Atmospheric Measurement Techniques Discussions

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

Anonymous Referee #3

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General comments

The manuscript describes the coupling of an existing continuous ice-core melting head to a commercial (Picarro) laser-based water vapor isotope ratio analyzer. An essential part of the system is the custom-built flash evaporator (previously published: Gkinis et al., 2010) that enables the water from the melting head to be delivered as vapor to the analyzer in a manner that assures the integrity of the isotope ratio signals. The paper is clearly within the scope of AMT and should be of interest to all those researchers that have an interest in paleo-climate reconstructions based on data derived from ice-cores. The research is generally well executed and presented. As should have been expected from the Johnson group, which has a reputation to live up to as it comes to

dispersion and diffusion effects in ice-core analyses, a lot of attention is paid to the deconvolution of the final isotope records with the instrumental function, in order to account for smoothing of the isotope signals by the dispersion of the sample between the melting of the ice-core in the melting head and its arrival as water vapor in the laser spectrometer gas cell.

However, I agree strongly with referee #2 that a serious shortcoming of the paper is that no attempt was made to introduce the isotope step function at the melting head. If two synthetic ice-cores would have been sandwiched together, with the two parts composed of two different waters with well-known and different isotopic composition, the effect of sample dispersion could have been assessed directly. Very importantly, such a measurement would also have allowed assessing both precision (repeatability) and accuracy (trueness) unambiguously, of the entire system, including the melting head, without resorting to a convoluted statistical analysis of real time-series data. At the very least, the paper should discuss why such an obvious measurement was not carried out.

As pointed out by referee #1, the precision and accuracy depend on both averaging time (measurement band width) and humidity (personally, in this case, I prefer to speak of the water concentration or amount of water inside the spectrometer gas cell in order to avoid confusion with atmospheric humidity, as in atmospheric water vapor measurements). However, in this particular case, the deviation from 20,000 ppmv of the water mixing ratio inside the spectrometer is supposedly small enough that the precision of the spectrometer is not noticeably affected. It may be helpful to specify in the paper to what degree the water mixing ratio is stable. Clearly, the observed variations in the mixing ratio are still large enough that the measured isotope ratios do deviate significantly from their true values (accuracy). The correction factors (alpha in Eq. 1) are in general different between different instruments and can also be expected to change over time with environmental conditions, a realignment of the spectrometer optics, etc. To me, it is therefore not sufficient to see that the values determined in 2010 are given

in the paper, but I would like to see that these factors have been re-determined for this particular study (and hopefully, but not necessarily, have been found to agree within their uncertainty with the previous values). Or is this what the authors are actually doing in practice, but is their account of the experimental procedure (page 4080, lines 24-26) not sufficiently clear? In any case, they should mention what exactly is meant with "frequent VSMOW calibrations".

I believe the integral of Eq. 2, that is the integral of the power spectral density over all frequencies, equals the total power in the time series signal. Using Parceval's theorem, this can be shown to equal the zero-delay autocorrelation function, and thus the square of the root-mean-square-deviation. The latter only equals the square of the standard deviation if the mean of the time series is equal to zero. The paper does not define what measurements exactly are taken to constitute the time series. Also, considering only the flat high-frequency value of the power spectral density, instead of performing the integration over the full power spectral density function of Fig. 4, as would be required to obtain the standard deviation as defined in Eq. 2, effectively removes all low-frequency contributions (the largest part) to the estimator of the standard deviation. This may be a useful number to determine, but inexplicitly assumes that all lower frequency components are true signal, whereas it is very much conceivable that they are caused by instrumental artifacts, such as water flow instabilities (e.g., due to gas bubble formation, as mentioned elsewhere in the paper). In other words, the standard deviations mentioned in the text are absolute lower limits. It is more than likely that a continuous measurement on isotopically uniform synthetic ice will yield a higher standard deviation than the one reported here, even after averaging over the optimal averaging time (which will need to be determined through an Allan variance analysis).

Specific comments

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 mentioning Picarro here.

p4074, line 10: VSMOW-SLAP scale.

p4074, line 12: replace humidity by water volume mixing ratio or concentration or amount (see comment above).

p4074, line 25: Was the measurements performed at NEEM, as suggested here, or on ice-core material carried back to Copenhagen?

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.

p4076, line 5: replace "consumables and standard and carrier gases" by "consumables, isotope standards, and carrier gases".

p4076, line 7: processing.

p4076, line 12: Kerstel, 2004.

p4076, line 18: over, e.g., hot uranium. Note that zinc and chromium have also been used for this purpose.

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

p4078, line 24: purchased from Picarro.

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

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.

This should be mentioned in the text.

p4080, line 18: I assume that the unit is ppmv (per volume, not mass).

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.

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

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)?

p4089, Eq. 22: The numerical value equals 0.00048 or 0.48 per mil, not 0.48.