**Atmospheric
Measurement
Techniques
Discussions**

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Interactive comment on "Water isotopic ratios from a continuously melted ice core sample" *by* V. Gkinis et al.

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We would like to thank the three referees and the editor for a set of useful comments and corrections on our manuscript. After carefully considering these comments and performed the necessary changes we hereby propose a revised version of the manuscript. In the following we answer to the general comments posted by the referees. We also address the specific comments separately for every individual review.We particularly focus on comments about the water concentration correction and the performed VSMOW calibrations. As a result of that we modified section 3.1 for a more clear explanations of the followed procedures.

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1 General Comments

1.1 Estimation of the σ^2_{CFA} quantity and the stacked ice experiment

We agree with referees 2 and 3 that introduction of an isotopic step at the melter would characterize the whole system in terms of sample dispersion. Additionally it would not impose the need for the application of spectral methods on discrete data. In fact such attempts were made in the field. "Sausages" of milli-Q water have been left to freeze, and after they have been processed on the ice saw they were melted and analyzed by our system. What seemed as a simple and straight forward experiment, proved to be an experimental challenge for us. Despite the fact that the isotopic composition of the liquid water can be controlled relatively accurately by the adjustment of the deuterated water used, we never managed to produce an isotopically homogeneous ice rod. As a result the isotopic steps were disturbed and not usable. We do not know the exact cause of this effect but we assume that fractionation effects during the phase change from liquid to ice cause this problem. As a result we choose to overcome this problem by following the approach presented in the manuscript.

1.2 Sensitivity to water concentration

The measurements reported here as well as the measurements that we have gathered during the NEEM project in general, are performed in the area of 17,000 - 23,000 ppmv. In this range of water concentrations we see that the stability of the water vapour delivery to the system is significantly more crucial than the absolute level of the water concentration. Thus answering to the comments of referees 1 and 3 we would say that the obtained precision is in fact not a function of the water concentration. This is not the case for the low water concentration regime (< 15 kppmv) where the performance of this specific analyzer deteriorates considerably. For a more illustrative example please

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refer to figure 5 in Gkinis et al. (2010).

Practically, during a typical day the water concentration does not vary more than 300 - 500 ppmv. As reported in the manuscript all the raw data are corrected for the dependence on water concentrations to the level of 20,000 ppmv. Thus all data and SMOW calibrations are in fact reported at this water concentration level. We agree that this is not clearly stated in the text and thus we have performed the necessary changes in section 3.1

Regarding the value of the correction coefficients in section 3.1 we would like to comment that based on personal experience they are certainly instrument dependent. As far as their stability is concerned we can comment the following. We compiled data from 6 calibrations that span a period of approximately 2 years (07/2009 - 10/2011). We focus in the range 15,000 - 23,000 where we observe a linear response of the isotopic signal to changes of the water concentration. Performing linear regressions in the same manner as in Gkinis et al. (2010) we get $\alpha_{18} = 1.83 \pm 0.09$ and $\alpha_D = 4.05 \pm 0.77$. No apparent drift is observed with time. We choose to use the same values as reported in the submitted version of the manuscript as they were obtained chronologically closer to the reported measurements. If the mean values of 1.83 and 4.05 would be used instead, for deviation of 1000 ppmv the difference in δ^{18}O and δD would be

$$\left(\frac{19,000}{20,000} - 1\right) 1.94 - \left(\frac{19,000}{20,000} - 1\right) 1.83 = -0.0055 \tag{1}$$

and

$$\left(\frac{19,000}{20,000} - 1\right) 3.77 - \left(\frac{19,000}{20,000} - 1\right) 4.05 = 0.014 \tag{2}$$

respectively. Both these deviations are well below the precision levels we currently achieve.

1.3 VSMOW calibrations - accuracy

VSMOW calibrations are ideally performed using 2 water standards to obtain a slope and an intercept and a 3rd standard for linearity and accuracy check. All water standards have been transfered to the field using the necessary precautions to avoid evaporation (amber glass containers, airtight sealing, storage in low temperatures). They have been calibrated in Copenhagen with respect to SMOW and SLAP water on an IRMS system (Thermo Delta V) with a high temperature conversion system (Thermo TCEA). For the specific case of the data series we present in this manuscript a calibration had been performed the same day. This is the desired frequency for VSMOW calibrations.

However during the field operation of the CFA system, the need for high throughput does not always allow for sufficient time to perform these calibrations properly. The timing and sequence of events is also very irregular and depends on the measurement status of other parameters (the chemical analyses count analytical systems for 16 components). As a result automating the VSMOW calibration procedure is also not feasible. Consequently the normal frequency at which VSMOW calibrations were performed was one every 3-4 days. In the specific case of the ice core measurement we present here the D_{xs} signal can be used as a check of the quality of the calibration. Apparent drifts will affect the D_{xs} signal considerably. It is important to mention here that the water isotope measurement was an add-on to the existing CFA setup that was deployed at NEEM and was mainly dedicated to chemistry measurements. The main focus was to prove feasibility and thoroughly test the system with a secondary objective being gathering high resolution data from the NEEM core especially over sections of particular interest as some climatic transitions.

We modified the text in the manuscript accordingly to provide the reader with more information on VSMOW calibrations (p4081 l10). We have also added plots of the VSMOW calibration used for the dataset presented here. The calibration is performed with

3 water standards. A slope and an intercept is calculated using two of the standards and the calculated value of the third standard constitutes a check for the linearity and accuracy of the system.

The idea of plotting a 5 cm binned version of the CFA data so a 1:1 comparison can be obtained is interesting. It is the opinion of the author though that for various reasons such a plot can be misleading. This is mostly due to the fact that because of the instrumental diffusion we describe in this work, averaging the CFA data on a 5 cm resolution would yield a dataset that is more smoothed than the discrete 5 cm data. One way to account for that is to use the deconvoluted data we present in section 3.5. The use of these data as a starting point yields a better agreement between the binned CFA and the discrete data. The deconvolution of the CFA data is based on an estimate of the instrumental diffusion length σ^2_{CFA}. The estimation of this quantity carries of course an error. This is visible in the comparison we attach here (figure 1 of this document). The disagreement between the two datasets can be seen mainly at the extrema of the signal. These are the points that are more sensitive to the deconvolution technique. Using the data before the deconvolution binned in 5 cm resolution, we calculate an rms standard deviation $\sigma_{rms} = \sqrt{\frac{\sum (\delta_{binned} - \delta_{5cm})^2}{N}}$. From this calculation we get $\sigma_{rms} = 2.29$ for δD and $\sigma_{rms} = 0.3$ for δ^{18}O. The correlation between the two datasets is $R^2 = 0.92$ for δD and $R^2 = 0.94$ for δ^{18}O. Using the deconvoluted data we get $\sigma_{rms} = 1.97$ for δD and $\sigma_{rms} = 0.27$ for δ^{18}O. The correlatioin in this case increases with $R^2 = 0.986$ for δD and $R^2 = 0.998$ for δ^{18}O. These calculations show how this comparison is sensitive to the estimation of the instrumental diffusion. Based on the results of the VSMOW calibration we can also verify that the σ_{rms} values we calculated above heavily underestimate the performance of the system and thus such a comparison does not provide a proper insight in the accuracy estimation.

Additionally by estimating the accuracy of the system via this comparison we assume that the discrete dataset is in some way based on a "perfect" sampling and measuring procedure. We can comment that this is not true as already at the ice processing

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Discussion Paper

stage that happens in the field, the thickness of the samples can be different than 5 cm. This is due to the thickness of the saw blade (≈ 1 mm) and the human error involved. The latter is unavoidable considering the extremely high throughput of the ice core processing line during a field season (up to 35-40 m a day). As a result small fluctuations in the sampling resolution will yield high discrepancies at the extrema of the isotopic signal. Keeping the figure in its current form provides an indication of the way the isotopic cycles are sampled with our technique compared to the discrete sampling procedure. Having updated the section that deals with VSMOW calibrations, with updated text, data and plot we believe we give the reader an overview about the accuracy that can be obtained by the system and thus we would like to propose leaving the CFA-discrete data comparison plot at its current form.

1.4   Averaging and estimation of precision based on the power spectrum

As mentioned in section 3.2 we report our results on depth scale of nominal resolution equal to 5 mm. Considering a melt speed of 3 cm/min this corresponds to one data point per 10 sec. The analyzer reports data at a rate of approximately 1 data point per 5 seconds (acquisition rate is not constant). Thus we indeed average slightly.

As far as the estimation of the variance based on the power spectral density is concerned, we can comment the following. The variance reported is the variance of the white noise of the signal. The power spectral densities presented in figure 4 are calculated based on the data of the depth interval $1382.152 - 1398.607$ m (N = 3291, $\Delta x = 5$ mm). Injecting a sample of a constant isotopic value would also make it possible to assess the performance of the system. However with this method we can characterize the variance based on the ice core measurement itself. We rephrased the text in the beginning of section 3 (p4080 l5) as well as in section 3.2 (p4081 l23) so this is more clear to the reader.

The mean value of the data is subtracted before the power spectral density is calcu-

lated. The flat part of the spectrum defines the level of the white noise signal $\hat{\eta}(f)$ and the integral is calculated over the whole range of frequencies. Since we are considering the variance of the white noise signal we expect that its power spectral density is flat over the whole range of frequencies. We have good indication that all of the low frequency components belong to true ice core signal. If that was not the case one (or more) of the following would most likely happen. We would see a obvious drifts during the sections of milliQ water between the melt runs (figure 2). These sections do not appear to present any low frequency variations and the longest one of those is about 2500 sec long. In Gkinis et al. (2010) we have reported Allan variance plots and optimum integration times equal to approximately 5000 sec. This quantity would be considerably lower if indeed the low frequency power density was partly due to instrumental drifts. Last if parts of the low frequency components of the power spectral density were due to instrumental drifts we would expect an obviously poorer agreement between the discrete and the continuous data as presented in figure 5. Regarding the bubble formation and in general abrupt water level deviations of high intensity we can say that they affect the isotopic signal but their effect lies in the area of high frequencies. This can be demonstrated in figure 2 where around t = 19000 sec the water delivery was disturbed due to a scheduled change of the milliQ water tank. As seen the response of the isotopic signal is equally fast and seen as a clear spike in both the δ^{18}O and the δD signal.

2 Referee 1

- **Abstract, line 2** replace build with built.
  Done

- **Abstract, line 16** .. limits the resolution of the technique. You may want to add that you refer to the resolution in terms of age. It might be confused with

resolution in terms of δ-values.
replaced *resolution* with *temporal resolution*.

- **P. 4078, line 12** explain what mQ stands for. The unfamiliar reader would have to google..
  Added footnote

- **P. 4078, line 24** replace and correct purchasecd by with purchased from.
  Corrected

- **P. 4079, line 14** replace affects with effects.
  Corrected

- **P. 4080, line 4** add units to 1281.5–2200.55
  Added unit

- **P. 4080, line 21** replace a with α. same for the D.
  Replaced

- **P. 4080, line 25** You state that you perform frequent calibrations. The interested reader (like myself) would be keen to learn how often you do calibrations, what the ac- curacy of the instrument is when you calibrate frequently, and in par ticular how instrumental drifts affect your correction terms (Eq. 1) regarding humidity. This could be combined with another depiction of the data of Fig. 5 (see my comments there).
  See answer in the general comments.

- **P. 4081, line 22** remove the comma.
  Removed

- **P. 4081, line 26** why do you use M=300 when a lower number works equally well?

Interactive
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Interactive Discussion

Discussion Paper

There is in fact no particular reason for that. We removed the text "imple-mentations with a lower number of autoregressive coefficients can perform equally well" to avoid causing confusion to the readers.

- **P. 4082, line 5** From the power spectral density of a time series âĂŤ which is not shown âĂŤ you determine the precision of your δ^{18}O and δD measurements. The precision is, however, a function of the humidity, and you should at least state at which humidity you have determined the precision. It is furthermore a function of the averaging time. This seems to be seen by the increasing spectral density towards lower frequencies. However, the underlying time-series data and a more detailed description would be interesting to show how this measurement was performed (constant humidity and isotopic ratios or not).
  See the general comments section

- **P. 4082, line 6–20** and Fig. 5 This is a very important comparison measurement indeed. I think you should present the data in Fig. 5 in a different fashion. If you were to group the IR-CRDS data to the same depth scale than the discrete mass-spectrometer data you could plot them 1:1. Adding respective error bars as well as slope and intercept will give the reader a better feeling for the accuracy of the IR-CRDS in direct comparison with another state-of-the-ar t technique. Then you can discuss in a more quantitative fashion any differences.
  See general comments section

- **P. 4083, line 8** remove the comma
  Removed

- **P. 4082, line 23** remove the comma
  Removed

- **P. 4082, line 24** remove the second comma
  Removed

- **P. 4084, line 12** replace on by in
  Replaced

- **P. 4086, line 13** replace sceme by scheme
  Replaced

- **P. 4087, line 15** the term wavelength of the isotopic signal is at least confusing when discussing results obtained with a laser spectrometer. Maybe you can find a less ambiguous term.
  Unfortunately the term wavelength fits the need of describing attenuation effects on the isotopic signal and thus we kept it in the text. We have added a footnote clarifying the use of the term in this section of the manuscript. Based on this correction we also refined the mathematical description in sections 3.4 and 3.5 making a more consistent use of the units in the equations describing fourier transforms.

- **P. 4089, line 7** As mentioned previously, the precision of the δ-values is dependent on the humidity level and the averaging time. As such, the uncertainty of the deuterium excess is a function of these parameters, too.
  In the range we operate the noise level does not seem to be dependent on the water concentration. See our comments in the general comments section

- **P. 4089, line 9–10** I'm not so sure whether your optimal filtering is the cause for the cleaner Dxs signal. I believe a simple low-pass (averaging or running mean) would enhance the signal-to-noise ratio similarly. The optimal filtering seems to be useful to enhance the uncertainty in absolute terms rather than relative, which is what I see in Fig. 9. Furthermore, what is the consequence of your error estimation. Is it sufiňĄciently good enough to do what you want to do?
  We mainly use the optimal filtering technique to correct the signal for the diffusion imposed during the transfer and measurement of the sample by

C1937

the analytical system. At this step it is important to characterize the noise
level via the power spectral density estimate and account for it when we
invert from the frequency to the length domain. This is illustrated by the
restoration filter curves plotted in figure 8b. Otherwise this inversion pro-
cedure will amplify high frequency components resulting in an overampli-
fied reconstruction. Using a running mean filter one can reduce the noise
level but in this case excess diffusion is imposed (simple averaging). This
is not what we are aiming for in this work. So to conclude the optimal filter-
ing is used to correct for the instrumental diffusion and in order to perform
the technique it is necessary to account for the noise of the signal. Thus
an estimate based on the power spectral density can be used.

- **P. 4090, line 1–5** As mentioned before, the verification of your calibration is not
quanti- tatively shown in Fig. 5. Note that this accuracy is also rather independent
of the noise level you determine. Please quantify.
See the general comments section

- **P. 4090, line 14** remove ïňA̧rst the
Removed

- **P. 4090, line 17–18** Sentence needs to be rephrased
Rephrased

- **P. 4090, line 17–18** change *The non destructive, continuous and on-line tech-
nique, of- fers the possibility for analysis of multiple species on the same sample,
in high resolution and precision and pottentially performed in the ïňA̧eld.* to *The
non de- structive, continuous, and on-line technique offers the possibility for anal-
ysis of multiple species on the same sample in high resolution and precision and
can potentially be performed in the field.*
Changed

- **Fig. 4** add a legend
  Added legend

- textbfFig. 5 show as direct 1:1 comparison
  See the general comments section

- **Fig. 7** in the 2nd line of the caption change *represend* to *represent*
  Done

- **Fig. 9** add a legend
  Legend Added

3 Referee 2

- **p. 4, l. 16f**.: The high susceptibility of d18O measurements via CO to interference
  with NO (m/z = 30), generated in the ion source of the mass spectrometer, could
  also be mentioned here, which is a major drawback of the simultaneous analysis
  of d18O and dD with high temperature pyrolysis-CF-IRMS.
  Added a line on the subject

- **p. 7, l. 18**: "ka b2k" should be explained at its ïñẠrst use for the non-ice-core
  expert reader, e.g. "thousand years before 2000 AD (ka b2k)"
  Footnote added

- **p. 8, l. 3**: Here it should be made clear that it's the delta values (d18O, dD)
  that show the nearly linear response to water vapor concentration ïñĆuctuations
  around 20000 ppm.
  Replaced *the system shows a linear response.." with ..the δ^{18}O and δD signals show a linear response.."

- **p. 8, l. 6**: Here it should be made clear to the reader that these values were obtained for the same individual analyzer, as each individual analyzer has its own characteristics, e.g. the response might not be linear or the slope of the response might be different. This information should be amended by the calibration details for the analyzer, i.e. frequency of calibrations, precision, accuracy, drift.
Corrected see the general comments section

- **p. 13, l. 8f.**: It should not have been too difficult to introduce an isotopic step change at the melting unit, i.e. around P1 in Fig. 1. This would have avoided the "detour" using power spectral densities. **See the general comments section**

- **Figure 8**: The numbers for σ_{cfa} are a bit confusing here. The numbers in the legend do not correspond to the numbers given in the ïňAgure caption. **Numbers are now correct**

- **p. 4074, l. 3**: Change"build" to "built"
Changed

- **p. 4075, l. 16**: Change "usefull" to "useful"
Changed

- **p. 4075, l. 16**: Change "it's" to "its"
Changed

- **p. 4075, l. 20**: Change "is introduced" to "has been introduced"
Changed

- **p. 4076, l. 7**: Change "requires the process of" to "requires processing of"
changed

- **p. 4076, l. 28-29**: Change "similary" to "similarly"
Corrected

- **p. 4077, l. 13**: Change "evaporatotion" to "evaporation"
  Corrected

- **p. 4079, l. 5**: Change "VSMO" to "VSMOW"
  Replaced *VSMO* with *VSMOW standard*

- **p. 4081, l. 17, and p. 4086, l. 13**: Change "sceme" to "scheme"
  Corrected

- **p. 4086, l. 13 and 15**: Change "on a 5 cm resolution" to "at a 5 cm resolution"
  Corrected

- **p. 4090, l. 17**: Change "With the use" to "The use"
  Changed

- Figure 8 is mentioned in the text before Figure 7. Thus, swap the two ïňĄgures.
  Changed the figures

4 Referee 3

- **p4074, line 4**: Why introduce (yet) another abbreviation for the laser-based technique used here? Picarro, and practically all of its users refer to the measurement technique as Wavelength Scanned CRDS (WS-CRDS). I believe it is useful information for most readers to be able to identify the analyzer already in the Abstract, so I suggest men- tioning Picarro here.
  Replaced IR-CRDS with WS-CRDS in the text and mentioned in the abstract that the unit was purchased from Picarro

- **p4074, line 10**: VSMOW-SLAP scale.
  Replaced with "SMOW – SLAP"

- **4074, line 12**: replace humidity by water volume mixing ratio or concentration or amount (see comment above).
  Replaced "humidity" with "water concentration" throughout the document

- **p4074, line 25**: Was the measurements performed at NEEM, as suggested here, or on ice-core material carried back to Copenhagen?
  Measurements were carried out in the field. Similar measurements for chemical species and methane concentration occluded in the bubbles of the ice have also been performed during this project. We rephrased the text.

- **p4075, footnote**: delta = Rsample/Rvsmow -1 : Per mil is NOT a unit! Thus here no per mil sign is needed. If you insist on drawing attention to the fact that the numerical value will be given in per mil, then multiply the result by 1000 per mil (which is exactly equal to unity . . .). Numerator and denominator in the definition of R are usually placed in square brackets in order to signify atomic concentrations.
  Corrected footnote

- **p4076, line 5**: replace "consumables and standard and carrier gases" by "consum- ables, isotope standards, and carrier gases".
  replaced

- textbfp4076, line 7: processing. **Corrected**

- **p4076, line 12**: Kerstel, 2004.
  Corrected

- **p4076, line 18**: over, e.g., hot uranium. Note that zinc and chromium have also been used for this purpose.
  We add a reference to the work of Ghere et al. (1996) where use of chromium is made.

- **p4078, line 14**: replace "99.8% in D2O" with "containing 99.8 atom% deuterium".
  textbf
  corrected

- **p4078, line 24**: purchased from Picarro.
  corrected

- **p4078, line 25**: replace "sml min-1" by "sccm" or "standard mL/min".
  Corrected

- **p4079, line 5**: How many different local water standards were used and what isotopic range do they span? I assume that as in any good ice-core laboratory, you used a two- point (VSMOW and SLAP) isotope scale calibration as recommended by the IAEA.
  See the general comments section

- **p4080, line 18**: I assume that the unit is ppmv (per volume, not mass).
  Yes it is ppmv. Added in the text

- **p4081, line 6**: insert "measurement" into "the measurement time scale to a depth scale", in order to clearly distinguish between the time at which each individual isotope ratio measurement is made and the age of the ice, which results in a completely different time scale.
  inserted

- **p4081, line 21**: I suggest to change the title to "Noise level and accuracy" or "Precision and accuracy".
  Changed to "noise level and accuracy"

- **p4082, second section**: Since both data sets are calibrated to yield values on the VSMOW-SLAP scale, it is no surprise that the average values of the data sets agree. But, it is difficult to get a good idea of the accuracy of the measurements

from Fig. 5 as is. The deviations between the two data sets can be plot on the same horizontal scale, above the current isotope depth profiles, provided the laser data are binned or averaged to the same sampling interval size (5 cm) as the IRMS data. The RMS value of these deviations is than a measure of the accuracy of the laser method relative to the conventional IRMS method.
See the general comments section

- **p4088, line 10**: Autoregressive model of order 1 (AR1). Does the value of a1 in Eq. 21 support the assumption of red noise (i.e., a1 is negative but larger than -1)?
  The expected values depend on the definition of the AR1 process. We use $Y_t - \alpha_1 Y_{t-1} = \varepsilon_t$ **where** ε_t **the variance of the white noise Thus for a stationary process we expect** $0 < \alpha < 1$**. The optimization routine typically yields values in the range of 0.1 – 0.2.**

- **p4089, Eq. 22**: The numerical value equals 0.00048 or 0.48 per mil, not 0.48.
  Added ‰ sign

References

Gkinis, V., Popp, T. J., Johnsen, S. J., and Blunier, T.: A continuous stream flash evaporator for the calibration of an IR cavity ring down spectrometer for isotopic analysis of water, Isot. Environ. Health S., 46, 1–13, 2010.

Gehre, M., Hoefling, R., Kowski, P. and Strauch, G.: Sample preparation device for quantitative hydrogen isotope analysis using chromium metal, Analytical Chemistry, 68, 4414–4417, 1996.