

RC1

(edits are shown in red)

1) The uncertainty propagation due to reference materials (RMs) (authors call it as standards) in use, calibration procedures and measurements is not clear. Table 2 demonstrate obvious problems, namely the uncertainty in dD for several lab-standard waters (calling as secondary standard is confusing) is 0.2 to 0.3 per mille, equal or even smaller than the uncertainty assigned for the primary international RMs VSMOW2 and VSLAP2 (0.3 and 0.3 per mille respectively). This cannot be true; the uncertainty for any lower level material (secondary RM or lab standards) must include the uncertainty of the higher RMs, which was used for calibration. Thus, for lab standards one can expect about 0.5 per mille in the best case and larger if GISP was taken for calibrations (GISP has ± 1.2 per mille). The 0.2 per mille uncertainty stated for lab-standards clear demonstrates a problem; the same is valid for uncertainties for lab-standards given in d18O data in table 3.

Response:

We have changed the name of “secondary water standards” to “laboratory water standards” throughout the paper.

We have changed Table 2. Laboratory standards are now reported as a precision, with the combined uncertainty of each lab standard and all primary standards, given in parentheses.

“Table 2: Water isotope standards in units of per mil (‰). The laboratory standards (BSW, ASW, GSW, and PSW) were calibrated to primary standards (VSMOW2, SLAP2, and GISP) in March 2010. The primary standards are reported with errors given by the IAEA. **The laboratory standards are reported with a precision value given by the average standard deviation (1σ) of multiple isotopic determinations across multiple analysis platforms (IRMS and CRDS). In parentheses, the combined uncertainty of the laboratory standard and each primary standard are given, added in quadrature.**”

Table 3 gives Allan Deviation values, determined directly from a 7-hour analysis of isotopically homogenous water. If the reviewer meant Table 6 (instead of Table 3), we have modified the caption to show that we are reporting precision values, rather than combined uncertainty values.

“Table 6: The isotopic measurement **precision** (1σ) of varying parts of the CRDS-CFA system (‰). The difference in quadrature of the **full-system precision derived from GTI (System) and the precision derived from IHW (Vapor-Side) gives an estimate of the noise added on the preparation side of the system (Prep-Side). The Prep-Side values include noise added to the isotopic signal upstream of the Valco valve, while the Vapor-Side values include noise added to the isotopic signal downstream of the Valco valve.**”

2. Correspondingly, the uncertainty for sample results appear to be largely underestimated, at this must include the uncertainty of lab-standards (see above) in use as a single component.

Response:

Throughout the paper, in regards to the CRDS-CFA system, we have changed the text to indicate that we are reporting precision values, rather than uncertainty values. We have removed mention of repeatability. Bias (instead of accuracy) is now used in Section 2.4.2. And, in any case where we define a precision, we fully explain how that precision value was determined. We mention 3 types of precision measurements in the paper: vapor-phase precision downstream of the Valco valve, a similar precision measurement using isotopically homogenous waters, and a full-system precision determined from replicate ice sticks.

Furthermore, to improve clarity of the stated precision values in the paper, we add the following:

In the first paragraph of Section 2.4.2:

“We also use the laboratory isotopic standards to define **precision and bias of the CRDS-CFA system, occurring downstream of the Valco stream selection valve. Except for a small section of tubing between the**

Valco valve and the nebulizer, these values account for vapor-phase noise added to the isotopic signal. We use the following definitions of precision and bias. Precision is defined as the degree of internal agreement among independent measurements made under specific conditions, while bias is defined as the difference between the expectation of the test results and an accepted reference value. The vapor-phase precision is determined by taking the average standard deviation of each of the last 5 minutes of each 20-minute laboratory standard run, while the vapor-phase bias is defined as the difference of the measured GSW value from its known value. These values can then be compared over the long-term to monitor the performance of the CRDS-CFA system. The average vapor-phase precision (1σ) and average vapor-phase bias for δD was 0.49 and 0.39 ‰, respectively. For $\delta^{18}O$, these values were 0.05 and 0.01 ‰, respectively. In Section 3, we define a precision value that takes into account all components of the CRDS-CFA system.”

In the second paragraph of Section 3.1:

“The isotopic data for the seven 1-meter long GTI sticks analyzed on the CRDS-CFA system was measured at sub-millimeter resolution. These data were then averaged to 1 cm successive values (GTI-1cm) for each stick, resulting in seven values at each 1 cm increment, from which a standard deviation was determined. This resulted in a total of 100 standard deviation values, and the mean of these values is used to estimate the full-system precision (Figure 7). We find full-system precision values (1σ) for δD , $\delta^{18}O$, and dxs of 0.55, 0.09, and 0.55 ‰, respectively. For comparison, traditional IRMS measurements using water equilibration methods for δD , $\delta^{18}O$, and dxs are commonly reported with a precision of about 1.0 0.1, and 1.3 ‰, respectively.”

In the third paragraph of Section 3.1:

“The full-system precision can be subdivided into two parts: noise added to the isotopic signal on the preparation side of the system (i.e. noise occurring prior to the Valco stream selection valve, including depth registration) and noise added to the isotopic signal on the vapor side of the system (i.e. noise occurring downstream of the Valco stream selection valve, including the nebulizer and CRDS laser cavity). We can isolate the noise added on the vapor side of the system by analyzing a continuous stream of isotopically homogenous water (IHW) inputted directly into the nebulizer from the Valco valve and subsequently analyzed on the CRDS instrument. We take averages of the IHW over consecutive 24-second intervals (supplement), which correspond to the time needed to melt 1 cm of ice at a melt rate of 2.5 cm/min. The standard deviation of 100 consecutive 24-second averages of the IHW (the equivalent of a meter long section of ice) yields an IHW precision value, which is an estimate of the noise added to the isotopic signal on the vapor side of the system (similar to that determined in Section 2.4.2). The difference in quadrature of this IHW precision value and the full-system precision value (determined from GTI) gives an estimate of the noise added to the isotopic signal on the preparation side of the system upstream of the Valco valve (Table 6). We find that the added preparation side noise is significantly larger than the noise added on the vapor side of the system. This highlights the importance of limiting mixing in the system and achieving high-quality depth registration measurements.”

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In the last paragraph of Section 3.1:

“As a final analysis using GTI, the reproducibility of GTI-1cm CRDS-CFA data and 1 cm discrete CRDS data are compared. **We define reproducibility as the closeness of the agreement between results of measurements of the same measure and carried out under changed conditions of measurement. In this case, the same water samples are analyzed using a Picarro L2130-i, but the exact conditions of measurement are different, in that some samples are analyzed on the CFA-CRDS system, while others are analyzed by discrete sample injection into a CRDS instrument.** A scatter plot and linear regression of the resulting data for the two measurement types gives a slope, y-intercept, and R^2 value (Figure 8). The coefficient of determination values (R^2) for δD and $\delta^{18}O$ are 0.99 and 1.00, respectively, while dxs remains inherently more difficult to measure with an R^2 value of 0.88. Because this test shows the comparison of seven GTI sticks analyzed on CRDS-CFA compared with a single ice stick measured discretely on CRDS, the R^2 **values represents the reproducibility of the average of seven ice sticks vs. a single ice stick carried out under changed conditions of measurement. We explore the reproducibility of sets of single ice sticks for IRMS and CRDS in the following section.**”

Additional edits are made throughout the paper, especially related to changing “system uncertainty” and “external precision” to “full-system precision”. For example, see revised Tables 2 and 6 in comment #1 above.

3. Given continuously changing isotope signals of continuous-melted ice (due to natural variability in ice core) one may ask how the integration time of CRDS contributes to the smoothing of the natural variability measured on the melted ice by CRDS.

Reponse:

We give a short explanation below:

We add the following as the last paragraph of Section 2.4.2:

“Relative to a set flow rate, an increase in integration time decreases the resolution of measured ice core data. Therefore, a choice must be made between the integration time and the amount of smoothing introduced to an ice core record. Maselli et al. (2012) tested integration times for two CRDS instruments (Picarro L2120-i and L2130-i) using isotopically homogenous water injected directly into the CRDS instrument. This is essentially the same testing protocol as we have described in this section. However, as we show in Section 3.1, it is important to use replicate ice sticks to determine a precision for the entire CRDS-CFA system, which includes additional components of the system not considered in these Allan deviation tests. Furthermore, we use the minimum integration time of the system, which is the data-sampling rate (1.18 Hz, 0.85 sec). In this regard, the test of Allan deviation is done to show that the CRDS is stable over time.”

To the first paragraph of Section 3.1, we add the following sentence for clarity:

“As stated previously, these ice sticks are melted at a rate of 2.5 cm/min, and data is recorded on the CRDS instrument at 0.85 second intervals.”

4. Referring to the traditional mass-spectrometry, the authors have missed to mention TCEA method which is widely used for discrete sampling of ice (e.g. <http://digitalscholarship.unlv.edu/cgi/viewcontent.cgi?article=1917&context=thesesdissertations>), resulting in 1 StDev of under the best conditions at 0.5 and <0.1 per mille for dD and d18O correspondingly (e.g. see <https://tools.thermofisher.com/content/sfs/brochures/D21627.pdf>)

Response:

We have added the following reference:

Sharp, Z. D., Atudorei, V., & Durakiewicz, T. (2001). A rapid method for determination of hydrogen and oxygen isotope ratios from water and hydrous minerals. *Chemical Geology*, 178(1), 197-210.

And in the 4th paragraph of the Introduction, we write:

“Systems have been developed that continuously deliver water vapor into LAS measurement devices. The technique, known as continuous flow analysis (CFA), is accomplished by slowly melting a solid ice stick into a continuous liquid stream, which is then vaporized and injected into the LAS instrument. Gkinis et al. (2010; 2011) established the CFA framework for water isotope analysis using LAS. In particular, Gkinis reproduced traditional IRMS water isotope measurements in Greenland ice using a Picarro L1102-i CRDS instrument. Gkinis found that the precision of hydrogen isotope measurements was comparable to IRMS, while oxygen isotope precision was slightly decreased. Substantial increases in depth resolution and shorter analysis time were realized. Maselli et al. (2012) expanded on Gkinis’ technique by testing multiple new-generation Picarro devices (L2120-i and L2130-i) and found similar results. Later, Emanuelsson et al. (2015) used OA-ICOS to continuously analyze water samples from an ice core, achieving reductions in isotopic step-change response time and memory effects. Other water isotope CFA techniques (not considered in this paper) have utilized a platinum catalyst for continuous mass spectrometry measurements (Huber and Leuenberger, 2005) or a Thermal Conversion Elemental Analyzer (TC/EA) coupled to a mass spectrometer (Sharp et al., 2001). CFA has also widely been used for chemical measurements in ice cores (e.g. Rothlisberger, 2000; Osterberg et al., 2006; Bigler et al., 2011; and Rhodes et al., 2013).

5. The uncertainty cited for traditional mass-spectrometry (p 12 line 24) - does it refer to water equilibration methods or to TCEA?

Response:

This refers to water equilibration methods.

The text now reads:

“For comparison, traditional IRMS measurements using uranium reduction for δD and CO_2/H_2O equilibration for $\delta^{18}O$ are commonly reported with a precision of about 1.0 and 0.1 ‰, respectively. The resulting dxs precision using these two measurement techniques is about 1.3 ‰.”

6. The authors are not very careful in references, for instance reference given to (Lin et al. 2010) when referring to dD and d18O values of VSMOW2 & VSLAP2 is not correct. (This publication was aimed to determine d17O, without effecting d18O and dD values accepted for VSMOW2 & VSLAP2.) The initial manuscript submitted in April did contain numerous incorrect and irrelevant references, for instance those related to 17O which is not addressed in the work; I have not fully checked this version being under discussion.

Response:

We have removed the Lin et al. 2010 reference.

7. When one discusses effects of corrections, not to forget that the magnitude of corrections may be rather significant, reaching 1 per mil in d18O for mixing corrections (Fig 4) and about 20 per mille for diffusion-mixing corrections (Fig 6). What about the uncertainties of the corrections? In particular interesting is whether the corrections (introduced for dD and d18O separately) may result in an artifact for d-excess values (means – whether uncertainties in dD and d18O are well correlated or not?) Please provide a clear explanation on this.

This is a very valid question, and in Figure 5, the impulse response of the system for dD and d18O are indeed slightly different, which could introduce an artifact in dxs. However, in Figure 7, we compare 7 Greenland replicate ice sticks measured on CRDS-CFA to discrete samples measured on CRDS (which

have no issue with different impulse responses). The dxs values correlate quite well with an R^2 value of 0.88. We feel this replicate experiment is a very important part of this study, and adds new confidence to the method in general.

In the conclusion, we state:

“One exception to these solid ice results is found in the deuterium excess (dxs) measurements. At the highest frequencies (multi-year to decadal), we found discrepancies in comparisons of both inter-lab CRDS measurements of dxs and in CRDS and IRMS measurements of dxs. Additional studies at high resolution and between different labs are necessary to better understand these high-frequency discrepancies in dxs. Contrary to this, however, are the dxs results measured solely on the CRDS-CFA system presented in this paper. We found that dxs can be replicated at high frequencies, demonstrated by tests of identical Greenland ice core sticks. Furthermore, despite slightly different impulse response functions for δD and $\delta^{18}O$, the dxs measured from replicate ice sticks on the CRDS-CFA system is correlated ($R^2 = 0.88$) with discrete CRDS dxs values measured on the same replicate ice. This indicates a negligible artifact in dxs calculations arising from the differing impulse response functions, and shows that CRDS-CFA system measurements of dxs can be used reliably as a climate proxy.”

Furthermore, in Section 2.4.3, we write:

“In our data output file, values of $\sigma_{mock\ ice}$ and melt rate are included for all depths to allow for CRDS-CFA mixing length corrections (i.e. deconvolution techniques), and for comparison to diffusion occurring naturally in an ice sheet. It is at the discretion of the output file user whether to make these corrections.”

And Table 4 now includes 1σ variability for mixing lengths across 50 determinations:

“Table 4: Mean mixing length values from 50 determinations of mock ice step changes ($\sigma_{mock\ ice}$) and for laboratory isotopic standards step changes (σ_{LS}). The difference in quadrature of $\sigma_{mock\ ice}$ and σ_{LS} is the amount of mixing occurring in the liquid phase of the CRDS-CFA system (σ_{LQD}). Mixing length values for both skew and normal impulse response functions are given in seconds and in meters (in parentheses), based on a melt rate of 2.5 cm/min. Values with an asterisk represent 1σ variability in meters.”

In terms of dxs corrections done for mixing lengths (similar to that shown in Figure 6), the affect of the deconvolution on dxs is not tested in this paper. However, varying spectral methods can be used, similar to Johnsen et al. (2000) or Jones et al. (2016, in review at JGR), to determine the original dxs strength of signal under varying white noise or red noise background climate assumptions. Again, it is up to the reader to determine the best course of action. As noted, we provide mixing lengths for both dD and d18O, so that the mixing effects of the CRDS-CFA system can be removed, allowing for a corrected dxs to be calculated.

Johnsen, S. J., Clausen, H. B., Cuffey, K. M., Hoffmann, G., Schwander, J., & Creyts, T. (2000). Diffusion of stable isotopes in polar firn and ice: the isotope effect in firn diffusion. *Physics of ice core records*, 159, 121-140.

Water Isotope Diffusion in the WAIS Divide Ice Core During the Holocene and Last Glacial, T. R. Jones, K. M. Cuffey, J. W. C. White, E. J. Steig, C. Buizert, B. R. Markle, J. R. McConnell, and M. Sigl, JGR, in review.

For the isotopic step-change correction (Section 2.4.4), we now include a new table that provides uncertainties for this correction. Again, it is up to the user whether they want to include or discard the isotopic step change correction values...

The new caption reads:

“Table 5: Standard deviation of the mean for 50 determinations of isotopic step-change corrections using mock ice (δD step-change values of approximately -240 to -120 ‰). All values are given in per mil (‰). Each data bin includes 20 consecutive data points (spanning ~17 seconds of analysis time), increasing from $c_n = 0.5$. The data in each bin are averaged for each determination. Corrected values of dxs are calculated from the corrected δD and $\delta^{18}O$ values. From $c_n = 0.5$, about 100 seconds are needed to achieve greater than

98% of the expected mock ice value of -120 ‰. For comparison, the calculation of the standard deviation of the mean for 50 determinations of 17 second averages of isotopically homogenous water yields values for δD , $\delta^{18}O$, and δx_s of 0.01, 0.01, and 0.05 ‰, respectively. The isotopically homogenous water was allowed to run through the CRDS-CFA system for 1 hour before the 17-second averages were determined.”