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Atmospheric Measurement Techniques Discussions
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Interactive comment on "A new setup for simultaneous high precision measurements of CO_2, δ^{13}C-CO_2 and δ^{18}O-CO_2 on small ice core samples" *by* T. M. Jenk et al.

Anonymous Referee #2

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General comments:

T.M. Jenk and colleagues present a new method for measuring d13CO2, d18O(CO2), and [CO2] on small ice samples. In addition to a thorough description of the setup and procedure, problems with the measurements (such as a non-zero blank measurement) are appropriately discussed. Furthermore, a technique for determining outliers based on d18O(CO2) values is presented. This paper is a good candidate for publication in AMT, as it is very appropriate to the content and aims of this journal.

Specific comments:

I would consider rephrasing statements about the "high precision" of this method, for

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Discussion paper

example in line 37, to put this in perspective: yes, the precision is good, but it's actually not as good as the published values of the Cheese Grater in Oregon (0.02 permil for d13C, Bauska et al., 2014) or the Sublimation system in Bern (0.07 permil). The precision for [CO2] is also not as good as other published methods, such as Bereiter et al. (2013)

353: Please describe the advantage of having three sample aliquots.

Section 4.3: Note that the equilibration equations from Siegenthaler et al. (1988) do not seem to fit all datasets perfectly (e.g. Bauska et al., 2014). Using this relationship requires making an important assumption, which I think you should at least mention in the text.

830: Is there corroborating evidence that these samples should indeed be discarded as outliers? Are there other samples that may also be outliers for [CO2] and/or d13C? What is the probable cause of such outliers? Problems in ice? analytical system?

Suggestions for minor changes/technical comments:

53-58: add Schmitt et al. (2011), Bauska et al. (2015)

58-59: "constantly improving precision and accuracy" - I question the use of "accuracy" in this statement, as new results typically agree with previously published records

68-69: maybe add references for examples of the different extraction methods (e.g., Schmitt et al, 2011, Bauska et al., 2014)?

75: "clathrates coexist, that CO2 is enriched"

95: delete comma

95-145: A table would be useful and could replace a lot of this text

99: "(m/z 44, 45 and 46)." [new paragraph] "The laboratory"

99-119: This is confusing; there are three systems in Bern:

CIM - only [CO2]

Cracker (no longer used) - only d13C

Sublimation - [CO2] and d13C

103: please reference the lowering of temperature statement (personal communication?)

119: New paragraph: “At the Laboratoire”

125: New paragraph: “The ice core”

134: New paragraph: “At CSIRO”

135: not M. Rubino, pers. comm.?

150: compare “high precision” to Bauska et al. (2014)

170: I would recommend using SS for stainless steel, as this is a commonly used abbreviation, and SST is reserved throughout the literature for sea surface temperature

174-5: “In comparison to the..., which requires..."

176-8: consider rephrasing as: “resulting in an inner volume of half the size (110 cm3; 63 cm3 with the bellow compressed) ... reduced by about one-third” (or two-thirds?)

194: “Using this sealing mechanism”

194-5: consider rephrasing to: “This sealing mechanism reduces the amount of time required to open and close the vessel compared to systems using bolts and nuts.”

206: space needed between 10 and Ohm

224: please clarify: “Compared to a common operating temperature of -30 C” - not all systems are operated at this temperature!

246: “cryofocusing” instead of “focusing” (otherwise it’s confusing why the abbreviation

should be CF)

251: amount of what? Please clarify

273: no “m,” as the ratio is defined as rare-to-abundant; include the permit conversion in the equation

294: reference for laser spectrometer?

318: what temperature?

328: 30s should be separated by a space

344: 30°C, 10μm should be separated by spaces

349: you have already defined CF in line 246

350: exclusively (hopefully not present in your standard!)

352: “In parallel. . . one after the other” This is confusing; are they are lifted at the same time? What do you mean by “in parallel?”

355: 35°C should be separated by a space

355: What is the ID? What is df?

356-7: Please be consistent with the dimensions of the columns (length x ID as in line 355)

359: Briefly explain what on/off peaks are

364: ultimately instead of finally

366: “ice sample measurements, as these include section A of the system”

378: either “flasks” or “cylinders”

379: delete “require and”

383-4: “decontaminated by removing the top layers”

385: delete “in addition”

386: “separated into” instead of “distinguished in”

388: “These standards” instead of “used standards”

389: “and the amount of gas introduced was varied”

398: “Lastly,”

403: “both the upper and lower parts”

406: New paragraph: “Each time..."

407: “time the NC is opened,”

Can you be sure that no carrier N2 is present in the samples? Tests, maybe by analyzing d15N?

414: “into the NC, thus preventing water”

415: What is the high vacuum pressure in the NC?

419: This is confusing; I assume you mean that the line to the HV pump is closed. In that case, perhaps: “the chamber is closed off from the vacuum”

423-4: “After a trapping time of three minutes,”

426: “the He gas flow is then directed”

431: delete “again”

432: delete “it would be”

441: “first and last valves”

442: “conditions of the entire system”

446: “(with the valve at inlet 12 having previously been closed)”

448: “After the pressure has been recorded,”

449: This is confusing; do you mean “expanded into the NC, which has been disconnected from the vacuum?” I would delete the latter clause, as you’ve already stated that.

449-50: air sample or standard gas?

452: “allows us to record”

458: “At this point, the air”

463: “Subsequently, the outlet valve”

464-5: “In the case that the next sample in the sequence (Table 2) is to be measured”

469: “Here, as opposed to”

473: In what case are additional steps necessary?

474: “the procedure described here does not”

476: “while the current measurement is running in section B.”

477: This isn’t obvious. “However, the amount of time required increases for runs” Figure 4B: Perhaps also show the typical sample size in this plot as a gray region?

495: you have already defined QCS in 279

529: “runs 16, 21”

530: “run 17 is treated as a real sample”

533: “independence of the final results of the sampled amount of gas”

554: delete “finally”

561: either “in the following referred to as” or “in the following denoted by”

578: CF has already been defined

579: “Thereby injection of CO2”

591: “will vary based on both the CO2 mixing ratio”

593-4: “carefully separate effects related to system blanks from those influencing the observed isotopic signal”

595: “at least as a first-order approximation.”

598: “sample, will be”

598: “Shown in Fig. 5B is the linear relationship derived for”

606-7: “This demonstrates that the blank isotopic values are heavily depleted”

619: delete “happening”

635: “This again adds to our confidence in these depleted values”

638: “air amount dependence presented in Fig.”

645-6: “the the subsequent measurements with the pins also being moved”?

648: “then allows us to calculate” or “then allows for the calculation of”

650: “isotopic composition of the total gas is known.”

651: “results in values of”

658: “the measured heavily depleted”

658: delete “finally”

671: Maybe indicate briefly why this is crucial?

676: delete “finally”

680: “contribution, which is variable”

682: “As this is unlikely to be the case,”

698-9: “As discussed in Sect. 4.1.2, even for blanks constant in CO2 contribution and isotopic composition, the size”

701: “CO2 blank-to-sample ratio”

710: “and small compared to”

716: “higher blank-to-sample ratios”

721: “natural ice samples”

725: you have already defined QCS in 279

726: “over natural and artificial ice”

727: “CO2 mixing ratios and isotopic compositions”

732-3: “no statistically significant trend”?

733: “in the two standards, and”

749: perhaps “Note that DE08 was dry-drilled”

752: delete “leftover”

757-8: While the agreement between d13C results is high (average CIC - CSIRO = 0.02 permil)”

776: delete “therefore,” as this doesn’t follow directly fromm what came before

781-784: I don’t think you’ll be able to measure any seasonal cycle, as the CO2 has already had time to equilibrate with the ice

837: “allows for high resolution”

841: “natural and BFI”

842: “resulted in”

857: “could be achieved through”

860: “advantageous.”

References:

Bauska, T.K., E.J. Brook, A.C. Mix, High precision dual-inlet IRMS measurements of the stable isotopes of CO2 and the N2O/CO2 ratio from polar ice core sample, Atmospheric Measurement Techniques, 2014

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Schmitt, J., R. Schneider, H. Fischer, A sublimation technique for high-precision measurements of δ13CO2 and mixing ratios of CO2 and N2O from air trapped in ice cores, Atmospheric Measurement Techniques, 4/7, 1445-1461, 2011

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