

Atmos. Meas. Tech. Discuss., 5, C3583–C3591, 2013

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AMTD

5, C3583–C3591, 2013

Interactive  
Comment

## ***Interactive comment on “A centrifugal ice microtome for measurements of atmospheric CO<sub>2</sub> on air trapped in polar ice cores” by B. Bereiter et al.***

**B. Bereiter et al.**

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The points mentioned by C. Stowasser are listed below. Each point is followed by our answer/editing.

Page 7868, line 26: The authors state that it took decades to reach a precision better than 5%. Can this be backed up by one or several references? A precision of  $\pm 5\%$  seems to be high, since it corresponds to  $\pm 14$  ppm for preindustrial concentrations. Do the authors refer to reproducibility or accuracy rather than precision?

The history of CO<sub>2</sub> measurements at trapped air in ice samples goes back to the  
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1950th (Scholander et al. (1956), Coachman et al. (1956)). It took until the early 1980th (Delmas et al. (1982), Neftel et al. (1982)) to find a difference between glacial and pre-industrial air, however, the accuracy (based on what we know today) of these results was in the range of 10% or more. The period until the late 1990th showed different problems with these CO<sub>2</sub> measurements regarding the contamination from the dry-extraction mechanics, the ice, the sealing, the used materials... Clearly, from Indermühle et al. (1999) onwards the results became much more reliable and accuracy was well below 5% from this point on. The explanation given here still does not cover the whole story of CO<sub>2</sub> measurements and many more works should be mentioned in this context. A fairly complete history of CO<sub>2</sub> measurements is given in Ph.D.-Thesis of Bereiter (2012). To not go beyond the scope of this paper we would like to add the works of Coachman et al. (1956), Neftel et al. (1982) and Indermühle et al. (1999) and refer to the work of Bereiter (2012) for further historic details. Besides, we replace precision with accuracy.

Page 7869, line 7: The reference (Anklin et al., 1995) focuses on CO<sub>2</sub> contamination due to the carbonate-acidity reaction. To also cover organic substances, I suggest the e.g. the reference (Tschumi and Stauffer, 2000), who focuses on both the carbonateacid reaction and the oxidation of organic substances.

We add the reference (Tschumi and Stauffer, 2000).

Page 7869, line 14: For the interested reader references should be added referring to e.g. CH<sub>4</sub> and N<sub>2</sub>O measurements using a wet extraction technique.

We add following brackets at the end of the sentence: (e.g. Baumgartner et al. (2012) and Schilt et al. (2010)).

Page 7869, line 28: I believe the extraction efficiencies from bubble and clathrate ice have been switched: The references given by the authors yield the following extraction efficiencies for bubble/clathrate ice: 62/52% (Schaefer et al., 2011); 75/54% (Sowers and Jubenville, 2000); 70/50% (Luethi et al, 2010); 80-90% (Ahn et al., 2009; clathrate

extraction efficiency not explicitly stated but lower). Thus, “. . . release only 60%–90% and 50%–80% of the enclosed air in pure bubble ice and in pure clathrate ice, respectively. . .” would be correct.

That’s correct. We change the numbers as proposed.

Page 7870, line 16: The authors mention “our cracker system”. To introduce this system I suggest a phrasing like “the needle cracker system used previously at our lab”. Later in the text the phrasing “our cracker system” is appropriate (e.g. on page 7871, line 12).

We replace “our cracker system” with “the needle cracker system used to date at our lab”.

Page 7871, line 9 and page 7876, line 11: The diameter given in the reference (Uchida et al., 2011) is for clathrates only. Other enclosures like bubbles have different diameters. Thus, the sentence should be rephrased. E.g.: “The diameter of air enclosed as clathrates in polar ice...”.

On page 7871 we change the wording as proposed. On page 7876 we write the corresponding sentence as follows: With this size distribution also the CIM will not extract 100% of the trapped air in clathrated ice since the diameter of clathrates in polar ice cores lies between 0.02 - 0.2 mm (Uchida et al., 2011).

Page 7871, line 26 and page 7874, line 5: The authors write that the sample holder is rotated until the ice is consumed totally. How is his time determined? Is he sample consumption monitored somehow, e.g. by weighing the powder? Please specify.

On page 7871 we add “which can be identified acoustically by the absence of the noise originating from the impact of the sample on the knife” to the corresponding sentence.

Page 7873, lines 14-15: Are  $\pm 0.02C$  and  $\pm 0.1C$  the standard deviations (1) or maximum fluctuations (peak to peak)? Please specify.

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It's peak to peak. We add this information in brackets at the end of the first sentence.

Page 7873, lines 17-20: For the ease of the reader the authors could provide some references regarding the measurement techniques and sensitivities of the different optical spectrometers. Examples are (Baer et al, 2002) for the Los Gatos technique and (E. Crosson, 2008) for the Picarro technique. Something similar probably exists for the LI-COR principle.

We add the two proposed references in this paragraph in the following way: "...analysers (i.e. of Los Gatos Research (Baer et al., 2002) and Picarro (Crosson, 2008))". The principle behind the LI-7000 is very old and simple for which reason we only found specific application papers about the LI-7000 but no basic peer-reviewed paper as the ones for the newer devices. The manual of the LI-7000, which is available online, explains well the basics of the device for which reason we add this reference for the LI-7000 in the paragraph.

Page 7874, lines 21-26: Could the authors be more specific about the pressure inside the sample cell of the LI-7000? Is this pressure identical to the pressure that is measured with the pressure gauge (determined by the amount of sample gas)? In other words: Is the LI-7000 actively controlling sample cell pressure or is this pressure determined by the sample size and the LI-7000 is passive?

The pressure inside the LI-7000 is controlled by the membrane bellow as mentioned at the end of the section. However, the discussion was a little too short. We therefore rewrite the section as follows and hope to clarify this point: When the detection is finished, the sample air is pumped out of the LI-7000 measuring cell and reloaded with standard gas from one of the standard gas containers. Thereby, the pressure in the cell, which is measured by the pressure gauge P, is adjusted to the pressure of the sample before by changing the volume of the membrane bellow (deviation between the two pressures within 1.5 per mill).

Page 7874, lines 26-28: The authors use the raw data of the LI-7000 of both the sample

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and standard gas measurement to determine the CO<sub>2</sub> concentration in the sample. Thus, it seems the LI-7000 is used in a customized way. I think more explanation (1-2 sentences) on how the concentration is calculated would be helpful for the reader.

We add the following sentence after the section: Since temperature and pressure are equal for the sample and the standard, the sample concentration is directly proportional to the ratio of the two measured absorption signals.

Page 7875, lines 8-13: What was the reason to add the dry ice powder? Was it to keep the sample powder cool? Please specify. Also, I suggest to replace the wording "no optical difference with "no visual difference" to make clear that no optical analysis of the powder took place.

Yes, the dry ice is used to cool the powder. To make this clear we extend the first sentence of the section as follows: A dewar was cooled down and filled with dry ice powder in order to keep the dewar cool. We also change "optical" to "visual".

Page 7876, line 20: Reference to Fig.9 is wrong. It should be Fig. 7.

That's right. We correct this.

Page 7879, line 7: The authors state here that direct expansion towards the measurement cell is the optimal case. However, on page 7874, line 18 it is said that 2.3 times more the amount of sample gas can be transferred to the measurement cell when the bellow is used in between. Reading this, I assumed that the bellow way is optimal. Is the bellow ideal only if the sample size is small or if the ice is fully clathrated? Please be more specific about that.

The direct expansion in the context here is misunderstood by the reviewer. It means that no break takes place in the process in contrast to other cases where breaks of up to 5 minutes are introduced. Hence, the below is used in all cases but if it says that expansion took place directly, the air was transferred to the bellow and the cell right after the shaving process has been finished. We clarify this issue by replacement of

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the word "direct" with "immediate" where it is used in this context and by adding the brackets "(i.e. no break in the process)" where "immediate" is used the first time.

Page 7879, lines 17-20: Why have two different options been used? Does it take more time for the gas to expand from the CIM when BCTZ or clathrate ice is used? Please specify (this may be related to my comment above).

Yes, the options have to do with the different ice types. To clarify this we replace the first three sentences of that paragraph with the following text: The different options of the procedure have been introduced in order to account for slowly decaying clathrates. Therefore, for pure bubble ice the option of immediate expansion towards the measurement cell is used whereas for (partly) clathrated ice (Fig. 6 and 7) the option with a waiting time is applied. The option of connecting the CIM to C2 or not during the waiting time did not influence the measurements on polar ice performed in this work. Since the different options have an influence on the system accuracy, two cases from the measurements with gas-free ice are selected to provide a range of the system accuracy.

Page 7879, line 19: "Figs. 8 and 9" do not exist. I believe the authors refer to Figs. 6 and 7.

That's right. We correct this (see above).

Page 7883, lines 4-5: The sentence "Due to this good reproducibility. . ." should be made specific for fully clathrated ice (and fully bubbly ice). E.g.: ". . .future measurement series on fully clathrated ice . . .". Even though this sentence occurs in a paragraph where results from fully clathrated ice are discussed, it can be confusing since relatively large error bars (plus an offset) occur for BCTZ ice in the same figure (Fig. 6).

We change the sentence as follows: ...future measurement series with the CIM system on non-BCTZ ice might no longer require...

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Page 7888, line 8: See comment above.

We change the sentence as follows: ... future measurement campaigns on non-BCTZ ice.

Figure 3: A grid in the background would help to read the portions easier.

We add a grid (see below).

Figure 6: In the figure caption it should be mentioned that “no error bars” correspond to a single measurement as the authors did in the caption of Fig. 7.

We add the corresponding information similar to the caption of Fig. 7.

Technical corrections:

Page 7689, line 1: remove “how”

We would like to keep the "how" for better readability.

Page 7869, line 4: “,” missing after “(Kawamura et al., 2003)”

Typo during processing the pdf. “,” is added.

Page 7869, line 5: “,” missing after “(Zumbrunn et al., 1982)”

Typo during processing the pdf. “,” is added.

Page 7871, line 5: remove “,” after “LI-COR”

“,” is removed.

Page 7873, line5: Unclear. Suggestion: replace “. At latter part of the CIM” with “, where”.

We replace the sentence as follows: ... where an insulant is required and glass is used.

Page 7874, line 24: replace “and” with “, which is“

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With the "and" at this place it is clear that a first step is done AND then a second. The suggestion of the reviewer would make this more confusing. We would like to keep it as it is now.

We thank very much to the anonymous Referee #1 and C. Stowasser for reviewing the article and the detailed edits given to improve the article.

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Interactive comment on Atmos. Meas. Tech. Discuss., 5, 7867, 2012.

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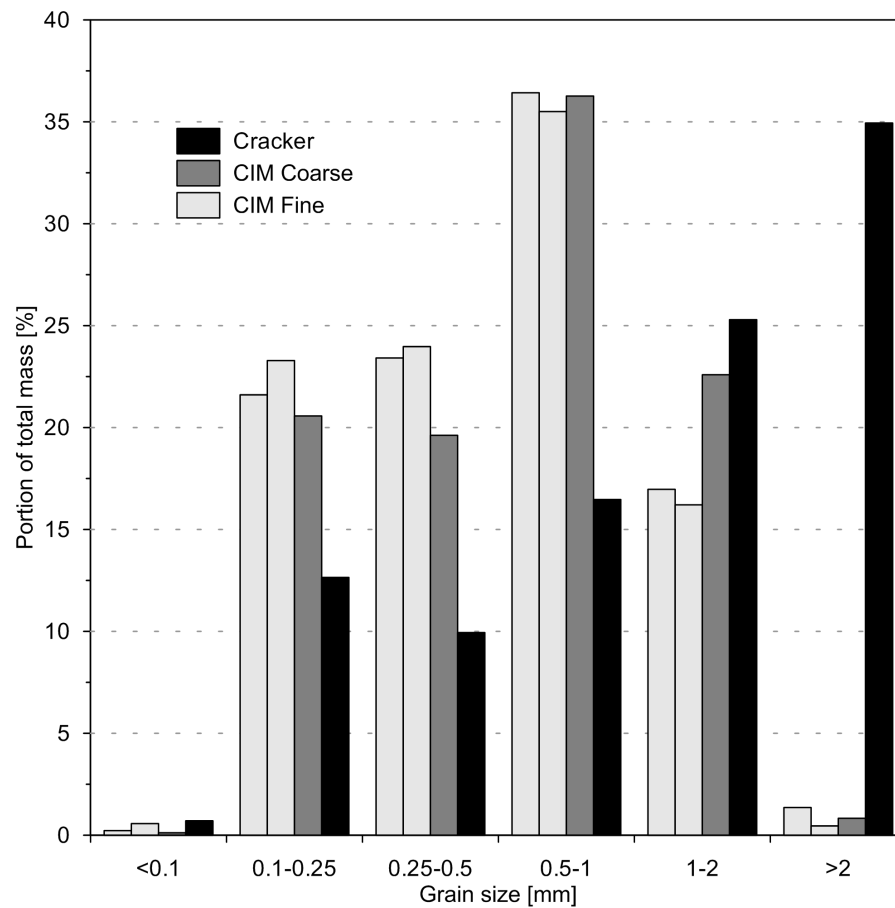


Fig. 1.

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