

Author response to Reviewer 1 (RC1) comments on:

Title: A system for analysis of H₂ and Ne in polar ice core samples

Authors: Eric S. Saltzman, Miranda H. Miranda, John D. Patterson, and Murat Aydin

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.

I think more information could be provided about long-term performance of the system (even if only on standard runs), as well as the calibration (I cannot tell from the text, for example, what is the range of compositions of the various prepared working reference gases used to calibrate the instrument).

The performance of the system during this deployment was messy, with variability in blanks and system response much larger than typical for this system under normal conditions. This was due to a combination of harsh and variable deployment conditions in a tent and a malfunctioning electronic pressure controller on the detector discharge gas that was not repairable in the field. We thought it would be confusing for the reader to present this level of detail in the main text. As an alternative, we present the requested performance data in a Supplement with figures (S1, S2) illustrating the changes in instrument response during the field deployment

Revised text in line 210 describes the range of compositions of the working standards: *“The field working standards contained concentrations ranging from 150 ppb to 500 ppb for H₂ and 10 ppm to 25 ppm for Ne.”*

It would be helpful to see a photo of the whole instrument setup including the piston/ linear actuator device.

Several photos of the system in the field and lab are included in the Supplement (Fig. S3-S5).

One of the stated goals of the instrument was to determine the rate of equilibration of ice core samples with modern air, but data toward this end are not shown. Are there preliminary results that can be included in this manuscript? If not, I recommend rephrasing this (line 42) so as not to build up the expectation for this paper.

The comment about equilibration was removed.

It would be helpful to gauge system performance if more data were shown that characterise the long-term stability of the system. Figure 6 is useful for demonstrating the linearity and gives some indication of the range of total variation, but it would be useful to see, e.g., the linearity-corrected standard data over a long period of time. I’m a little unclear how the sensitivity correction was determined. Perhaps showing the drift in a figure would help the reader gauge the timescale and magnitude of the sensitivity drift.

The sensitivity drift is shown in the Supplement figures (S1, S2). Fig. 7 (formerly Fig. 6) is the drift-corrected data.

Regarding calibration, the main text reads as if the three high-pressure cylinders had the same (or nearly the same) composition, though I think this is a mistake. Did you not measure standards of different compositions (especially standards with compositions like the ice core air) against one another to verify your calibration scheme? This seems necessary to me, especially given the lower concentrations of H_2 and Ne measured in the samples.

It is correct that the three high pressure cylinders were similar in concentration. The text in section 2.5 was clarified and includes additional information about calibration standard concentrations. Line 189: *“Calibration is based on three high-pressure gas standards (1000 psi) prepared in our laboratory in electropolished stainless-steel cylinders (Swagelok 304L-HDF8-1GAL, 3.8 L). These cylinders contained roughly 350 ppm H_2 , 18 ppm Ne, 600 ppm CH_4 , and 5 ppm CO with N_2 (99.99%) as the balance gas.”*

The working standards used to calibrate the system covered a range of concentrations (see revised text on Line 210).

Specific comments

I may have just missed it, but please make sure the ice sample size is stated somewhere.

The text at Line 64 was revised as follows: *“The ice cores samples in this study were 7 cm diameter, cut into 10 cm long sections for analysis (roughly 350 grams). The samples are scraped with a scalpel on all sides to clean the drilling fluid. The samples are melted in a 500 cm³ glass chamber.*

Line 38 This is a bit pedantic, but I’m not sure *in situ* is exactly appropriate here given the cores are first drilled and extracted from the ice sheet prior to measurement.

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

You should state what is the heating element of the oven in section 2.6. I didn’t realise it was an oven until line 196.

The description of the box has been to “insulated box”. The box was only heated by the GC oven. Line 221: *“To minimize these issues, we constructed a tubular aluminum frame insulation box with insulated sheathing boards, which was placed over the analytical system each night.”*

It would be helpful for the reader to see the temporal variability in the blank to judge for themselves how significant it is. Perhaps just show the spline fit and blank data (lines 233-237).

This is now shown in the Supplement (Fig. S1).

You might consider putting the calibration equations on Figure 6 instead of listing them in the main text in lines 243-260.

We considered this but decided that the equations are more easily understood in the text where they are explained.

Line 261 – Does “calibration uncertainty” refer to the uncertainty in the standard mixing ratios? Please specify if so, and if not please also address this source of uncertainty.

Revised text in line 292: *“Monte Carlo sampling is used to propagate uncertainty in the blank correction, drift correction, and standard mixing ratios. The resulting relative uncertainties in assigned mixing ratios average 8.6% (1σ) for H_2 and 10.2% for Ne.”*

Line 264 – I would change this to say, “The factors limiting system precision are different for H_2 versus Ne.”

Done

In Figure 7, please state what the red circles mean in the caption.

Done

Lines 267-268 There is only one sentence in section 2.4 that states the reasons for the detector limiting Ne precision (lines 168-169), so you might as well just say again here what those reasons are.

Revised text line (line 297): “The primary source of uncertainty in the Ne measurements is the generally low and non-linear response of the He-PDD detector. The mechanism of detection of Ne in the He-PDD involves reaction with metastable He^* rather than photoionization (as in the case of H_2), as a consequence of the high Ne ionization energy (Sect. 2.4).”

Line 272-273 Change to something like, “..., suggesting the atmospheric H_2 levels were constant within the measurement uncertainty over this period.”

Revised text line 302: *“The variability in the data is consistent with the uncertainty in a single measurement, suggesting that atmospheric H_2 levels were constant within the measurement uncertainty over this period.”*

Technical corrections

On the Figure 1 caption, also state what “MV” stands for. Done.

Figure 1 and Figure 2 could be combined to save space if desired. Done.

Line 99-100 Change to read, “This outgassing is associated with movement of the O-ring.” Done.

Line 101 “...polymer due to compressive or shear...” Done.

Line 103 “the O-ring did not outgas...” Done.

Line 145 “This prevented(?) major constituents from air...” Done.

Line 193 “...we constructed a tubular aluminum frame oven with insulated walls...” Done.

Line 204 “...and evacuation to the vapor pressure of ice” Done.

Figure 6 caption – “non-linear” rather than “non=linear” Done.

Figure 7 caption – references to Mitchell et al. and Rhodes et al. should have proper formatting. The age range 150-1750 is different than what is stated in the text on line 271 (1600-1730 CE). Done.