

Calibrated high-precision $^{17}\text{O}_{\text{excess}}$ measurements using cavity ring-down spectroscopy with laser-current-tuned cavity resonance

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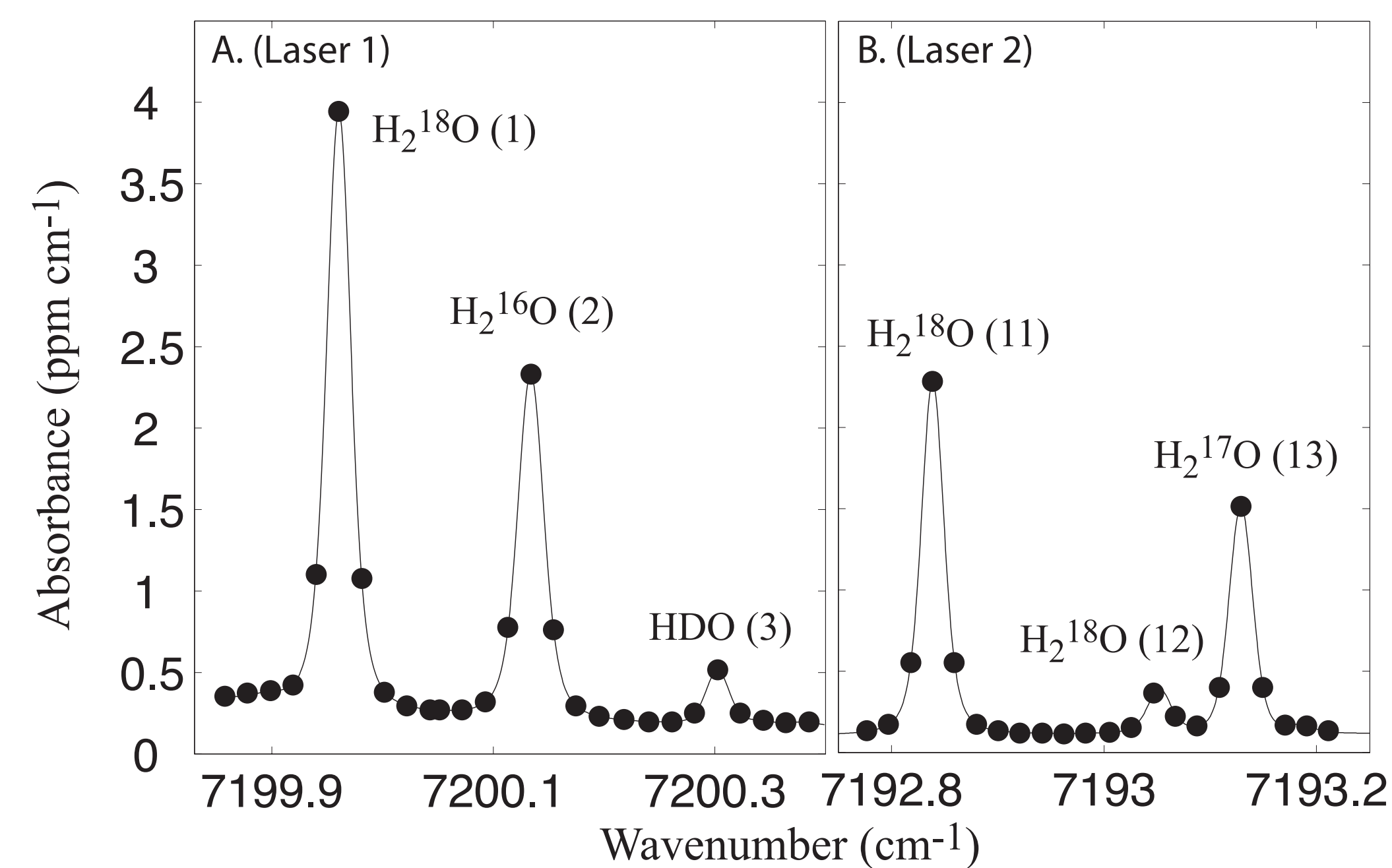
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Abstract

High precision analysis of the $^{17}\text{O}/^{16}\text{O}$ isotope ratio in water and water vapor is of interest in hydrological, paleoclimate, and atmospheric science applications. Of specific interest is the parameter $^{17}\text{O}_{\text{excess}}$, a measure of the deviation from a linear relationship between $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios. Conventional analyses of $^{17}\text{O}_{\text{excess}}$ are obtained by fluorination of H_2O to O_2 that is analyzed by dual-inlet isotope ratio mass spectrometry (IRMS). We describe a new laser spectroscopy instrument for high-precision $^{17}\text{O}_{\text{excess}}$ measurements. The new instrument uses cavity ring-down spectroscopy (CRDS) with laser-current-tuned cavity resonance to achieve reduced measurement drift compared with previous-generation instruments. Liquid water and water vapor samples can be analyzed with better than 8 per meg precision for $^{17}\text{O}_{\text{excess}}$ using integration times of less than 30 min. Calibration with respect to accepted water standards demonstrates that both the precision and the accuracy are competitive with conventional IRMS methods. The new instrument 20 also achieves simultaneous analysis of $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and δD with precision of $< 0.03\text{‰}$, $< 0.02\text{‰}$ and $< 0.2\text{‰}$, based on repeated calibrated measurements. This work is published in *Atmos. Meas. Tech. Discuss.*, 6, 10191-10229, 2013, doi:10.5194/amtd-6-10191-2013 and under review for the journal *Atmospheric Measurement Techniques (AMT)*.

Spectroscopy



Measured absorption spectrum for water isotopologues in the two wavenumber regions used by the L2140i prototype (L2130-i-C) and L2140-i CRDS analyzers. Filled circles: measured absorption for H_2O vapor 20 mmol mol^{-1} in dry air carrier, 66.7 hPa cavity pressure. The isotopologue associated with each peak is noted, with nominal peak numbers for reference (1–3 on laser 1, 11–13 on laser 2). Lines: least-squares fit to the data using Galatry profiles as discussed in the Steig et al. (2014).

Accepted Values of Reference Waters

	$^{17}\text{O}_{\text{excess}}$ (per meg)	$\delta^{18}\text{O}$ (‰)	$\delta^{17}\text{O}^a$ (‰)	δD (‰)	n
GISP ^b	28 ± 2	-24.80 ± 0.02	-13.1337	-189.67 ± 0.20	20
VW	3 ± 3	-56.61 ± 0.02	-30.3142	-438.79 ± 0.35	10
WW	27 ± 2	-33.82 ± 0.03	-17.9700	-268.30 ± 0.31	36
SW	33 ± 2	-10.55 ± 0.02	-5.5568	-75.63 ± 0.17	18
PW	30 ± 2	-6.88 ± 0.02	-3.6140	-42.12 ± 0.18	17
KD ^c	-0.8 ± 4	0.43 ± 0.01	0.2260	1.33 ± 0.13	5

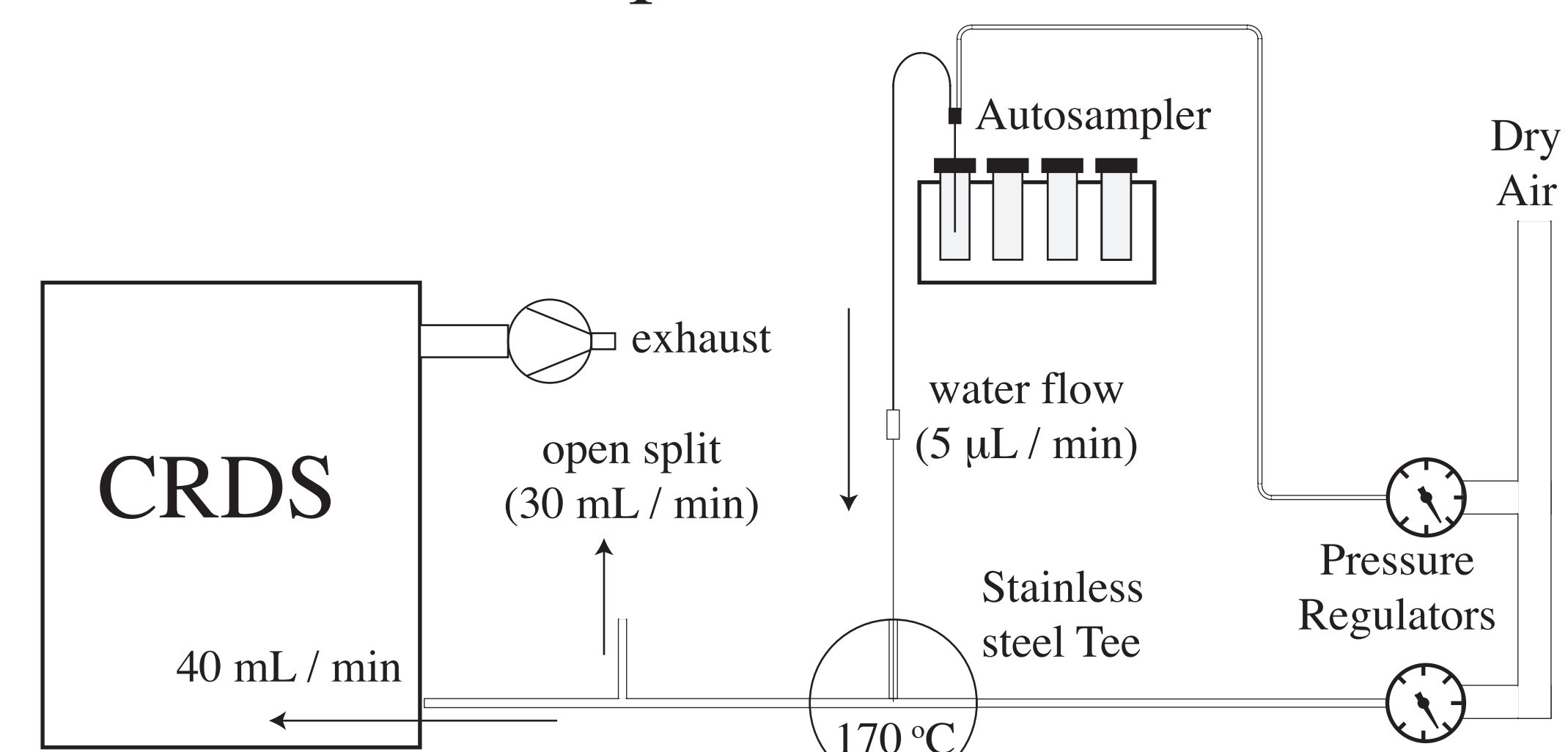
^a $\delta^{17}\text{O}$ calculated from $\delta^{18}\text{O}$ and $^{17}\text{O}_{\text{excess}}$. See Schoenemann et al. (2013).

^b CIAAW values for GISP are $\delta\text{D} = -189.73\text{‰}$ and $\delta^{18}\text{O} = -24.78\text{‰}$ (Gonfiantini et al., 1995).

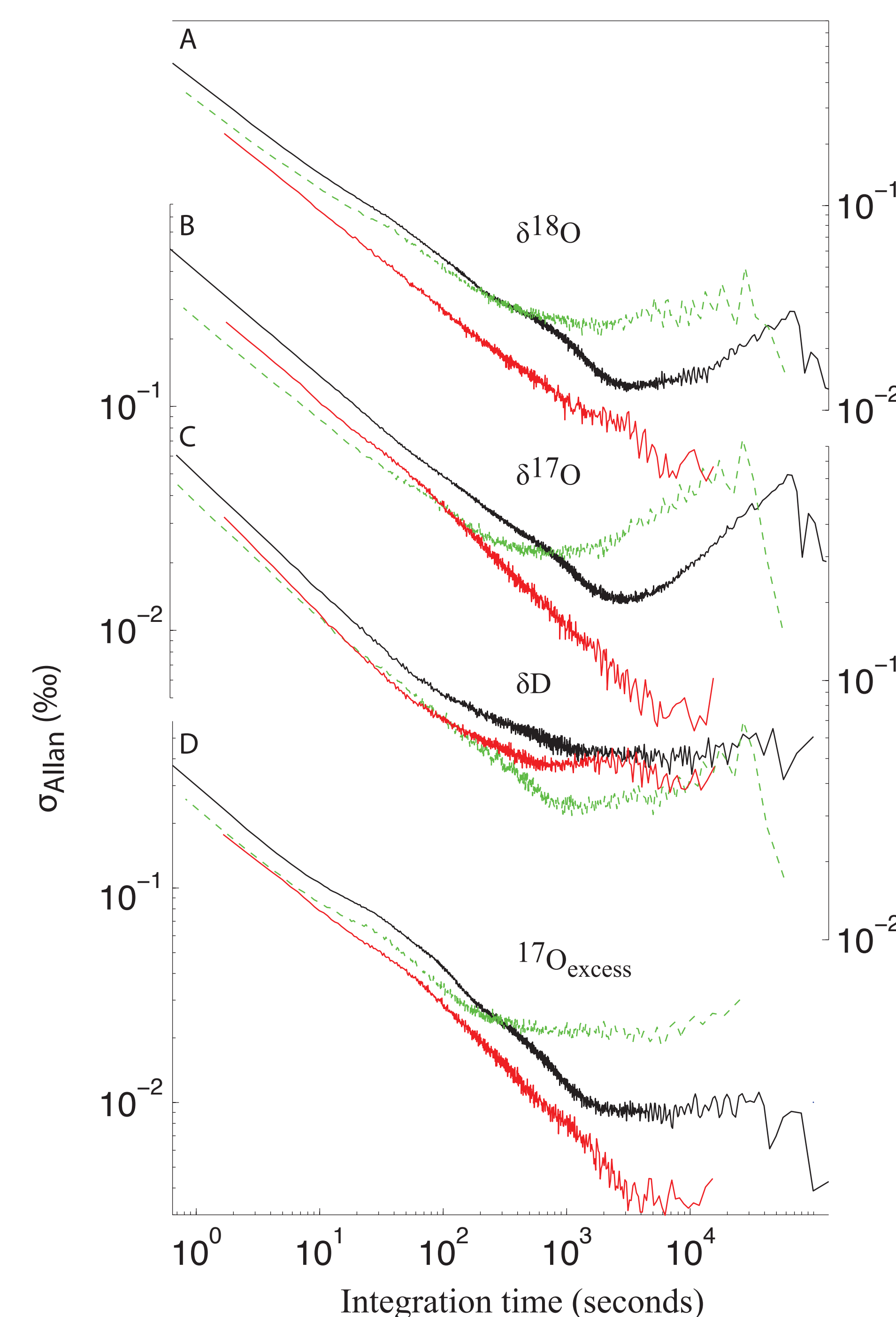
^c Provisional measurement. Long-term average data for KD (Kona Deep) are not yet available.

VSMOW-SLAP normalized isotopic ratios of reference waters analyzed at the University of Washington "Δ-IsoLab". $^{17}\text{O}_{\text{excess}}$ values are from long-term average IRMS measurements, updated from Schoenemann et al. (2013) to reflect the inclusion of additional data. $\delta^{18}\text{O}$ and δD values are from long term average laser spectroscopy measurements. $\delta^{17}\text{O}$ values are calculated from $^{17}\text{O}_{\text{excess}}$ and $\delta^{18}\text{O}$ (Eq. 5 Steig et al. 2014). Precision (\pm) is the standard error of the mean.

Continuous Vaporization

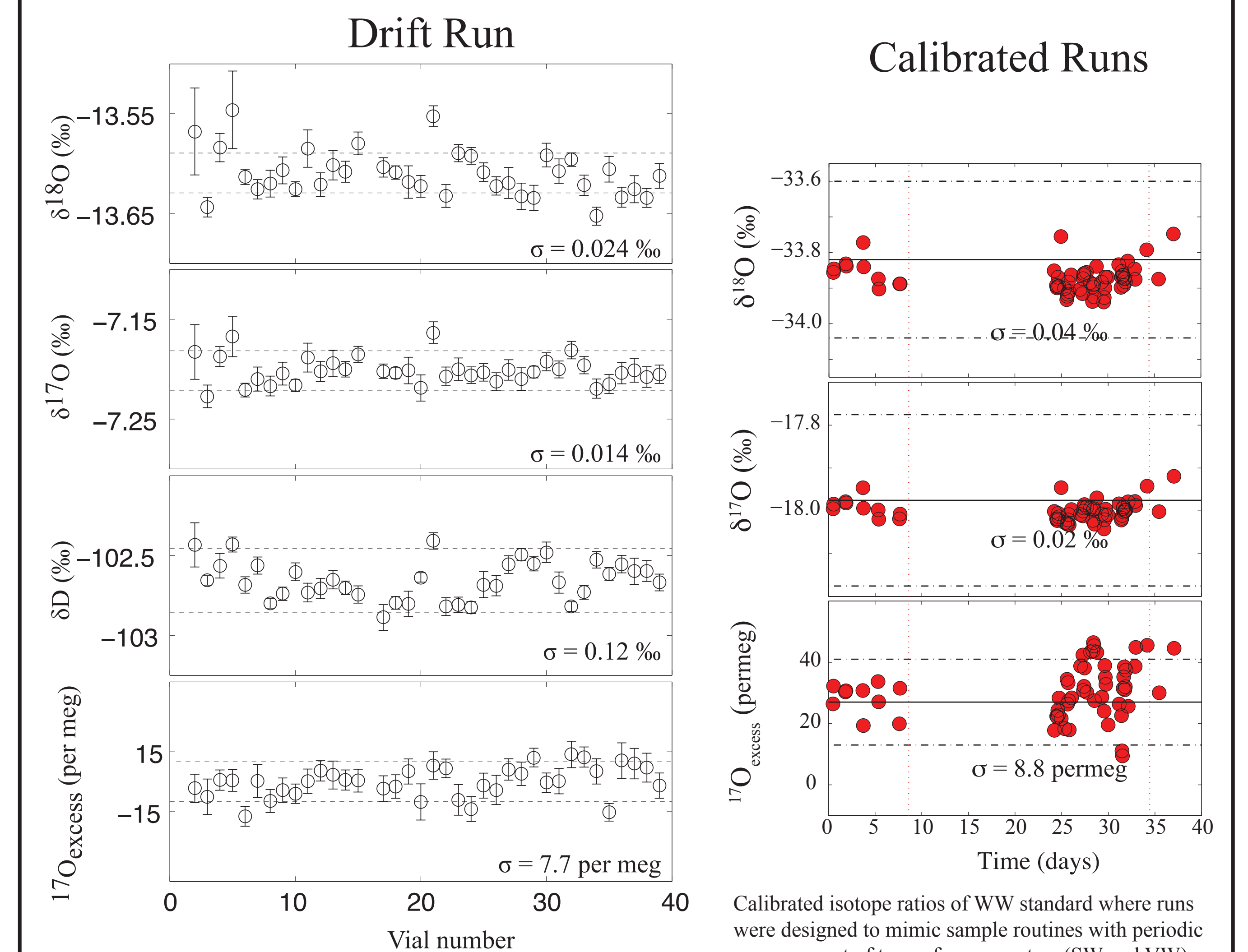


Schematic of custom vaporizer design used for isotope ratio measurements over long integration times. Double lines denote 1/16 inch and 1/32 inch stainless steel tubing (outside diameter). Single lines denote fused-silica capillary (0.3 mm inside diameter) exiting the vials, reduced to 0.1 mm where the capillary enters the vaporizer.



Comparison of Allan deviations for water isotope ratios with the L2140-i prototype (L2130-i-C) using conventional wavelength monitor and spectral peak amplitude (green dashed lines), and with the L2140-i using laser-current-tuned cavity resonance and integrated absorption (solid black lines). Green and black lines were generated using the above Continuous Vaporizer while the red lines are from a vaporizer at Centre for Ice and Climate, Niels Bohr Institute as in Gkinis et al (2010). (A) $\delta^{18}\text{O}$, (B) $\delta^{17}\text{O}$, (C) δD , (D) $^{17}\text{O}_{\text{excess}}$.

Discrete Vaporization



Isotope ratios from repeated measurements of 2 mL vials of identical water, using integrated absorption on the L2140-i. Each dot represents the average of ten 1.8 μL injections from one vial; the vertical error bars show the standard error of the $n = 10$ individual injections. The standard deviation of all vial means (σ) is given in each panel. Horizontal dashed lines are shown for reference at $\pm 0.02\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, at $\pm 0.2\text{‰}$ for δD , and at ± 10 per meg for $^{17}\text{O}_{\text{excess}}$. The experiment shown took about 60 h. No drift corrections or other post-measurement adjustments were made to the raw data.

	IRMS $^{17}\text{O}_{\text{excess}}$ (per meg)	CRDS $^{17}\text{O}_{\text{excess}}$ (per meg)	$\delta^{18}\text{O}$ (‰)	$\delta^{17}\text{O}$ (‰)	δD (‰)	n
GISP ^a	28 ± 2	27 ± 4	-24.77 ± 0.02	-13.13 ± 0.01	-190.19 ± 0.14	6
VW ^a	3 ± 3	-3 ± 3	-56.50 ± 0.03	-30.24 ± 0.02	-438.19 ± 0.35	6
WW ^a	27 ± 2	27 ± 4	-33.90 ± 0.03	-18.02 ± 0.02	-268.87 ± 0.40	6
WW ^b	27 ± 2	27 ± 2	-33.98 ± 0.03	-18.06 ± 0.03	-269.29 ± 0.26	6
SW ^b	33 ± 2	34 ± 4	-10.64 ± 0.04	-5.60 ± 0.03	-76.05 ± 0.24	6
KD ^a	-0.8 ± 4	-1.6 ± 3	0.43 ± 0.01	0.23 ± 0.01	1.33 ± 0.13	6
KD ^b	-0.8 ± 4	-1.6 ± 4	0.50 ± 0.03	0.26 ± 0.03	1.71 ± 0.22	6

^a VSMOW2 and SLAP2 calibration.

^b PW and VW calibration. Errors take into account uncertainty in calibration points.

VSMOW-SLAP normalized $^{17}\text{O}_{\text{excess}}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and δD values for reference waters determined by CRDS using (a) IAEA standards VSMOW2 and SLAP2 as calibration points and (b) using University of Washington standards PW and VW as calibration points. IRMS-measured $^{17}\text{O}_{\text{excess}}$ values are shown for comparison. Precision (\pm) is the standard error of the mean. n=sample size.

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