

First of all we would like to thank the Hinrich Schaefer 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.

### **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.*

All are now 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.*

What I mean in the text with the term „extraction efficiency“ is literally the efficiency during the actual extraction process, i.e. the release of enclosed gases from the ice sample. It does not include all the subsequent steps, like removal of the water vapour or transfer into the tube etc. The reasons for this distinction in the proper extraction step and follow-up steps are the involved physical processes:

The processes involved in the proper extraction step are closely related with the ice sample itself. In case of sublimation, the sample matrix is transformed into water vapour thereby releasing all “types” of gas into the gas phase, i.e. gas molecules in bubbles, in air hydrates (clathrates) and classically dissolved in the ice matrix. Mechanical extraction techniques have the potential to extract these three types of gases differently, thus, leading to fractionation of the gas species as a function of type of ice (bubble ice vs. clathrated ice). This does not necessarily mean that this fractionation affects all gas species, nor does it imply that isotopes are fractionated as well.

The second reason for this distinction is a more practical one. The follow-up processes can be modified more easily than the extraction itself. One can switch from one tubing material to another, or vary the temperature of cold traps in order to minimize adsorption or desorption processes. These kinds of specifications are to some extent independent from the extraction process applied.

To be more specific on that, I added a definition in the paper what is meant with “extraction efficiency”.

*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.*

Thank you for this comment. Indeed I wanted to implement that in the early phase of the technical development but it was already difficult to get certified NOAA air standards for  $\delta^{13}\text{C}$  with glacial  $\text{CO}_2$  concentrations and preindustrial  $\delta^{13}\text{C}$  values. For the  $\text{CO}_2$  concentration this was possible but unfortunately the  $\delta^{13}\text{C}$  values of the two “Boulder” tanks are close together and lighter than the average samples. But it is already 6 years ago that I ordered them and it could be that they have more possibilities to adjust both  $\delta^{13}\text{C}$  and the  $\text{CO}_2$  concentration. Yet, my favourite solution would be a conveniently large volume (tens of litres at several bars) of firm air older than 1940 AD. I added a short discussion on that in section 4.2.

#### **Detailed comments:**

*Page 1855, lines 20-23: This statement implies that dry extraction techniques are not suitable for  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  analyses. In fact, a recent study that the authors cannot be aware of suggests that a dry extraction technique can yield reliable  $\delta^{13}\text{C}$  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.*

Meanwhile, this paper is published and I could include the main findings of this work and adapted these sentences and statements elsewhere in the paper accordingly.

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

I reorganized this sentence.

*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”.*

I renamed the sublimation extraction as recommended to sublimation system. Additionally, I indicated that the tube cracker-GC-system is the inlet to the IRMS. However, during the text I stick to the term ‘tube cracker GC system’ as I already use the term inlet for the injection of air standards into the sublimation vessel.

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

Adjusted as proposed.

*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.*

Adjusted as proposed.

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

These sentences were updated accordingly.

*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.*

Adjusted as proposed.

*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).*

I introduced the term internal water trap at the appropriate place.

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

I added “corresponding” to make it clearer that the vapour pressure at this temperature is meant.

*Page 1861, line 16: U-shaped?*

Yes, adjusted as proposed.

*Page 1862, lines 18-22: The range in  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  (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.*

I added a discussion and an outlook for a future improvement on that issue. Practically, I do not think that our system suffers from an “isotopic scale compression” or similar phenomenon. Provided the good general agreement among the different labs this is probably a minor issue but becomes more important when the precision of contributing labs gradually improves.

*Page 1864, line 13: disentangle?*

Typo corrected.

*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.*

Corrected as proposed.

*Line 23: acts as a cold finger?*

Added as proposed.

*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?*

The transfer of the trapped gases from the air trap is monitored by the pressure transducer and the stable values read out.

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

I added this information in the text.

*Page 1871, lines 11-13: the fractionation observed by Lüthi 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  $\text{CO}_2$  relative to  $\text{N}_2$  and  $\text{O}_2$ ). 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 Lüthi et al. should be corrected to avoid confusion.*

I added that the extraction efficiency issue for dry extraction techniques is a unique problem for ‘partially clathrated ice’ to be clearer on that.

*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 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.*

The numbers in Table 1 are correct; each pulse introduces 8 nmol CO<sub>2</sub>. But the info in page 1873, line 3-4 was incorrect. It must read in total 24 nmol (3\*8 nmol).

*1874, lines 1-5: what about other CO<sub>2</sub> isotopologues that are trapped? Given the different elution times one would expect  $\delta^{13}\text{C}$  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.*

I added a sentence to clarify this point.

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

The CO<sub>2</sub> used for the pulses and the monitoring CO<sub>2</sub> (rectangular peaks, or std on/off) is identical and its isotopic composition given above.

*1875, lines 5-10: are the peak heights for CO<sub>2</sub> 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.*

Yes, we apply a 1-point calibration using Boulder 2. However, when we measure both Boulder 1 and 2 within one session, we calculate Boulder 1 relative to Boulder 2 to check for deviations from its expected value. As these deviations usually fall within their measurement uncertainty, a 2-point calibration is not necessary and we regularly check this relationship between the two standards.

*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?*

In fact this correction step is done at the beginning and at the end of the correction routine as described in the text. Like for example in the ISODAT routine, all  $\delta^{13}\text{C}$  values are calculated against selected peaks. Usually, the rectangular peaks are used for this purpose, but we already use the air reference peaks for this purpose. Then we apply the correction steps, including the air reference peaks. As the reference peaks will be shifted due to these corrections, a final off-set correction to the assigned tank value of the air references is calculated.

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

I added a few sentences on this topic, to point out that our measurement precision is independent on the type of ice (bubbly, partially clathrated or fully clathrated ice). Also beyond the scope of this technical paper is a careful comparison of measurements done on different ice cores, with different types of ice, covering the same time interval. This work is underway and will be published later on.

*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 GCIRMS measurements of these tanks.*

I added this information to the sentence.

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

I corrected this and added EDML and EDC ice cores as examples.

*1878, lines 10-13: This sentence implies that for mechanical extraction the accuracy of CO<sub>2</sub> concentration analyses depends on extraction efficiency. This is incorrect, as long as there is no fractionation between extracted and remaining gas. Given the importance of CO<sub>2</sub> reconstructions and the fact that mixing ratios derived with dry extraction from clathrated ice (e.g., Lüthi 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 Lüthi et al. (2008)?*

For sure, you point at a critical issue. Given the importance of the accuracy of CO<sub>2</sub> reconstructions from ice cores, a proper discussion on that topic is not feasible in this technical description of a new analytical system. Moreover, a serious comparison between classic dry extraction techniques and our sublimation must cover several different ice cores and different depth intervals to capture the possible range of effects. This certainly has to be done, but our limited data set is not sufficient to make a clear statement at this point. We agree that a joint paper by all the groups measuring CO<sub>2</sub> in ice cores on this topic would be beneficial.

*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).*

In the Elsig et al. (2009) paper we only state that our data “is entirely consistent” with the Law Dome record from Francey et al. (1999). Providing a hard number on how good both records overlap is difficult given the entirely different gas enclosure characteristics of the two sites and the observed trend in the Law Dome record where EDC provides only a certain mean value. We therefore go not beyond our original statement that the data overlap is entirely consistent.

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

I rewrote this sentence to be more specific. We obtain 0.05‰ under optimal conditions for both the ice core quality and measurement conditions.

*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.*

I connected the fore vacuum line accordingly and also the optional connection for the He purge.