

***Interactive comment on “New technique for high-precision, simultaneous measurements of CH<sub>4</sub>, N<sub>2</sub>O and CO<sub>2</sub> concentrations, isotopic and elemental ratios of N<sub>2</sub>, O<sub>2</sub> and Ar, and total air content in ice cores by wet extraction” by Ikumi Oyabu et al.***

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General remarks:

The paper by Ikumi Oyabu and co-authors presents a new technique to extract and subsequently measure a large suite of key parameters on a single ice core sample. Since so many and diverse parameters are obtained from this new device, this paper is quite extensive. Not only the technique is described, but also new results for sev-

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eral parameters are presented and compared with previous records. Thanks to the fact that the manuscript is both well-structured and clearly written, the reader is not overwhelmed and can find the necessary information without too much effort.

The introduction provides the reader with sufficient information of the key applications of the individual parameters that are obtained with the new device. This chapter nicely captures the general advantages of multi-species measurement systems, i.e. to save precious ice and, more importantly, to obtain a large suite of parameters from the same piece of ice. Obviously, this feature is advantageous to improve the palaeo-climatic interpretation (no age difference between parameters), it is also very useful for troubleshooting and scrutinizing the parameters. As the ice core community continuously improves the precision and accuracy of these parameters, more and more previously unknown effects (e.g., production of species in the ice or preferential loss of some gas species from the ice) emerge from the noise level that alter the archived information of the ice core. Multi-species methods that provide a wide array of parameters without compromising the individual precisions are the key techniques to help identify and quantify those effect. In that sense, the new method presented by Oyabu and co-authors is very welcome and sets a new standard for these analyses.

Overall, the paper is already in good shape. Below I commented only on minor issues to improve the accessibility of the text and figures.

Minor comments on the text:

Line 77: Beginning of Chapter 2. You immediately start describing your procedure and then you compare/discuss it afterwards with other options to extract air with wet extraction techniques. While OK, you may add a short introductory section to briefly discuss the different wet techniques and point out their advantages and drawbacks. This may help readers not familiar with wet extraction techniques to put your technique into a wider perspective; e.g. . . .three different types of wet extraction techniques have been developed that. . . 1) melt-refreeze techniques (you already mention it with their

drawbacks) 2) melting under vacuum with the vessel closed, with subsequent helium purging (takes long and consumes lots of helium often used for isotope work on greenhouse gases e.g. Bock et al. 2014, AMT); 3) melting under vacuum with immediate removal of the released air (Kawamura et al., Schmitt et al. 2014, AMT, Bereiter et al. 2018). Method 3) is the preferred way to achieve sufficiently high extraction efficiencies for precise values of soluble trace gases (e.g. N<sub>2</sub>O, Xe) and high-precision ratios of atmospheric main components (e.g. O<sub>2</sub>/N<sub>2</sub>).

Line 83: please clarify: “Also, the pressure over the meltwater is relatively low (~100 – 200 Pa),...” The reported 100 to 200 Pa is not the air pressure over the meltwater (within the vessel) as this value is measured far away downstream at P<sub>1</sub>, after the water traps, if I got it right. The air pressure after the first water trap is modulated by the individual flow resistances of the tubing etc. between the vessel, the water trap, and the He cryostat. To my knowledge, there is no simple solution to come up with a robust estimate of the air pressure over the meltwater. One option would be to install a pressure sensor close to the vessel and before the first water trap and measure the total pressure (pH<sub>2</sub>O at 0°C around 600 Pa plus the air pressure) and subtract the water vapour pressure. Using bubble-free ice as a comparison allows to get an estimate of the actual pH<sub>2</sub>O while the ice melts, which might be warmer than 0°C since you melt the ice quite quickly with the hot water bath. Line 108: you might add here that this H<sub>2</sub>O + O<sub>2</sub> pre-treatment is sufficient for the (relatively short) extraction step. However, O<sub>2</sub>/N<sub>2</sub> ratios are not stable in these sample tubes over a longer time, therefore we use a different set of dip tubes after splitting (GEPW tubes).

Line 111: you might remove this extra info “(i.e., on weekends and holidays)” to help keep the paper short.

Line 122: remove “highly”. unclear: “the surface of ice samples”. Actually, the fractionation happens on the exposed outer parts of the stored ice core sections (for me the term “ice sample” refers to the piece of ice that is prepared prior to the measurement in the lab).

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Line 123: "... removed to precisely measure" add: ... and accurately the archived composition for these ratios.

Line 127: "... not important for greenhouse gas ...large molecular size...". This sentence could be better phrased to prevent misunderstanding. For example, CO<sub>2</sub> concentrations could indeed be biased by gas loss if O<sub>2</sub> (or if O<sub>2</sub>, N<sub>2</sub>, Ar, are lost without relative fractionation) is preferentially lost from the ice, while CO<sub>2</sub> is preserved due to its larger diameter. Consequently, CO<sub>2</sub> conc. would be biased higher as CO<sub>2</sub> conc. is just the ratio of CO<sub>2</sub> against total amount of (remaining) air. This process might occur but it is not yet visible due to limitations in the measurement precision. Gas loss biases for CO<sub>2</sub> were discussed as a potential option to explain the observed offsets among different ice cores of the same age (e.g. Eggleston et al. 2016 doi:10.1002/2015PA002874).

Line 133: remove the word vessel after Dewar.

Line 137: "laboratory room", remove the word room after laboratory;

Line 144: regarding the impact of the ice + gas loss during sublimation on TAC: can you estimate how much ice is lost due to sublimation (e.g. weighing the sample before and after 90 +30 min of pumping?

Line 149: "After the evacuation, all vessels, except for one for the first extraction, are. . ." please rewrite

Line 156: "The hot water bath is removed after the completion of ice melting." At that point, I wondered how the operator detects when the ice is gone because the vessel where the ice is melted is full metal, thus there is no visual control of that point. I guess it is done via a sudden drop in the pressure reading at P1? Also, all valves of the entire system are manually operated, right?

Line 159: "The time required for melting the ice sample is <~3 minutes, and the total time for the air transfer takes ~10 min (including the ice melting)." Perhaps it is easier for the reader if you write that the ice melting takes ca. 3 min and the pumping step

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after melting is completed takes additional ca. 7 min (i.e. the duration of the individual steps). Also: convert the mTorr unit into Pa to use only one pressure unit throughout the paper.

Line 163-165: this sentence could benefit from rephrasing. I am not sure if I got it.

Line 170: "one night" perhaps just write the hours that are physically needed for this equilibration step and not "one night"

Line 173: Does that mean you measure two sets of 6 samples each day?

Line 182: "...depletion of the O<sub>2</sub>/N<sub>2</sub> ratio" just to be on the save side, explicitly say that O<sub>2</sub> is consumed at the metal surfaces leading to lower O<sub>2</sub>/N<sub>2</sub> values (to exclude the option that extra N<sub>2</sub> causes lower O<sub>2</sub>/N<sub>2</sub> ratios)

Line 184: perhaps add a sentence stating that the stainless steel sample tubes lead to an unacceptable trend in the O<sub>2</sub>/N<sub>2</sub> ratio as O<sub>2</sub> is consumed (perhaps provide numbers if available so the reader gets a handle on the size of this O<sub>2</sub> depletion).

Line 187: delete "(e.g., during nights and weekends)",

Line 191: replace "(measured at the head of a turbomolecular pump with an ionization gauge) with (P3)

Line 198: perhaps add the reason for the -196°C cold trap: ..to remove CO<sub>2</sub> and N<sub>2</sub>O...

Line 201: is the lowering of the tube by a few cm an essential step or rather precautionary or does it speed up the process?

Line 204: unclear "Sometimes the samples are measured on the following day of the splitting".

Line 209: "the air left in the original sample tube" can you roughly provide the reader with an estimate of how much the rest is (e.g. fraction of the original amount)? You

provide this info (80% vs 20%) only in the conclusion.

Line 211: FID = flame ionization detector

Line 223-: This GC section is nicely written too, yet due to the inherent complexity of the system it still took me a while to jump from one valve to the next and figure out which way the gas goes. It is hard to come up with a better description but you could help the reader by optimizing details, e.g. you write “we use small sample loops (1/16" o.d., 0.5 cm<sup>3</sup>, Valco)” here, it would help that you use the same unit as in Fig. 3 (rather than 0.5 cm<sup>3</sup> in the text and 500  $\mu$ L in the figure). . .write e.g. we use two 500  $\mu$ L sample loops (Loop 1 and 2 in Fig. 3 [mentioning the names Loop 1 and 2 helps the reader locate the object quicker])

Line 229: 400 – 600 hPa. . .

Line 241: let? “At 1.74 min, V2 is switched to lead CO<sub>2</sub> from column 1 to pass through. . .”

Line 346 : “. . . but the first cycle is discarded and only the latter 16 values are used.” Delete “and only the latter 16 values are used” as this should be clear already.

Line 351: “. . .by simply opening the tube valve”. Just curiosity: is the valve opened quickly?

Line 359: (at  $\Delta P = 0$ , +100 and -100 ‰. In line 347 you write “. . . imbalancing the sample pressure by  $\pm 10 \%$ ”. It is already clear that the  $\pm 10 \%$  refer to the +100 and -100 ‰ but using the same “unit”, either % or ‰ could save a few seconds for some readers.

Line 437: “The standard gas thus transferred to the sample tubes is (are) measured . . .” check is/are.

Line 465: as you assume that a constant amount of O<sub>2</sub> is consumed independent of the sample size you could use a Keeling plot style fit (i.e. 1/V) and work with a linear

system instead of the exp function.

Line 501: please rephrase this sentence

Line 511: "...112.88 – 157.81 m (bubbly ice, 2.0 – 0.2 kyr BP)," please arrange order, the same a line below for the NEEM core

Line 551: "In any case, we exclude these anomalously high concentrations from the calculation of pooled standard deviation and comparison with other ice core records". Perhaps rephrase: I am not so convinced by your statement that these anomalies should not be compared with other records as CH<sub>4</sub> anomalies have been observed for NEEM and GISP2, therefore these anomalies are valuable and important observations. You might also cite and have a look in Mitchel et al. 2013, Supplement figure S1: there are several instances where GISP2 shows elevated CH<sub>4</sub> that are not an analytical artefact but features of the ice (see Rhodes et al. papers 2013, 2016). Just my curiosity: 2 out of three of anomalous samples from 361 m show also elevated CO<sub>2</sub> values. Do the corresponding dO<sub>2</sub>/N<sub>2</sub> values for these samples also deviate from their neighbors (e.g. lighter values due to microbial O<sub>2</sub> consumption)?

Line 561: The comparison of your N<sub>2</sub>O measurements with previous measurements can be improved (especially in Fig. A1) as many records exist and the evolution during the Late Holocene is rather flat with only little fine structure. To make this comparison easier for the reader, you might use the Late Holocene Monte Carlo N<sub>2</sub>O spline with 2s error envelopes and compare your DF and NEEM records with that spline as in Figure 4 of Fischer et al. 2019, Biogeosciences, doi: 10.5194/bg-16-3997-2019. <https://www.ncdc.noaa.gov/paleo-search/study/28890>, the direct link to the Late Holocene N<sub>2</sub>O spline is: <https://www1.ncdc.noaa.gov/pub/data/paleo/icecore/fischer2019/fischer2019spline3k-2o.txt>

Line 578: to be complete, you might add "... generally measured with mechanic dry extraction techniques (references) and sublimation (Schmitt et al. 2011, doi:10.5194/amt-

4-1445-2011).

Line 585 and the following line: It might be better to mention in an introductory sentence that reliable atm. CO<sub>2</sub> reconstructions are only possible in Antarctic ice cores because impurity levels in Greenland are too high and lead to excess CO<sub>2</sub> (refs). . . .so it is no wonder that your NEEM data also shows higher values.

Line 595: “. . .outer ice pieces were. . .”

Line 599-601: these two sentences have almost the same meaning, combine.

Line 601: “. . .indicating significant size-dependent fractionation in the outer ice“. Without further information, the reader has no clue why you immediately state that these observations are due to a size-fractionating process. May be O<sub>2</sub> has a higher permeation rate due to solubility in the ice matrix compared to N<sub>2</sub>. Either provide more background or just write e.g. gas species-dependent gas loss

Line 603: “. . .but not for N<sub>2</sub>, in the outer ice.” Unclear: because N<sub>2</sub> is not lost at all.

Line 609: please better specify what is plotted in Fig. 14: While it is clear that Fig. 13 shows the differences between samples with 5 or 8 mm removed this is not so clear for Fig. 14.

Line 612: “. . .more than 8 mm is sufficient” message not clear: is 8 mm enough?

Line 624: “ $\delta^{18}O_2$  as originally trapped. . . can be reconstructed (delete measured) from the 20-year old samples. Also, the overall match of the corrected old data and the new data is a good sign that the relatively large gas-loss correction was accurately done at that time.

Line 625: regarding the d<sub>18</sub>O values in Fig. 15b it seems that the old values that experienced gas loss (thus mass-dependent fractionation of the O<sub>2</sub>) are consistently heavier and is thus in line with the idea of the mass-dependent fractionation during the O<sub>2</sub> loss from the ice (a scaled correction factor that was used to correct the O<sub>2</sub>/N<sub>2</sub>



data from gas-loss effects might work as well). Comment regarding the d15N values: The new measurements of the clathrate ice look, on average, ca 0.03‰ higher than the old Kawamura values. This systematic offset is not visible for the young ice, thus calibration is not the reason. Yet for gas loss, the sign is in the wrong direction.

Line 648: technique?

comments on the figures and tables:

Fig. 1 typo in the scheme: “He ditector”, should read detector. Note, the schematic is quite large and in the final version it might get squeezed a bit to fit the page. To allow readability of the labels please increase the font size a bit (in most cases the distances allow that).

Fig. 2: you might help the reader find the “small volume (1.4 cm<sup>3</sup>) between the valves” by adding colors to this section.

Fig. 3: the “:” symbol in the legend seems not necessary. electronforming (without n); explain SuS

Fig. 4: I guess the y-axes are arbitrary units, please add any label to that axes. CH<sub>4</sub> panel, please add labels to the O<sub>2</sub> and CH<sub>4</sub> to make it more intuitive for the reader which peak is what. Since your paper has many figures (15) and tables you might want to save a bit space here and try plotting Fig. 4 more compactly, e.g. plotting all three gases on one x-axis without showing the others (like you did in Fig. 5)

Fig. 5: there seems to be a typo at the x-axis labels (16.7.1), also Fig. 7. To better differentiate the symbols (filled vs open markers), you might increase the symbol size. Panel c. For the O<sub>2</sub>/N<sub>2</sub> ratio it seems that with each new filling of the reference can the trends get smaller, i.e. less O<sub>2</sub> is consumed for a certain time interval. Is this an indication that consumption ceases over time as all of the oxygen-reactant is consumed?

Fig. 6: there is a typo in the equation: there is + and - before 0.078802, equation (7)

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says -0.078802. you may add the equation into the figure rather than in the caption

Fig. 8: it looks like that the new CO<sub>2</sub> measurements are slightly higher between 100 and 150 m and after 1800 m compared to the old ones? perhaps calc. the difference of means for the 100-150 m. Is it due to better extraction efficiency (or lower headspace pressure air reducing CO<sub>2</sub> solution in the meltwater) or longer reaction time for the chemical CO<sub>2</sub> production pathway in the meltwater?

Fig. 9: Caption: remove "from other groups". Panel c: you don't need the connecting lines for South Pole and EDML and WDC. just keep it for Law Dome.

Fig. 10: Caption: write "The line connects the blue markers..." since there is only one line, therefore, there is no need to specify this line it as "dotted line (blue)" Actually, I am not sure if you need the blue line at all as the next neighbouring points to the right side are quite a bit older and thus outside of the gas age distribution. For me this situation with the artefact samples is convincing already as the age difference of the plotted data is smaller than the NEEM gas age distribution. Additionally, you might indicate these two artefact depth levels already in Fig. 9 panel a) e.g. with a red circle around the artefact samples that you zoom in in Fig. 10.

Fig. 11: caption. unclear statement: "For single (non-duplicate) measurements, "a" piece is not cut.". I am not sure if I got it right. If you do a single measurement, piece "b" is measured only, but you need to do the cut between a and b anyway? Further, how did you cut the curvature between the inner and outer pieces?

Fig. 12: you might consider producing a single figure (as e.g. nicely done in Fig. 15) out of the four panels because you don't need four-times Depth(m) and the depth scales. The same applies to Figs. 13 and 14. Also, you might consider using a Delta symbol (e.g.  $\Delta$  d Ar/N<sub>2</sub>) to indicate the "pair differences" to prevent too long y-axis labels every time and write this in the caption (Pair differences (Delta) between the inner and outer ice piece.

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Fig. 14: figure: go for the same design: the dashed line at zero is plotted as a thick line in d) while thin for a, b, c. please chose one thickness, e.g. the thin line style. Caption line 955: add pieces: between the two inner ice pieces: and also specify if it is a-b or b-a.

Fig. 15: figure top x-axis label: replace Air age with Gas age because you use gas age throughout your manuscript. Legend between panel c) and d) the names for the grey and red crosses are switched, the red symbols refer to the values After gas loss correction? caption line 1001: delete dotted lines, because there are none (crosses connected with dotted lines, Kawamura, 2000; Kawamura et al., 2007). Table A1: typo: TALDICE not TALDAICE; the Eurocore ice core and project is mostly written Eurocore (in some cases EUROCORE, but EURO core would be new)

Fig. A1: panel a) this panel is a bit busy. you might consider plotting more records without the connecting line (EDML, TALDICE Schilt, Siple Dome) typo. EDML (Schilt et al. 2010), et al. And for the legend, TALDICE add a blank between 4.06 and ppb.

panel b) this is a busy panel and you might consider plotting only some records (your data and perhaps NEEM from Prokopiou et al) with a connecting line while removing the line for others (Eurocore, GRIP, GISP2, EDC, TALDICE, EDML)

Finally, a few technical things: Most of your subscripts and superscripts in your manuscript have been moved up or down. Please check but the usual style convention for AMT papers is that the units % and ‰ are written without a blank, e.g. 0.23‰ while all others come with a blank. Also, the unit liter is written L, e.g., 25 mL.

Please also note the supplement to this comment:

<https://amt.copernicus.org/preprints/amt-2020-171/amt-2020-171-RC2-supplement.pdf>

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2020-171, 2020.

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