Author response to Reviewer 2 (RC2) comments on:

Title: A system for analysis of H_2 and Ne in polar ice core samples

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We appreciate the insightful comments received from the reviewer. The manuscript has improved as a result. Below are our responses to specific comments raised in the review. Excerpts from the review are shown in blue and our responses are in black. Revised manuscript text shown in italics and with quotation marks. For brevity, we include only the reviewer comments requiring a response.

Questions mainly relate to the materials used within the setup, as Hydrogen is quite material sensitive- Line 52: It is known that Hydrogen is very material sensitive, also to aluminium, which can be exposed if a Synflex line is slightly damaged at a union for example. Further down in the text, the authors also describe how the material of the piston seal matters regarding influences on the Hydrogen concentration in the sample. In various wetted parts of the setup non-stainless-steel materials are used. Did the authors make material choices based on tests they conducted, or based on references? I think it is worth emphasizing at a suitable place in the text (possibly in the section describing the blanks) why PFA, PTFE, PEEK, etc. are readily usable; or give some references where that was shown.

We revised the text to provide additional information about how materials used in the extraction line were tested (Lines 54): *"Nafion is a fluoropolymer membrane that acts as a very selective, semi-permeable membrane to water* vapor. *The materials used in the extraction line (stainless steel, PFA, PTFE, Nafion, Viton, Synflex 1300) were tested for H_2 loss and outgassing on timescales of 1-2 hours, relevant for the extraction of the gas from the ice core."*

Flow chart of the GC-PDD would be helpful to follow the descriptions in the text. Line 142: I think a flow schematic of the GC-PDD setup (including getters, flow controllers, valves, etc.) would be helpful (if there is still allowance for another display item).

We added a schematic illustrating the components of the GC-PDD system (Fig. 4)

More background information needs to be added on the preparation of standards and on the implementation of the calibration. This is necessary to fully trace the entire process of deriving the sample concentrations. At last, I was wondering whether the instrumental drift was associated with the running time of the instrument, or could be characterized in any other way?

We added details in section 2.5 to better explain the preparation of standards and how they were calibrated. Line 225 explains the running time and temperature stabilization of the instrument: *"Gas flows, GC oven temperature, and detector temperature were maintained at the normal operating values overnight (~20 ºC). The nighttime power usage was approximately 80W which was sufficient to heat the insulated box. The in-line fan was activated in order to cool the box if the temperature in the box reached 20 ºC, which did occur during the deployment."*

We did not observe measurable drift in our high-pressure standards. We believe the drift in the calibration curves resulted from instrumental drift. Line 196: "*Working standards diluted from two of the high-pressure cylinders gave no indication of drift of the high-pressure cylinders over the course of six months (Fig. 5).*"

Line 38: I think with "in *situ*" the authors intended to emphasize that the measurements are happening at site, so I would slightly rephrase to "determining H_2 and Ne levels *in situ*".

The text was revised (Line 36) to: "*The instrument was developed to extract and analyze samples in the field immediately after recovery recovered from the ice core drill to avoid possible subsequent changes due to permeation during storage.*"

Figure 1: Please make sure that the reader knows that "ultra-torr" means an "ultra-torr adapter", like it is phrased in the text.

Fig. 1 caption was revised accordingly.

Line 62: I have some difficulty understanding the sentence: "The lower portion of the chamber is a flask constructed from one side of a 75 mm borosilicate glass O-ring joint (Ace Glass, 7646-18) with the tube end closed." What does "from one side" and "the tube end closed" mean? Could the authors please rephrase this sentence. Or, if this is a special technical term, then it would probably help if a real picture or some labels were added to the schematic.

The text was revised as follows (Line 66): *"The flask is built from a 75 mm borosilicate glass O-ring joint (Ace Glass, 7646-18). The Viton O-ring exhibited outgassing of H_2 during initial tests with melting ice. This outgassing did not occur when the flask was dry, so we suspect the outgassing was related to contact of Viton with liquid water. The other side of the glass joint is glass-blown into a dome shape to close the joint and to create the lower portion of the glass chamber (Fig. 2).*"

We also added additional labels toFig. 2 to differentiate more clearly between the sample chamber top and bottom.

Line 63: If there is a specific reason for the choice of a ground flat O-ring joint, please briefly mention it.

We expanded the text in Sect. 2.2 to more clearly explain why we ground the O-ring joint.

Line 65: "limit compression" in general, or on a specific part? If meant for a specific part, please mention, e.g. "limit compression on the O-ring".

Addressed in previous comment.

Line 66: To avoid confusion between the plastic rings and the O-ring, please write "The outer plastic ring....".

Revised text (Line 74): *"The outer plastic ring is held in place by a ¼" lip that fits over the outer wall of the glass joint."* We also added a top view of the plastic rings to Fig. 2 for clarity.

Line 96: This may be lack of knowledge on my side, but was a standardized test developed to check on the state of the seal or on which criterium is it replaced every 1-2 months?

Revised text (Line 104): *"These seals required replacement in the field, most likely from exposure to wide ranging temperatures. In laboratory conditions, the wearing of the encapsulated O-ring became noticeable in the piston "standard" blanks after 1-2 months of use. Higher H_2 levels in the daily blanks were followed by the replacement of the O-ring. More information about blanks is found in Sect. 3."*

Line 103: Please quickly check that when speaking of permeation rates in polymers, you really mean polymers in general, and not the polymer types that were tested in this study (as PTFE is also a polymer, but this was used in the setup).

Revised text (Line 114): *"This H_2 likely originates from chemical reactions in the Viton rather than from permeation of ambient air because the O-ring did not outgas detectable Ne or CH_4. Permeation rates of Ne and H_2 in Viton are relatively similar due to their similar atomic/molecular size (Brehm et al., 1987)."*

Line 142: Maybe change the title to something including the detector as well.

Section 2.4 title revised to: *"2.4 Gas chromatograph and helium pulsed discharge detector"*

Line 143: A 10 port two-position valve?

Revised text (Line 155): *"The field gas chromatograph is an SRI Instruments 8610C equipped with a heated 10 port two position valve (VICI) with a 3 cm^3 injection loop."*

Line 145: High purity helium of grade 5 or 6?

*Revised text (Line 158): "Ultra-high purity He (99.999% purity) carrier gas was passed through getters to remove traces of H_2 and other impurities" (*see Fig. 4.)

Line 145: How many getters of each model?

Revised text (Line 159*): "Three helium gas flows (carrier, backflush, and discharge) were controlled by electronic pressure control (EPC) units on the gas chromatograph. A high-capacity getter (VICI model HP2) was used on the He supply, and three smaller capacity getters (VICI model HPM) were used in the downstream of the three electronic pressure controllers (Fig.4.)"*

Line 146: Were the flow controllers already described before? Where are they located?

The electronic pressure controllers are first described in line 159 *"Three helium gas flows (carrier, backflush, and discharge) were controlled by electronic pressure control (EPC) units on the gas chromatograph."* The new Fig. 4 shows the flow configuration.

Line 152/ Line 154: Do I understand it right, that water vapour and CO_2 do not even reach the main column, but O_2, N_2 and Ar do? If so, then please specify, e.g. "and other high boiling compounds from reaching the main column and the detector".

That is correct. We revised Line 167 to: *"This prevented water vapor, CO_2, and other high boiling compounds from reaching the main column and detector."*

Line 152: Was it tested how much water vapour is still left in the sample after Nafion drying? Would this have an influence on the targeted gases in the sample?

We did not measure the water vapor levels after the Nafion but expect them to be well below 1% (molar ratio to air). The purpose is to avoid possible condensation during expansion of the sample into the sample loop and to make our samples directly comparable to dry calibration standards. The permeation of major air components (N_2, O_2, Ar) through the membrane is undetectable in our system and we have not observed any effect on calibration standards containing H_2 and Ne.

line 156: This is not a two-position valve, correct? Is this also heated? The second valve used as a bypass valve as referred to in line 171 is also a 10 port two position valve and is not heated. Revised line 171: *"A second 10 port two position valve (VICI) was used as a detector bypass valve"*.

Line 157: Please specify "for roughly 3.5 minutes (minute xxx-xyz through the run) during elution…"

Both comments are addressed in revised text (Line 168): "*Backflushing of the precolumn was delayed until Ne and H_2 were detected to avoid flow-induced disturbances to the baseline. This allowed major constituents from air (O_2, N_2, Ar) to elute from the precolumn onto the analytical column. Allowing these high abundance gases to reach the detector causes contamination that disrupts the detector baseline for several minutes. A second 10 port two position valve (VICI) was used as a detector bypass valve. The detector bypass valve diverts the flow effluent from the analytical column to waste. This valve is actuated for 3.5 minutes during elution of the major air peaks (minutes 3-6.5 of the run).*"

Line 159: Is it ever mentioned somewhere at what temperature the GC oven and the PDD are operated?

Revised text (Line 156): *"The heated 10 port two position valve and the chromatographic column were heated to 30 ºC via the GC."*

Revised text (Line 175): *"A stand-alone He-PDD (VICI model D-3) was mounted on the gas chromatograph with 200V power supply. The detector temperature is maintained at 100 ºC using a PID controller."*

Line 160: Is the temperature controller for monitoring and setting the PDD temperature? Is it not done via the GC?

In our system, the He-PDD electronics (temperature control, electrode voltages) are stand-alone. The temperature controller sets the PDD temperature. From the GC, we only use the oven, electronic pressure controllers, electrometer, and data system.

Line 166: "orders of magnitude", including the range of atmospheric H_2 abundance?

Yes. Novelli et al. (2009) demonstrated linear response of this detector to 2ppm.

Revised text (Line 179): *"This mode of detection results in a linear response to H_2 over several orders of magnitude, including the range of atmospheric H_2 abundance (Novelli et al., 2009)."*

Line 174 & Line 183: Hydrogen can drift depending on the cylinder material and cylinder batch. Was there some sort of longer-term stability testing of the used cylinders or comparison to a sample filled into

another type of cylinder to exclude drift in the cylinders? Or could you exclude simultaneous drift in the three cylinders with the comparisons you made and this question I already covered in Line 183?

Revised text (Line 181): *"The high-pressure cylinders were filled prior to the field project and were intercompared prior to shipping, in the field, and after completion of the field work."*

Revised text (Line 195): *"Intercomparison of these standards yielded agreement within ±2% (1σ) which is consistent with our estimate of the uncertainties in their preparation. The high-pressure gas standards prepared for this study are not intended for multi-year use and have not yet been intercompared with gas standards from other laboratories. Working standards diluted from two of the high-pressure cylinders gave no indication of drift of the high-pressure cylinders over the course of six months (Fig. 5)."*

Line 176: Do I understand it right, that you prepared your own scale? Or is it planned to reference (at least Hydrogen) to an external scale like the WMO scale? I am not sure if an established scale exists for Neon. Is this preparation of calibration cylinders a refined procedure in your lab (e.g. at the level of a metrological institute) and is there a literature reference that describes the details? What was taken into account to derive the 2% uncertainty? I think this section either needs referencing or should be described in a bit more detail.

Yes, we did prepare our own calibration scale for this project. We have been preparing high pressure gas standards in our laboratory at UCI for numerous trace gases for more than 20 years and have participated in formal and informal interlaboratory intercomparisons. We do plan to intercalibrate for H_2 with an external scale like the WMO scale but have not yet done so. Like the reviewer, we are not aware of an external scale for Ne.

Additional details regarding preparation and analysis of standards have been added to the text on lines 188-206.

Line 179: What were the resulting concentrations in the working standards? How many working standards did you produce and use? Same question for Line 238 with the part of the sentence saying "several concentrations". Please specify at least in one of these text passages.

Revised text (Line 207): "*The weekly preparation of the working standards ensured that the 2L flask wouldn't show any H_2 drift over the course of the analysis. Prior laboratory measurements showed that the 2L flasks would drift over the course of 3-4 weeks. Four sets of field working standards (about 25 total) were prepared over the course of 1 month. The field working standards contained concentrations ranging from 150 to 500 ppb for H_2 and 10 ppm to 25 ppm for Ne."*

Line 180: Did you see a difference whether N_2 or zero air is used as the balance gas, or does it not matter?

There is no difference between N_2 and zero air in terms of response. Zero-air did exhibit higher levels of H_2 in blanks upon arrival from the supplier (Airgas). We removed mention of zero air in the text, since only N_2 was used in the field.

Line 183: Were working standards analyzed once or multiple times daily? Please specify in the text (or in Line 238). How was the necessary frequency of working standard analysis assessed?

Revised text line 207: *"Each day, four different working standards were analyzed. The standards were run in duplicate or triplicate throughout the day for a total of 8-10 working standard runs each day."*

The working standards were run before, between, and after ice core samples.

Line 183: I assume that the weekly preparation of working standards has to do with limitations at this remote site? If there was a method-related reason, please specify in the text.

Daily dilutions were not possible due to time limitations on the field. The weekly preparations fit better in these time constraints. Line 207 explains: "*The weekly preparation of the working standards ensured that the 2L flask wouldn't show any H_2 drift over the course of the analysis. Prior laboratory measurements showed that the 2L flasks would show H_2 over the course of 3-4 weeks."*

Line 187: connected to the "vacuum line" (I presume)

Revised caption for Fig. 5: *"The low-pressure flask and high-pressure gas standard are connected to the vacuum line using PFA tubing."*

Figure 4: Please also mention the calibrated volume briefly in the text – or is this meant by the stainless-steel vacuum line?

This text was revised for clarity in line 192: *"The high-pressure cylinder standards are prepared by expanding the pure gases (H_2, Ne, CH_4,CO) from a section of the stainless-steel vacuum line at known pressure, volume, and temperature into the evacuated stainless-steel cylinder. N_2 is then added to the cylinder through a high-pressure transfer line. The added N_2 is determined gravimetrically."*

Line 198: What was the eventual temperature range that the aluminium frame box could create?

Revised text (Line 225): *"Gas flows, GC oven temperature, and detector temperature were maintained at the normal operating values overnight. The nighttime power draw of the system was approximately 80W which provided heating for the insulated box. The in-line fan was activated in order to cool the box if the temperature in the box reached 20 ºC, which did occur during the deployment."*

Line 212: I understand that the GC and detector were always restarted anew before an analysis batch? The stabilization of a GC-PDD can take some time after restart. Did you observe this issue? In case yes, I assume the GC and the detector were already running some test runs before the actual sample analysis, to have the baseline stabilised?

See revised text at line 225 (above).

Line 252: I have already commented on this above, but could this daily variation of residuals be an artefact of restarting the instrument every day? Or is the instrument running continuously, or is it in idle over night?

See revised text at line 225 (above).

Line 218: The level of detector output/ baseline varies over the runs. Is this the drift you are addressing later in the text and that needed correcting? What is the reason for this, i.e. is there a connection with the operating time of the instrument, or parameters like temperature or pressure, or is it a random pattern?

The baseline did not actually vary from run to run. We revised the caption of Fig. 6 to explain that: "*The detector signals are shifted vertically so as not to overlap.:*

Line 240-259: I am not familiar with this procedure for calibrating measurements. I presume the purpose of all these steps is to, firstly, establish a calibration curve and secondly, to apply a drift correction. Please specify this at the start of the description of the steps, e.g. in Line 239. Also, if possible, please reference to respective literature for this data treatment method.

That is correct. The correction process was unusually complicated for this project due to the harsh conditions and sensitivity changes caused by a faulty electronic pressure controller. Under normal operating conditions, more typical chromatography calibration procedures would suffice. There is no literature that we are aware of to cite for the data treatment we used.

Line 245: If injection loop temperature should actually also be accounted for, why was it not included, even if it did not improve or even worsened the regression statistics? If including it did not have a large effect on the statistics, then it could still have been included, or the sentence should at least be rephrased saying "did not change the regression statistics" or similar.

Revised text line 276: *"In theory, injection loop temperature should also be accounted for in the regression, but including it did not improve the regression statistics."*

Line 8: the abbreviation needs to be "He-PDD", not "He-PPD"

Done

Line 101: a "to" is missing, "due to compressive"

Done

Line 103: a "the" is missing, "because the O-ring"

Done

Line 192: a "to" is missing, "due to"

Done

Line 204: an "of" is missing, "of the ice"

Done

Line 246: I think "Ne" has to be "neon", as this is used throughout the text and to make the naming consistent; please check for consistent naming throughout the manuscript.

Done

Line 248: I cannot find section 2.1.3, please correct the number in the cross-reference.

Done

Figure 7: Maybe I missed it, but what are the red circles in the plot? Please add description to caption.

Done

Figure 7: I think the depth range “75-150 m” in the caption does not match the x-axis of the plot

Done

Figure 7: The gas age range “150-1750” in the caption does not match the age range in Line 271.

Done