

First of all we would like to thank the reviewer for his comprehensive comments and suggestions for technical improvements and pointing on the technical shortcomings of the current system. By incorporating these suggestions we considerably improved the paper.

A general point concerns the use of “Bubble free” ice. Is it known that this is also air free (i.e. There are no dissolved or invisible gases inclusions)?

As the term bubble free ice is misleading I replaced it by gas free blank ice. The used ice is produced with a zone melt technique, which generates almost single crystal ice. As the solubility of CO₂ and other gases in the ice matrix is low at atmospheric pressure, there is good reason to assume that the ice is essentially free from CO₂. However, this is difficult to verify experimentally as the procedure only works when the sublimation vessel contains some ice to establish a water vapour gradient. So it is not possible to just compare experiments with and without ice. However, we made two different kinds of experiments:

1. We put blank ice in the vessel and cooled it but did not run the sublimating step (light source off). The drawback of this procedure is that it is quite different to the default procedure: no ice is sublimated and deposited in the internal water trap; no light and thus heat is applied onto the glass vessel and consequently the cooling air stream had to be reduced.
2. We refroze some water within the vessel and sublimated this refrozen piece of ice in a similar way like the larger gas free blank ice or real samples. These experiments were difficult to reproduce as the resulting ice rod did not allow for a proper sublimation due to its too large diameter.

The outcome of all these experiments was that we did not find significant differences compared to air free blank ice. We did not report on all these experiments in the paper as it would blow up the paper even more to properly describe these experiments and their outcome.

Regarding the organic fluid effects:

- *Are all cores drilled with organic fluid affected, or are some types of fluid less or not contaminating?*

All measured ice cores used the same “EPICA drill fluid” which consists of the densifier HCFC-141b, a chloro-fluoro carbon and Exxsol D30, a mixture of alkanes and other hydrocarbons. A short section on the densifier is now added in section 2.3.1

- *Is it demonstrated that the system described here removes the vapour (for example, are the various organic fractions seen to emerge separate from the CO₂ and N₂O peaks)?*

We added a few sentences on that saying that the GC column strongly retains them and these compounds are removed only at higher temperatures in the stand-by mode (200°C).

- *Is it possible that the very low temperature of the water traps holds back the organics?*

At least for the densifier component HCFC-141b we know that a sufficient amount of vapour passes the low temperatures of the water trap. This became evident during the early phase of the development, when the GC column was not yet installed and we occasionally saw severe contamination on m/z 45. Additionally, I calculated the saturation vapour pressure of this component for the working temperature of the external water trap (-150°C). The calculation shows that the saturation pressure is still high enough to provide a sufficient amount of the drilling fluid component to pass this trap. I added a few lines on that in section 2.3.1

VDPB-CO₂ is often mentioned. I guess what is meant is VPDB.

YES, typo fixed.

There are places in the ms where only a narrow selection of publications is cited, when there is actually a broader body of published work in this area with relevant results that should be mentioned.

I added on many places more references to provide a broader spectrum.

Finally, the goal of this system is to measure CO₂, δ³C of CO₂ (and N₂O?) with high precision and accuracy. What are the precisions and accuracies required to expose and explain past changes in the atmosphere that are relevant to the biochemistry, geochemistry and climatic issues? Has this work approached that goal?

I added a sentence on that in the conclusions. However, we don't want to load this experimental paper with too many details about paleo-climatic issues. The references given in the introduction should provide a starting point on that.

Detailed comments follow:

Page 1854 Line 1 $\delta^{13}\text{C}$ of CO_2

Typo corrected.

Line 16 and elsewhere mechanical.

Typo corrected.

Line 26: "knowing the causes of these changes is also relevant to the future behaviour of CO_2 "

Added: Knowing the underlying natural causes of these CO_2 changes is key to predict its future dynamics.

P 1855 Line 4 explain what is meant by fragmentary:

I meant that until now no continuous record over a longer time interval was constructed with the same method and currently the differences between overlapping intervals of the individual studies are considerably. I added the following "however, the data coverage of $\delta^{13}\text{C}$ measurements is still fragmentary due to methodological limitations; i.e. measurements were done on selected time intervals, using different ice cores and different extraction devices"

P 1855, Line 8 in situ production of CO_2 in the ice will affect all measurements of air extracted from bubbles. It seems that the melt extraction limitations are due to the effects in the following sentence, Line 10

Yes, this sentence was misleading: I rewrote this sentence as follows: However, wet extraction methods, often used for other atmospheric trace gases, might lead to CO_2 production within the melt water due to acid/carbonate reactions (Kawamura et al., 2003).

Line 14 Need to explain what is meant by pure bubble and clathrate ice

The term pure is indeed misleading. I omitted pure and used the term bubble ice, for ice which contains only bubbles but no clathrates. Similarly, I use partially clathrated ice and fully clathrated ice (also, see comments on that below).

Line 25 ..only extraction technique for CO₂ for ice core samples.

I added CO₂ to be specific...

Page 1856 Line 1 date for Siegenthaler reference:

Date added.

Line 10 to create a highly resolved record in deep ice cores with thin annual layers:

Added

Line 11 please provide a reference for the drill fluid observation.

I provided references on that and extended the discussion on that in section 2.3.1

Line 21 to take advantage:

Added

Line 24 changes over time? Explain a little

I added: This is crucial as changes in the performance of the IRMS measurement, like source tuning, variations in the H₂O background are a common problem.

Line 28 ...are discussed:

corrected

Page 1857 Line 8 What about the impurities e.g. Drill fluid vapour?

At least parts of the drill fluid components are trapped together with CO₂ and N₂O and then transferred into the glass tube and subsequently in the GC-IRMS system. We noticed that during an ice core measurement in the early phase of the development of the system when the GC column was not yet installed. As the drill fluid components were not removed on the GC column the CO₂-N₂O peak had extremely positive $\delta^{13}\text{C}$ values. In two cases we measured extremely high 45/44 ratios yielding highly enriched $\delta^{13}\text{C}$ values (8570‰ and 1420‰). I added the following: After the sublimation of the ice sample is finished, the trapped fraction (CO₂, N₂O and organic impurities like components of the drill fluid) is transferred into a small glass tube (Fig. 4).

Line 14 Sharp peak or pulse of gas?

Pulse is the better one.

Line 18 Does the reference device introduce only air or air from ice- the latter more closely mimics the actual ice sample analysis.

I am not sure if I correctly understand what you mean. Do you mean air that was previously extracted from an ice sample and afterwards used to mimic the sample extraction? No, air from the cylinder is introduced by this device. Indeed it would be a good idea to use compressed old firn air as a reference gas.

Line 25 Why choose all metal components when only 2 lines previously it is said that these (and glass) surfaces most notably degass CO₂?

That's true, for CO₂ analysis the best choice would be to omit all kinds of surfaces. Glass surfaces are probably better than metal surfaces. However, there are no appropriate "all glass valves" available for this purpose. The second best solution - and a realistic solution - are all-metal valves, since they are better than valves with polymers. We adapted the sentence accordingly.

Page 1859 Line 13 becomes unstable.

corrected

Page 1861 Line 22 are permanently heated:

corrected:

Page 1862 Line 13 Except for the possibility of impurities, mentioned above.

Yes, but the steps are the same". We added ...and possible impurities

Page 1863 line 24. The sample process rate is an important feature of the system and could be mentioned earlier.

This information is now given already in the section general layout: Although the sublimation step takes about one hour, the overall processing time is about 4 hours, which limits our sample throughput to two samples per day.

Page 1864 “The recent 2000 years of the Holocene is covered in detail in the Law Dome ice records (MacFarling Meure et al, Etheridge et al).

The two Law Dome references were added.

P1865 line 13...is organic...

corrected.

Line 20 Francey et al did not report this. In fact they say they found no difference between ice drilled with or without fluids.

Yes, Francey et al. did not report actual problems with drill fluid, but they were aware of the problem. And in section “8.4 Ethanol contamination” they discuss the issue of ethanol entering the source and thus producing enriched $\delta^{13}\text{C}$ values. They were aware of this problem and solved it successfully. I included this reference as it is the rare case that problems with organic solvents (drill fluid or ethanol used stored in the cold room in this case) are adequately discussed in a paper. So it’s a very valuable reference, therefore, I did not remove it, but added the “or from organic solvents used in the lab, which both can interfere in the MS measurement”

P1866 line 12 (and elsewhere) I think Figure 3 is meant.

Yes.

Line 24 Explain what is meant by Alternatively....

I rewrote the sentence to be clearer on that: Instead of the $\text{CO}_2/\text{N}_2\text{O}$ pulses described above, a sealed sample tube containing the trapped $\text{CO}_2\text{-N}_2\text{O}$ mixture from an ice core sample can be introduced via the cracker device.

Page 1870 line 11 More detail of the CO_2 absorption issue would be nice.

I hoped that the information given in the following sentences (and in the two very valuable references) would provide some clues about the behaviour of CO_2 on surfaces. Conducting experiments which provide a firm interpretation on that issue is extremely difficult. Therefore, we conservatively stick to the two hour pumping step in order to be on the safe side.

Page 1871 line 5 Were any extractions done to 100% completion to demonstrate this?

Yes, a few sublimations were done with the purpose of total air content measurements (Kaufmann et al., 2008), but experiments are difficult. One problem with 100% sublimation is the variable duration of the sublimation. Dependent on the form of the original sample and on subtle parameters during the sublimation the actual form of the last grams of ice is highly variable and as a result also the time needed for complete sublimation (about 70 min to 100 min). A second problem is overheating of the upper glass vessel when only a small piece of ice is left at the bottom of the vessel as the IR light source cannot be adjusted for a different configuration. Already both mentioned effects lead to difficult experimental conditions and thus higher scatter of the results. I added a comment on that in the respective line.

line 12 Does this fractionation occur only to clathrated ice?. I think so, as for bubble ice sublimation and mechanical extractions result in the same mixing ratios, which is not necessarily the case for clathrated ice.

Yes, this sentence is now more precise.

Line 23 ...section on data...?

corrected

Page 1876 line 24 Talos Dome ice core is more reliable than from other cores, which other cores? Has the inorganic impurity content be measured and compared with others? Is the N₂O in situ production observed for all other cores? Are the processes behind that expected to be the same for CO₂? More detail is needed in this section, and on line 12 of the next page.

I added more information and added a reference for dust measurements on Talos Dome ice on that issue. I made also clear that these observations refer only to the dust rich period of the glacial, thus, do not refer to the Holocene sections of the Law Dome ice cores.

Page 1877 line 9 the 3 references given cover only some of the well known ice core measurement techniques

Three more references were added for comparison.

Line 17 as for CO₂, there are other N₂O measurement techniques not mentioned

I added two more references.

Page 1878 line 23 Several Law Dome cores were measured by Francey et al and subsequent studies.

More studies using ice cores from the Law Dome were included in the references.

Lines 25 and 28. What are the uncertainties of the matches with the overlapping periods of the various ice, firn and atmospheric measurements? This is important as it is one of the only ways that the ice core technique can be verified (although only for recent ice and therefore not clathrate ice).

A discussion was added on this topic. Although the depth of information given in Francey et al. 1999 cannot be reproduced here.

Figure 7 caption. This cracker system is different from the tube cracker presented in this paper- it should be called “ice air extraction cracker” or similar to avoid confusion.

We named the other device “mechanical extraction device” to prevent confusion...

Also, “pure bubble ice” presumably refers to ice with no clathrates as compared to ice with no impurities.

Yes. I changed this misleading terminus and use only the following three categories: bubble ice (air is present only in bubbles and the ice was never clathrated), ice from the bubble/clathrate transition zone (contains both bubbles and clathrates), clathrate ice (was entirely clathrated and remained so after storage). The forth “type” (originally fully clathrated ice that partially transformed back to bubble ice after long, and preferentially warm storage conditions) is not discussed here.