, "Why did you not use the most recent one given in Brand et al. (2010), Pure Appl. Chem., Vol. 82, No. 8, pp. 1719–1733?"

The (Santrock et al., 1985) formulation was implemented with our in-house software. Experimentation with different formulations suggests that systematic errors introduced by this effect are small (unless the original Craig, 1957 formulation is used). If the reviewer feels this important we can discuss this aspect further or reformulate our corrections.

Pg 9 Line 20, "Can you add uncertainties to the values?"

Yes. We will add uncertainty quoted for the NOAA scale calibration relative to NBS-19 in (Troler et al., 1996)(95% C.I. = 0.02 per mil for $\delta^{13}\text{C-CO}_2$). Our in-house calibration to NBS-19 is based on long-term runs of NBS-19 (as well as other standards) on MAT252 equipped with a Kiel Device. In the body of the text describing the calibration procedure we now include the following (Pg 11. Line 16):

"With the NOAA1 standard being measured over 400 times against the working reference, the INSTAAR-SIL and in-house calibration converge within 0.001‰ for $\delta^{13}\text{C-CO}_2$, well-within the estimated $\pm 0.02\%$ uncertainty of the NOAA calibration scale relative to NBS-19 scale (Troler et al., 1996) and the long-term reproducibility of our in-house measurements of NBS-19 (1-sigma standard deviation, $\pm 0.02\%$)."

Pg 9 Line 25, "Why not use the date on the x-axis? That would also show the 6 month break in the analyses"

We prefer our current scheme as we believe it more readily displays the drift and random noise in the calibration scheme.

Pg 9 line 30, "You could call the upper and lower parts of Figure 2: Figure 2a and Figure 2b"

Good idea. We will change during typesetting.

Pg 10 line 30 "I think you should attribute an uncertainty to all the isotopic values. The uncertainty should reflect the uncertainty associated with the calibration against NBS-19"

As stated above, for the NOAA calibrations we can provide the accuracy relative to the NBS scheme of 0.02 per mil for $\delta^{13}\text{C-CO}_2$ as stated in Trolier. et al. 1996.

Pg 11 line 13 "Why don't you write the equations explicitly?"

We feel that the equations are well-described in the referenced paper.

Pg 13 line 1 "Is it not decreasing in Figure 4?" ..." I would write ‰/volt instead of ‰ per volt"..."per volt" is missing"

Correct, typos will be fixed.

Pg 13 line 15 "Consider specifying that this assumes no horizontal concentration gradient"

We modified the sentence to read "In the case of WDC05A, the sampling allows for true duplication assuming horizontal homogeneity, that is two samples from the same exact depth."

Pg 14, line 2 "How about different graters? Previously, you said that you use 2 graters."

There are no statistically significant differences so we did not report them. Also, we use a randomized sampling scheme such that any differences between the graters should be aggregated into the apparent random error we observe in the reproducibility results (ie precision)

Pg 14 line 7 "Accuracy might not be the right term because d13C measurements are expressed relative to standards. They provide with differences while the concept of accuracy suggests to me something more related to absolute values.

We will change the language to always refer to the accuracy relative to the NOAA/NBS scale as follows:

Pg 14 line 24 "Evaluating the accuracy of ice core gas measurements relative to an accepted standard is a significant challenge,"

and....

Pg 18 line 28. "The external precision of $\pm 0.018\text{‰}$ and accuracy relative to the NOAA/NBS scale of $\pm 0.04\text{‰}$ "

Also, we will note that the NOAA /NBS scale itself is itself only accurate in absolute terms to within the uncertainty reported in Trolier et al., 1996 (0.02 per mil). However, we do feel strongly that we are using the correct and commonly accepted terminology to describe the "precision" and "accuracy".

Also, Bubble Free Ice tests don't completely simulate "real" samples. Therefore I would rather talk about blank correction and compatibility between different datasets"

This is an excellent suggestion. When describing the experiment in detail we replaced "accuracy" with "procedural blank offsets" to read "We performed experiments in which a gas-free piece of ice (made in the laboratory) is grated along with an aliquot of known NOAA standard gas to examine potential procedural blanks offsets after the release of occluded air from ice." We also changed the subheading from "Accuracy" to "Accuracy and compatibility with other methods"

Pg 14 line 8, "One way of estimating the compatibility of ice core gas measurements with contemporary atmospheric measurements is to compare them through firn measurements. This has been done in Rubino et al. (2013). Could you do anything like that?"

Unfortunately, not with the data at hand. A comparison to Rubino et al., 2013 will be submitted soon and more data could of course be collected in the future.

Pg 14 line 10 "The assumption here is that bubble-free means gas-free."

No, the ice is produced with a method that drives off dissolved gases from ultrapure water through a combination of heating and slow-freezing. The ice is widely used in our lab for similar blank experiments for CH₄, CO₂, N₂O concentration measurements and N₂O isotopic and CO₂ isotopic measurements.

Pg 14, Line 30 "I would rather call this "total uncertainty". To me, the accuracy is the difference between measured and expected values for references, as defined by the Joint Committee for Guides in Metrology (2008): "closeness of the agreement between the result of a measurement and a true value of the measurand"."

We hope the changes in language regarding the procedural blank measurements are sufficient. "Total Uncertainty" is probably also a fine term for the summation of the type of errors (both random and non-random) we are attempting to describe. But we again feel that precision and accuracy are also appropriate and in our opinion more commonly recognized.

Pg 15, Line 10, I would move "probably" after compromised: we know that it changes in the firn, but we are not sure about the reason."

Okay. Removed

Pg 18, Line 16 "6 % of 0.3 per mil is 0.018 per mil, which corresponds to the external precision. To resolve isotopic variations of 0.018 per mil, the authors should demonstrate a total uncertainty equal or less than 0.018 per mil. However, the total uncertainty, that the authors call the accuracy, is higher than that (0.04 per mil). Given that this is not simply a bias, but a random uncertainty (because it is propagated from random uncertainties), I

would say that the authors cannot resolve variations of less than 0.04 per mil. This is actually 13 % of the glacial-interglacial range.”

We are trying to argue that if our method alone was applied to construct a record of the glacial-interglacial changes in $\delta^{13}\text{C-CO}_2$ then we should be able to resolve changes of 0.018 per mil. One could argue that if we need to splice together two or more methods, or if the metric of interest was the difference in our measurements of the glacial atmosphere to the modern measurements by another laboratory, then we would have to account for non-random biases and the uncertainty in determining these biases. In that case, yes, we could only resolve the changes down to the accuracy of our measurements. To make this clear we amended the sentence (pg 19, line 10) to read “To put this some perspective, the precision of the method can resolve isotopic variations of about 6%....”

Additional References:

Bertolini, T., Rubino, M., Lubritto, C., D’Onofrio, A., Marzaioli, F., Passariello, I. and Terrasi, F.: Optimized sample preparation for isotopic analyses of CO₂ in air: systematic study of precision and accuracy dependence on driving variables during CO₂ purification process, *J. Mass Spectrom.*, 40(8), 1104–1108, 2005.

Huber, C., Beyerle, U., Leuenberger, M., Schwander, J., Kipfer, R., Spahni, R., Severinghaus, J. P. and Weiler, K.: Evidence for molecular size dependent gas fractionation in firn air derived from noble gases, oxygen, and nitrogen measurements, *Earth Planet. Sci. Lett.*, 243(1-2), 61–73, 2006.

Leuenberger, M. and Siegenthaler, U.: Ice-age atmospheric concentration of nitrous oxide from an Antarctic ice core, *Nature*, 360(6403), 449–451, doi:10.1038/360449a0, 1992.

Santrock, J., Studley, S. A. and Hayes, J. M.: Isotopic analyses based on the mass-spectrum of carbon-dioxide, *Anal. Chem.*, 57(7), 1444–1448, doi:10.1021/ac00284a060, 1985.

Severinghaus, J. P. and Battle, M. O.: Fractionation of gases in polar lee during bubble close-off: New constraints from firn air Ne, Kr and Xe observations, *Earth Planet. Sci. Lett.*, 244(1-2), 474–500, 2006.

Trolier, M., White, J. W. C., Tans, P. P., Masarie, K. A. and Gemery, P. A.: Monitoring the isotopic composition of atmospheric CO₂: Measurements from the NOAA Global Air Sampling Network, *J. Geophys. Res. Atmospheres*, 101(D20), 25897–25916, doi:10.1029/96JD02363, 1996.