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Comment

Interactive comment on “Calibrated high-precision $^{17}\text{O}_{\text{excess}}$ measurements using laser-current tuned cavity ring-down spectroscopy” by E. J. Steig et al.

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This manuscript describes the use of a new instrument to measure stable isotopes in liquid water and water vapor, including the ^{17}O isotope. This is a timely and interesting topic which has seen much recent work. I, among many others I am sure, am looking forward to seeing what new questions are unlocked by the ability to more easily measure $^{17}\text{O}_{\text{excess}}$. The authors' careful treatments of calibration and noise contributions are applauded. I have several specific concerns and questions regarding the manuscript:

General comments:

First, Figure 3 shows Allan deviation plots, with the minimum σ_{Allan} for $^{17}\text{O}_{\text{excess}}$
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of ~ 8 per meg, indicating that in the limit of long-term averaging, the best precision achievable by the instrument is 8 per meg. However, the reported standard error is lower than 8 per meg for every 17O -excess measurement in Table 2 and Figure 6 (as well as the Results section). The use of the standard error is statistically incorrect if, in fact, averaging of measurements does not reduce the noise associated with those measurements by the square root of the number of measurements averaged. The Allan deviation plot presented in Figure 3 shows that the data indeed do not average statistically below 8 per meg. The uncertainty reported with all measurements should reflect the actual limit of the instrumental averaging as demonstrated in Figure 3.

Second, it is reported that a precision of 8 per meg for 17O -excess can be made in ~ 30 minutes. These precision numbers are indeed impressive, but a discussion of the accuracy of these measurements is also warranted. What is the accuracy? How are these measurements standardized? How much time is required for standardization of these measurements to reach said accuracy? How are instrumental memory effects accounted for?

Similarly, Figure 4 lists precisions for repeated liquid injections. Again, what is the accuracy? Since memory effects are generally far from negligible, the repeat precision (measured from repeated measurements of the same sample) is frequently not the same as the precision of measurements of unknown samples. Specifically, how long does it take (including standardization and accounting for memory effects) to measure the calibrated values presented in Table 2 and Figure 6? What precision and accuracy are obtained?

Are the experimental uncertainties associated with the $\delta 2\text{H}$, $\delta 18\text{O}$, and $\delta 17\text{O}$ values for the VSMOW2 and SLAP2 reference waters incorporated into the reported uncertainties for the measurements as reported vs. VSMOW-SLAP? Table 2 lists this for PW and VW calibration, but not for VSMOW2 and SLAP2 calibration.

Specific comments/questions

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P10209 line 3: It is not clear how the 17O-excess of GISP comparison between ICOS, CRDS, and IRMS is calculated or why the CRDS value is averaged with IRMS values. A more meaningful comparison may be afforded by averaging only those measurements taken with the same technology. For IRMS and assuming that “current” is in the last decade, from Schoenemann et al.: Barkan and Luz = 11 per meg and Kusakabe and Matsuhisa = 41 per meg. From Berman et al.: LSCE = 32 per meg and JHU = 25 per meg. The current manuscript lists an IRMS value of 28 per meg. These five IRMS laboratories give an average 17O-excess of GISP of 27 ± 11 (1σ) per meg. A weighted average may be more appropriate, but I do not have all of the uncertainties needed to calculate one. CRDS measurements are reported as 27 ± 4 per meg (see comment/question above about precision) and ICOS reports (Berman et al.) 23 ± 2 per meg. That these measurements all agree to well within the uncertainties is very exciting indeed and will certainly aid in the application of measurements of 17O-excess to hydrological and other applications.

P10209 line 14: ... σ_{18} is the precision of $\ln(\delta^{18}\text{O}+1)$ Also, in this paragraph you have neglected to reference Figure 7, where the data is displayed.

Finally, the distinction between “laser-current tuned CRDS” and “wavelength-scanned CRDS” was a bit unclear. It appears that the latter uses laser-current scanning as well and that the difference lies not in the scanning but in the way that the frequency axis of the spectrum is determined. If this is correct, it might help readers to be more specific about this difference.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 10191, 2013.

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