# Response to reviews of *High-Resolution Continuous Flow Analysis Setup for Water Isotopic Measurement from Ice Cores using Laser Spectroscopy by Emanuelsson, et al.,* AMTD 7 12081-12124, 2014.

We appreciate the constructive comments from two anonymous reviewers. We address their comments one by one below. Reviewer comments are in red, our responses are in black and changes to the revised manuscript are in blue.

#### **Response to Reviewer 1**

#### **General Comments:**

A customised experimental setup is proposed in this paper for high resolution (seasonally resolved) continuous flow measurements of water isotopes from melted ice cores using a commercial laser spectrometer and a calibration system from Los Gatos Research. Such a setup already exists in combination with a cavity ring-down spectrometer from Picarro. The setup proposed here tries to take advantage of the shorter response time of the off-axis integrated cavity output spectroscopy system of Los Gatos to further increase the (temporal) resolution of the isotope signal available from the ice core. Changes to the existing Water Vapor Isotopic Standard Source (WVISS) calibration unit include among others and most importantly a drastic reduction of the internal volume of the evaporation chamber to reduce the response time of the system, increased evaporation temperature, and the possibility to switch between several liquid water samples. This paper is in the scope of Atmospheric Measurement Techniques and presents a valuable new analytical setup for the analysis of water isotopes in ice cores that can be useful as well for the calibration of continuous water vapour measurements. The authors make a great effort to characterise their setup in a thorough way. I have the following major comments that I think the authors should address before final publication:

1) Characterisation of the response time of the full continuous flow analysis (CFA) system as already discussed in Gkinis, et al. 2011 for a full characterisation of the CFA-IWA system a step change in the water isotope composition should be done at the melt head to fully characterise the presented system.

Such an experiment may be beyond the scope of this publication but it should be discussed why this has not been done. Would it be possible to construct an artificial ice core with several distinct layers from different standard waters, so that the step change is introduced at the very beginning of the whole setup, i.e. at the ice melting unit?

The reviewer raises a valid and important point. We did perform an experiment to assess the response time via the entire CFA system. However, this experiment was very limited and only performed at the very end of the CFA campaign because there was concern that our water standards of different isotopic compositions (Table AR2) could contaminate some analyses, particularly for trace element concentration measured by ICP-MS. This contamination would have been a concern for all equipment upstream of DB1 (Fig. 2). As a result, we were only able to measure the response time from the melt head by applying a stream of liquid water of different compositions directly to the surface of the melt head, rather than a synthetic ice core with layers of alternating isotopic compositions. This experiment was only carried out at the end of the 2014 campaign, and never during the 2013 campaign.

In answer to the reviewer's question, we present the data from our limited experiment here as Figure AR1, below. The data suggests that when a step change between water standards was performed at the melt head, the response time was 43 s. This can be compared to 19 s when performed at the multi-port valve (V2). The difference between the two estimates indicates that the  $\delta$ -signal is smoothed between the melt head and the valve. The discrepancies between the data and the fitted curve suggests the response may be more complex than the fitted model, with ~70% of the response occurring more quickly, and the final portion of the response occurring more slowly than expected based on the fit for the 43 s response time.

The purpose of this manuscript is to characterize the isotope measurement system rather than the full CFA set up. Therefore, given the reviewers comment, we propose that it is appropriate to insert only a brief comment at the end of the section acknowledging that:

"To conclude discussion on this topic, we note that the response times reported above do not represent the full response time of the entire CFA system, as measured from the melt head. Limited experimentation produced an estimate of ~43 s for the response time of the entire 2014 CFA system. This is more rapid response than all systems reported in Table 3 except the Custom 2014 setup. Thus, to take full advantage of the fastest response times, the isotope analysis system could be placed closer to the melt head by changing the overall CFA design, or shortening the sample line between the melt head and DB1."



**Figure AR1.** Shows  $\delta$ -CFA data from a response time test performed by a switch in water standards at the melt head (blue dots), a LSO fitted curve (black line) and the 5% and 95% of change of the response (response time red line) for the custom 2014 setup.

2) Since another laser-based high-resolution CFA system already exists (Gkinis, et al. 2011) mention clearly the advantages of your system. E.g. that your system can potentially provide even higher time resolution ice core measurements due to the shorter response time of the laser instrument used.

The reviewer correctly identifies that Gkinis et al. (2010, 2011) have reported the development of a similar system. Maselli et al. (2013) also uses a similar system. We clarify that this study differs by developing a framework describing how the performance of the vaporizer/spectrometer system can be optimized, characterized and then integrated with other CFA analytical equipment. A key issue is that the ice core CFA campaign delivers an ice core melt-stream to many instruments, which produce nearsimultaneous measurements. These different instruments place different constraints on the overall CFA operation, and tradeoffs must be optimized. The reviewer suggests that we should expand on the reasons our system is optimal. Taken with the reviewer's further comments (below) that we deemphasize other elements of the manuscript such as calculation of Allan variance, these suggestions would reduce the ability of our manuscript to document the evolution of vaporizer/spectrometer systems from stand-alone equipment to integrated parts of multi-instrument CFA systems. We therefore propose to take further steps to clarify this overarching theme in our manuscript in two ways. First, we propose to add an additional paragraph describing this context within the introduction. Second, we clarify at the end of the introduction that we've documented the adaptation and integration of the vaporizer/spectrometer system into the RICE CFA campaign, but that other CFA campaigns may differ in their constraints and goals.

Addressing the second point, one of the important contributions from this study is the result from the comparison tests among four setups: our two custom setups, the WVISS setup and the UC setup. We show using response time tests and stability tests that the custom setups are more responsive (shorter response time), whereas the UC setup is more stable (lower Allan variance values). The purpose is not to single out one superior setup, but rather to highlight their differences and how these differences can be quantified. This information is valuable for research groups who are planning to purchase equipment and/or modify their setup for CFA. This is the first study within the field of ice core science that provides an in-depth characterization and comparison between water stable isotope CFA setups that are using the new generation of OA-ICOS and CRDS spectroscopy techniques.

We propose to address the issues raised with a thorough revision of the introduction. We believe that the introduction can be made more concise and can address issues of clarity by following the outline below, where each point is represented by a paragraph:

- Introductory importance of  $\delta$  from ice cores as records of past climate processes
- Interpretation of δ from ice cores
- Potential of laser spectrometry for  $\delta$  from ice cores
- Importance of vaporizer and calibration to isotope standards
- Aims in characterizing vaporizer and spectrometer performance.
- Challenge of CFA containing multiple instruments
- Application to RICE: optimized for our situation, but optimization tools applicable to other situations.

Removed from introduction

• Definition of  $\delta$  notation moved to beginning of Experimental section.

- Discussion of past performance of laser systems moved into the description of the laser systems in the Experimental section.
- We also removed the last sentence at the end of the introduction section, as this sentence gives the false impressions that establishing a CFA setup for ice cores that achieves δ -measurements with high temporal resolution is the only motivation behind this study, which, as already noted, has been achieved in earlier work (Gkinis et al., 2010; Maselli et al., 2013).

#### 3) Structure and conciseness of writing

The paper generally reads well. However several passages, especially the introduction and the results and discussion should be written in a more concise and better structured way (see specific comments below).

We believe the key opportunity to provide the enhanced clarity the reviewer requests involves improving the introduction (as described above) and addressing a number of points of clarity raised by the reviewers (below). These include removing Figure 11 and associated discussion, which reduces duplication.

#### 4) Abbreviations for different instruments and customised versions

In my opinion there are too many abbreviations for the different instruments and device versions used in this paper. LGR IWA, IWA, IWA-35EP, TIWA-45EP, WVISS system, custom 2013, 2014 custom setup, custom delta-CFA setup etc. It would help the reader a lot if a more consistent and simple naming system would be used.

We appreciate the reviewer raising this point about clarity.

To keep the naming more consistent we revised the text throughout and are now using the following names.

- Custom 2013 setup
- Custom 2014 setup
- WVISS setup
- UC setup University of Copenhagen setup

To increase the clarity we have also added a table (Table 1 in revised manuscript) that shows the properties and technical detail of the different setups.

Table AR1. Shows the technical detail and p	properties for the different setups.
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Setup name	Analyzer	Manufacturer	Technology	Vaporizer	Reference
Custom 2013	IWA-EP35	LGR	OA-ICOS	modified WVISS	This study
Custom 2014	TIWA-EP45	LGR	OA-ICOS	modified WVISS	This study
WVISS	TIWA-EP45	LGR	OA-ICOS	WVISS	
					(Gkinis et al.,
				Capillary and a	2010; 2011; Steig
UC	L2130-i	Picarro	CRDS	furnace, see ref.	et al., 2014)

#### Specific comments:

Abstract: p. 12082 L. 6 continuously analyse water samples, add water.

We agree and have added the word water to this sentence.

- Abstract: p. 12082 L. 15 The authors say « Another improvement... is that the modified setup has a reduced memory effect », is that really another improvement? To me this is not another result and simply comes along with the response time reduction.

We have used a cumulative log-normal distribution to describe the transitions between waters with known isotopic composition. This choice of function was introduced by Gkinis et al. (2010) and allows us to empirically fit data that shows true dispersion (represented by the cumulative normal (Gaussian) distribution, as reported in Gkinis et al. (2011), as well as a reservoir or memory effect, which would add an exponential response curve to that derived from dispersion. We empirically define a memory effect as causing an asymmetric tail in the last 5% of the step in  $\delta$  values, with an extended tail compared to our empirical fit. For the purposes of this study, this definition of a memory effect appears to be useful in that it clarifies memory effects that are problematic from a practical and analytical perspective.

We can clarify this further graphically. We distinguish between the response times, which we call the fast response (red curve fit in Fig. AR2), and memory effects, which we call the time it takes to reach the final isotopic value at the end of the transition (Fig. AR2). The reservoir effect due to the large volume of the vaporizer chamber in the WVISS is one example of a memory effect. It is identifiable, but not large.

We propose to address this issue by reordering the list in the abstract and introduction to group the response time and memory effects together as items (2) and (3) rather than (1) and (3). We then define the memory effect after discussing the response times, as follows:

"Alongside the response time, we define a memory effect as causing an asymmetric tail in the last 5% of the step in  $\delta$  values, with an extended tail compared to our empirical fit. Avoiding memory effects is desirable given the large range of  $\delta$  in ice cores and in the standards required for normalization."



Figure AR2. Comparison between the WVISS and the custom 2014 setup, the figure shows the differences in response time and memory effects between the setups.

- Abstract: p. 12082 L. 20 « For the WVISS setup... » and L22 « For the WVISS setup... ». The first one should be the 2014 modified setup.

Agreed this has now been changed.

- Abstract: p. 12082 L 24-26 this sentence has no verb.

This sentence has now been changed, i.e. " $\delta^{18}$ O of 0.30...." has been replaced by: " $\delta^{18}$ O are 0.30...."

- Abstract in general: to me the Allan deviations do not add any information in the abstract. The authors could mention that the stability is comparable in all the setups, shortly discuss the overall uncertainty and mention the longer response times but higher precision of the Picarro system.

A central contribution from this study is that we perform a detailed characterization of the custom setups (OA-ICOS), using stability and response time tests. We use stability and response time tests to compare the custom setups' performance with two other setups, the WVISS setup and the UC setup (CRDS). The detailed comparison and evaluation of performance of the different setups would not be feasible without the stability tests.

We therefore choose to keep the Allan variance as a central part of the abstract.

- Introduction: start with the broader context and a motivation for this study. The start in the present version of the paper is a bit technical and abrupt.

We appreciate this comment and we thank the reviewer for the opportunity to improve clarity. As noted earlier, we propose to fully revise the introduction.

- Introduction: p. 12083 L. 6 mention explicitly what i stands for

The i in the equation is not necessary and has been removed in the revised version of the manuscript.

- Introduction: p. 12084 L. 4 I do not understand what « replacing high resolution discrete measurements for delivering near-instrumental resolution » exactly means. Could you reformulate and explain the term « near-instrumental resolution ».

The end of the sentence "for delivering near-instrumental resolution" is referring to the fact that ice core records from high accumulation sites can provide proxy measurements with similar resolution to meteorological observational data from research stations data or from automatic weather stations (AWS). However, at other sites  $\delta$ -records are not directly comparable to high-resolution observational data due to physical processes (lower accumulation rate, diffusion, wind scour, etc.) that limit the resolution that can be derived from ice cores. The intent with this sentence was to emphasize that the CFA setup is much less labor-intensive than analyzing high-resolution discrete samples. We agree that this sentence was confusing, and it has been removed from the revised introduction.

- Introduction: p. 12084 L. 10-13 explain that this is the general aim of the project not of this publication.

We appreciate this comment, which has also been helpful in recognizing the need to restructure the introduction and clarify the purpose of the manuscript.

- Introduction: p. 12084 L. 21 this is a very incomplete list of publications please say (e.g. Johnson et al., 2011; Steen-Larsen et al., 2013)

Agreed this is not a complete list. This is also true for the ecology and hydrology example references. "e.g." has been added before these reference lists. We also took the opportunity to make the list more complete by adding an important reference in atmospheric sciences (Aemisegger et al., 2012).

- Introduction: p. 12084 L. 27 Sturm and Knohl, 2010 and not Strum

Thank you, this reference has now been updated at this location in the manuscript and at one more location where the same typo occurred (P. 12093 L. 19).

- Introduction: p. 12085 L. 2-3 in my opinion the references Rambo et al. 2011 and Tremoy et al. 2011 are not adequate here. These authors just used the commercial systems, and the mentioned values are not a result of their research. Rather cite the manufacturers directly.

We agree. These two references has now been removed.

- Introduction: p. 12085 L. 5 « During ice core CFA campaigns several analyses are performed simultaneously, with at times... »

We propose to clarify as follows: "The number of consecutive core sections that are stacked on top of one another and melted continuously without interruption for calibration can necessitate a compromise between the ideal time intervals of continuous melting for each analysis type."

- Introduction: p. 12085 L. 10 shouldn't it be « consecutive core sections » and not « consecutive cores »?

This has been corrected in the rewritten sentence (above).

- Introduction: p. 12085 L. 12 formulation unclear « between... and... » the and is missing

This has been corrected in the rewritten sentence (above).

- Introduction: p. 12085 L. 13 « with the following aims: (1) increase... (2)

Agreed. This sentence has been modified:

"Here, we present new experimental setups, and identify the following aims for the characterization of new and previously reported systems: (1) enable accurate calibration to several water standards, (2) increase the temporal resolution by reducing the response time, and (3) reduce memory effects."

- Introduction: p. 12085 L. 13 to me it is not a priori clear why you need goal (2). Shortly explain why you need to be able to measure several water standards in your setup.

We clarify that normalization traceable to two international standards, on the VSMOW/SLAP scale, is essentially a requirement for reporting  $\delta$  values in natural waters, with negligible changes since the VSMOW/SLAP scale was established in 1978 (Coplen, 1988, 1996; Gonfiantini, 1978). Normalization implies that at least two working standards must be run (both normalized against VSMOW/SLAP); measurements cannot be normalized based on a single standard. On IRMS systems, this was particularly an issue for  $\delta$ D because of instrument specific responses, but has been considered good practice for all isotope systems. Calibration slopes for OA-ICOS analyzers can differ from 1 (Aemisegger et al., 2012; Kurita et al., 2012), and have been shown to be instrument specific and to vary slightly over time (Kurita et al., 2012) due to instrumental drift. To correct for drift, our system is designed for calibrations performed at a time interval averaging 2.4 hours, as outlined in Section 3.3.

If one-point calibration were applied, the instrument specific calibration slopes cannot be calculated and accounted for, which makes the calibration of the raw measurement values less accurate. Additionally, a one-point calibration would also fail to enable both the detection and correction of small leaks of ambient air into the measurement system.

To clarify this issue within the manuscript, we have expanded the reporting of correction slopes as recommended by Kurita et al. (2012). We also inserted the following in the introductory paragraph: "With regard to the first aim, calibration to two standards allows us to properly normalize our results on the VSMOW/SLAP scale (Gonfiantini, 1978; Coplen, 1996)." In addition, we have added a column to Table 1 (Table AR2) which shows the purpose of the different water standards during calibration.

**Table AR2**  $\delta^{18}$ O and  $\delta$ D discrete-IWA measurements of water standards in relation to the VSMOW/SLAP scale and the different water standards role during calibration.

Standard	Ν	δ <sup>18</sup> Ο (‰)	±σ	δD (‰)	±σ	Calibration
WS 1	4	-10.84	0.099	-74.15	0.938	QA/QC
RICE						Slope and
MCL	30	-22.54	0.049	-175.02	0.193	normalization
ITASE	30	-37.39	0.046	-299.66	0.183	Slope

- Introduction: p. 12085 L. 15 « The response time mainly depends on the size of the evaporation chamber in of the vaporizer »

This sentence has been revised.

- Introduction: p. 12086 L.11 «is» innovative not «was»

This sentence has been removed.

- Introduction: p. 12086 L. 21 mention Gkinis, 2014 personal communication (or otherwise reference the publication in the references)

This statement referred to previously unpublished data that is part of this study. We have corrected this as noted in comments above by adding a new Table 1 that identifies the University of Copenhagen (UC) setup with published references (Gkinis et al., 2010, 2011; Steig et al., 2014) and refer to it here as:

"a similar  $\delta$ -CFA ice core setup, the University of Copenhagen (UC) setup."

- Introduction: p. 12086 L. 22 « presented in Sect. 3.3 (remove parentheses)

This has been corrected.

- Introduction: p. 12086 L. 26 replace «was» by «is»

This has been corrected.

- Experimental (is this section title really correct? Shouldn't it be Methods or Experimental methods?)

This section mainly describes experimental set up. 'Experimental' refers to development of an untested idea or technique, versus 'method' which refers to a usually established procedure for accomplishing or approaching something. Gkinis et al. (2011) used the section title "Experimental" in this journal for a section containing similar content. We therefore propose to leave the header for this section as is.

#### - Experimental p. 12087 L. 20 mention that T in TIWA stands for triple

The TIWA abbreviation is now explained on the line above this one where the acronym is used for the first time in the text (if you don't consider the header of this section).

#### - Experimental p. 12088 L. 24 replace complete by unaltered

We agree. This sentence has been changed.

- Experimental p. 12090 L.2 reference a sketch of the evaporation chamber

Agreed. A reference to Figure 1 has been added.

- Results and Discussion section 3.1: in my opinion section 3.1 is too long and prominent. What is the purpose of these tests? Is it to characterise the new setup or the laser instruments? It is of course necessary to shortly discuss the results of the very thorough stability tests that were performed by the authors but only with the aim of defining how frequently the measurement system should be calibrated and to show how the stability is affected by the changes made to the WVISS.

To me the results of the stability tests are not the innovative results of this paper and should be placed in the background, since the response time tests are the central aspect of the paper.

Furthermore, the stability section should be merged with the calibration section since information on instrument drift is gained from the Allan deviation analysis and thus the ideal calibration frequency can be deduced.

We reiterate that the purpose of this manuscript is to characterize the performance of the isotope measurement system in the wider context of a multi-instrument CFA campaign. The characterization we describe does identify the ideal calibration time, as the reviewer suggests. However, our stability analysis takes on much greater importance when another CFA measurement (methane in the case the RICE campaign) demands a maximum uninterrupted period. As a result, the stability analysis allows the maximum acceptable calibration time to be identified, rather than simply the ideal calibration time. Considering this purpose, we also note that the use of the Allan variance plots to describe the reproducibility of stability beyond the maximum precision appears to be novel in this field. It has correctly identified levels of instrumental drift that developed over time during the CFA campaign, and ideally should be reduced in future designs.

There are also other reasons as to why it is important to represent stability and response time as separate characteristics of a CFA system, and therefore we maintain sections for each. These center around our observation that the CFA isotope analysis systems reported to date all have different stability and response characteristics. Future campaigns can select systems with the characteristics that best meet the requirements of their study and the availability of funding to purchase and customize equipment. Where the opportunity to further customize equipment exists, these metrics enable separate focus on optimizing stability and response time.

Our response to this point is primarily the restructuring of the introduction to better explain the strong relevance of this material on instrument stability in the context of designing a multi-instrument CFA campaign and for comparison of performance of existing setups.

# - Results and Discussion Eq. 2: I don't think $\delta D$ and $\delta 180$ measurements are uncorrelated. If they are correlated you probably underestimate the error with this equation.

The reviewer is correct to identify that Eq. 2 assumes that the  $\delta D$  and  $\delta^{18}O$  measurements are uncorrelated, and this has been a useful point to examine. We are aware of and have reviewed the literature on the derivation of this formula, which can include a term to adjust for correlation. We clarify that the key assumption is that the  $\delta D$  and  $\delta^{18}O$  measurements are uncorrelated as a result of instrumental noise that we expected to occur in 15 s averages of measurements from analysis on a single water standard. We do not recommend thinking of the correlation as that which occurs while running analyzing an ice core, within which the two isotopes are correlated along the local meteoric water line. We have used our data from measurements on a single water standard (LHW) for extended time periods to check that this assumption is valid. By examining 15 instances of long runs on this single standard, we found only 3 instances where some aspect of measurements (with a 15 s moving average applied) showed correlation coefficients (R<sup>2</sup>) > 0.3 in  $\delta D$  and  $\delta^{18}O$  (due to drift).

To further investigate this approach, we have confirmed that it is valid by using our long-term stability tests to calculate Allan variance plots of d-excess, and using Eq. 2. Thus, in one approach we use the  $\delta^{18}$ O and  $\delta$ D co-varying raw-data measurement to generate a d-excess time series. In this method, the d-excess Allan deviation curves are derived using the d-excess time series (darker color in Figure AR3) resulting from the actual co-varying  $\delta^{18}$ O and  $\delta$ D; we refer to this estimate as "correlated". In the second approach (referred to as "uncorrelated") d-excess Allan deviation estimates are calculated from  $\sigma_{Allan, \ \delta 18O}$  and  $\sigma_{Allan, \ \delta 18O}$ , using Eq.2. The uncorrelated estimate curves from Eq.2 with (lighter color in Fig. AR3) are located above the raw-data d-excess measurement curve for both the 2013 and 2014 custom setups, which shows that the error estimate using Eq. 2 is conservative and that we are not underestimating the error using this equation. The offset (noise canceling effect) between the correlated and uncorrelated curves increase with longer integration times for the custom setups, about 0.05‰ at peak uncertainty (1.2 h) for the custom 2013 setup, but can be larger during certain runs (0.1‰) where more drift is present and the correlation is stronger.

To address this comment, we propose to insert the following sentence:

"We note that Eq. 2 assumes  $\delta^{18}$ O and  $\delta$ D are uncorrelated, which was verified to be true for the vast majority of our measurements on standards averaged at 15 s intervals."

Additionally, we propose to include Figure AR3 in the Supplementary Material to the revised manuscript.



**Figure AR3.** Allan deviation as a function of averaging time for d-excess from stability tests of the custom setups (2013 brown lines and 1014 setup blue lines), WVISS setup (green lines) and the UC setup (black lines). Darker colored lines indicates Allan devastation calculated from raw-data (correlated) and the lighter colored set of curves show error estimates calculated using equation 2 (uncorrelated).

- Results and Discussion Section 3.5: p. 12102 L 2 what is the « uncorrected bias in the CFA data »? I do not understand with sentence

We agree that this wording was unclear.

Figure 11 validates the calibration method and shows the slopes for the discrete and continuous data are similar. However, as an evaluation of the calibration method's performance is also provided in Sect. 3.5 and Figure 10 and 12, one could therefore argue that Figure 11 is redundant. We follow the reviewer's final suggestion (below) to remove Figure 11 from the revised version of the manuscript. As a consequence of removing Figure 11, the discussion associated with the figure was removed, which includes the unclear material.

- Conclusions: remove the reference to the figures in the conclusions.

We agree. This sentence has been changed.

- Conclusions: p. 12102 L. 17 «The» should be «This».

Agreed. Corrected.

- Conclusions: p. 12102 L. 18 « Direct measurements of water vapour of ambient atmosphere can also be performed ». This could be done before and without your customised setup, be more explicit, here. Your system could indeed be useful for the calibration of ambient air measurements, since it allows for automated switching between several liquid water standards, providing the basis for an easier and better calibration framework.

We thank the reviewer for this useful suggestion.

#### Text added to the revised manuscript:

"The custom setups can be applied to field of atmospheric science, enabling rapid, automated and robust calibration cycles using multiple water standards (two-point calibration). Compared to the one standard setup that the unaltered WVISS is fitted with by the manufacturer. Reducing the length of calibration, while including multiple standards should maximize data quality while minimizing the loss of atmospheric measurements during calibration cycles. Additionally, the setup has proven to be a robust system that can run continuously for months and operate unattended for days."

#### Figures: are Figs. 4-6 necessary or would a summarising table with the key figures be sufficient?

In response to the comment regarding the Results and Discussion (Section 3.1) above we argue for keeping stability tests as a central part of the paper, and the same arguments are valid for keeping Figure 4-5. Please see the response to General comment 2. However, as  $\delta^{17}$ O has a smaller role in the manuscript the  $\delta^{17}$ O Allan deviation figure (Fig. 6) was moved to the Supplementary Material.

#### To me Figure 11 is not helpful and could be removed.

We agree. Figure 11 provides confirmation that the calibration method works well, as the slopes for the discrete and continuous data are similar. However, evaluation of the calibration method's performance is also provided in Figure 10 and 12. Therefore, Figure 11 is somewhat redundant and has been removed in the revised version of the manuscript.

## **Response to Reviewer 2**

This paper outlines the continuous analysis technique used to measure water stable isotopes for an Antarctic ice core with an Off-Axis Integrated Cavity Output Spectrometer attached to a modified Water Vapor Isotopic Standard source Calibration unit. Modifications included the addition of a customized furnace and evaporation chamber inside the calibration unit which lead to reduced instrument response times and memory effects.

The paper discusses in detail the differences in precision between 4 different systems. The reduction in evaporation chamber volume in addition to the shortening of sample lines significantly reduced the system response time; which is important when sampling ice cores with high frequency changes in isotopic values along the length of the cores. The improved sample response time was however, at the expense of instrumental precision which was affected by an increased amount of signal drift. The paper is written in a comprehensive manner and provides significant detail about system performance which is helpful for those who which to setup their own water isotope system, whilst giving insight into the parts of the system which are potentially detrimental to factors such as system response, accuracy and precision.

Specific Comments.

p12082 L17. This paragraph is confusing. It is not always clear as to which modified

WVISS unit the authors are referring when quoting the Allan precision values. When the 'modified WVISS unit' is referred to, is this the 2013 or the 2014 version or both?

Perhaps it would be clearer if more distinct names were used for the different setups.

Also, it is difficult to follow when they are switching from talking about precision in one instrument to Allan value in another (line 19-21).

We appreciate the reviewer raising this point about clarity.

This comment is similar to the General comment 4 from Reviewer 1. To avoid redundancy we refer to our response to Reviewer 1, and specifically (1) more standardized names for the different experimental setups, and (2) the introduction of Table 1 that clearly defines the name and features of each setup.

P12086 L26. The objective of the study was stated as the establishment of a high temporal resolution  $\delta$ -CFA setup. This has already been achieved in other studies (such as Maselli et al. 2013), so this study is left to focus specifically on the application of a LGR-IWA spectrometer and modification of an established calibration unit to a high resolution  $\delta$ -CFA setup.

This comment is similar to the General comment 2 from Reviewer 1, and therefore was useful in identifying the need to improve clarity. We refer to our response to Reviewer 1, and the rationale for our revisions to the introduction to better clarify the purpose of the manuscript. We note again the focus on the development of metrics to characterize the performance of CFA isotope measurement systems and optimize decisions within the tradeoffs of a multi-instrument CFA campaign. Additionally, we would like to emphasize that the contribution from the comparison tests between different setups

that provides a detailed characterization and comparison between different water stable isotope CFA setups that are using the new generation OA-ICOS and CRDS spectroscopy techniques.

P12091 L3. "accomplished by a step in PFA tubing sizes," Unclear what the author is trying to say – how is a step (up or down) used in the setup?

To clarify this section we have changed this sentence and added a follow-up sentence to describe the open split.

#### Suggested revision:

"Preliminary results from the 2014 setup are reported here, and differ only in the vaporizer construction, and in delivery of mixed vapor to the IWA directly through an open split. The 2014 open split is a simple step down in PFA tubing sizes, rather than within the WVISS plumbing and exhaust system: 1/4" O.D. tubing is connected to the IWA, and inserted 5 cm and centered within the larger size tubing 1/2" O.D. carrying flow from the vaporizer."

P12092 L1. Why remove the gas from the sample line with DB1, and then immediately add the air again? Will part of the sample stream leaving DB1 be used for other analytical systems that require a degassed water sample? Please explain.

#### To clarify this we have added the following text:

"The old air entrapped in the ice is first separated from the water sample by a debubbler (DB1) and led to spectroscopic analyzers to measure  $CH_4$  and  $\delta^{18}O$  in the air. After this step air bubbles are introduced to the keep the water sample flow segmented. To keep the water vapor mixing ratio generated from the evaporation unit constant the introduced bubbles are removed in DB2 before the evaporation unit."

P12095. Do you have an explanation for why the modified setup experiences more drift? Since the ice core records are primarily focused on the larger frequency changes

(> annual) in the isotope signal should minimizing drift (which would affect the accuracy of the results) be a priority over precision of measurement? Perhaps the author should make some comment as to whether higher temporal resolution or precision or accuracy is of the greatest importance when analyzing ice core samples – thus indicating which system (including the Copenhagen setup) is the most appropriate to use for ice core analysis.

The reviewer asks an interesting question, but one where we feel there is no single answer. Ice cores being collected today vary considerably in their nature, and with depth. Measurement techniques can also vary from multi-instrument CFA campaigns to single-instrument CFA to discrete measurements.

A highly responsive system that can capture high-resolution seasonal signals in ice cores is advantageous when measuring a core from a high-accumulation coastal site or when the aim is to increase the depth by which annual peaks can be resolved. On the other hand, a more stable system can be preferable if measurements are performed on cores from low accumulation sites, where the annual signal is lost at a shallow depth and/or the aim of the project is to determine  $\delta$ -changes on longer time scales.

We hypothesize that a more responsive system can often become less stable, when optimized for responsiveness by reducing evaporation chamber volume or increasing the amount of dry air flow. This

could partially be due that it can be harder to control and keep environmental parameters constant in a more responsive system. For example, if the dry air flow is increased to reduce the response time, the system can become more sensitive to ambient temperature changes (as it will be harder to preheat a larger volume air) and can induce drift. We therefore emphasize that it is important to test both the stability and responsiveness of a system and then optimize for the purpose. However, another way to obtain a more responsive system would be to minimize the amount of dead volume and mixing volumes in the water sample lines, which would not necessarily result in a less stable system. The dead volume in the sample lines for the custom setups was not minimized due to lab space limitations and due to the fact that the  $\delta$ -CFA system shared sample lines with other CFA analytical equipment.

Both the custom setups and the UC setup are able to provide high accuracy and precision  $\delta$ measurements. The custom 2013 setup has an accuracy of (mean ± 1 $\sigma$ ) -0.07 ± 0.11‰ and -0.51 ± 0.75‰ for  $\delta^{18}$ O and  $\delta$ D, respectively. An important advantage with a more stable system (e.g. the UC setup) is that it requires fewer calibrations to achieve high accuracy and precision  $\delta$ -measurements, which can be advantageous when the setup is integrated with other analytical equipment which have large memory effects (e.g. CH<sub>4</sub> spectroscopy) and where frequent interruption for calibration is undesirable. When analyzing for secondary parameters, such as d-excess and <sup>17</sup>O-excess, a system that is optimized for stability, like the UC setup, has an advantage over the custom and WVISS setups (Fig. AR3) which to a larger extent is influenced by instrumental drift (with  $\delta^{18}$ O being more drift sensitive than  $\delta$ D). The susceptibility of OA-ICOS analyzers to instrumental drift for  $\delta^{18}$ O has also been shown by Aemisegger et al. (2012).

As a direct outcome from the question raised in here, we propose to update the manuscript d-excess discussion (AMTD P. 12094). A short paragraph about the advantage of having a system that is optimized for stability when analyzing for secondary parameters (d-excess and <sup>17</sup>O-excess) will be added. The d-excess Allan deviation plot (Fig. AR3) will be provided as Supplementary Material and referenced in this discussion. Additionally, the discussion regarding a potential trade-off between stability and responsiveness (AMTD P. 12097 L6) will be updated based on the more in-depth discussion here.

We also do refer again to our revisions to the introduction, which attempt to include these considerations of the need to characterize the performance of isotope CFA equipment so it can be matched to the needs of the ice core and measurement campaign.

#### Technical Corrections.

P12086 L16. Where previously the authors referred to the 'modified' unit it is now relabeled as the 'custom' unit. Consistent labeling will enhance clarity.

This comment is similar to the General comment 4 from Reviewer 1. We therefore refer to our response to Reviewer 1.

P12090 L2. "Glass was chosen to permit to form the desired shape". This sentence is unclear.

We agree. This sentence has been changed and it now reads: "Glass was chosen as material for the evaporation chamber because it can be molded when heated to form the precise desired shape of the chamber."

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