S1. Experimental Data

Table S1. Summary of experimental conditions. δD and $\delta^{18}O$ and [H_2O_v] were calculated using the average of measurements between 1800-2000 seconds after switching. Deuterium-excess was calculated using the average of measurements between 3400-3600s after switching because it took d-excess longer to equilibrate. The row "WVISS mV" gives the WVISS voltage setting used to achieve the WVISS [H_2O_v] in that experiment.

Tubing Type	Teflon (PTFE) long		Copper		HDPE		PFA		FEP (Thin-walled)		FEP (Thick-walled)		Thin-walled short PTFE	Thick-walled short PTFE	No filter long PTFE	No filter short PTFE
Tubing Information	Advanced Technology Products $^3/_{16}$ inch ID x $^1/_4$ inch OD 100 foot length (PTFE-0304X100)		McMaster-Carr cleaned and capped $^1/_8$ inch Tube Size, $^1/_4$ inch OD, 0.03 inch Wall Thickness (5174K21)		McMaster-Carr High-Pressure/ Vacuum Polyethylene Tubing $^1/_8$ inch ID, $^1/_4$ inch OD, $^1/_{16}$ inch Wall Thickness, White, 100' (50375K41)		Fluorotherm $^3/_{16}$ inch ID x $^1/_4$ inch OD 100 foot length (F015202)		Altoflo LLC $^3/_{16}$ inch ID x $^1/_4$ inch OD 100 foot length (200-0250-030-0C)		McMaster-Carr FEP clear tubing for chemicals $^1/_8$ inch ID, $^1/_4$ inch OD 100 foot' (2129T16)		Advanced Technology Products (PTFE-0304X100)	Advanced Technology Products $^1/_8$ inch ID, $^1/_4$ inch OD, $^1/_{16}$ inch Wall Thickness, (PTFE-0204X100)	Advanced Technology Products (PTFE-0304X100)	Advanced Technology Products (PTFE-0304X100)
Date ran	07 May 2022 to 08 May 2022	08 May 2022 to 09 May 2022	05 May 2022 to 06 May 2022	06 May 2022 to 07 May 2022	10 May 2022 to 11 May 2022	11 May 2022 to 12 May 2022	09 May 2022	10 May 2022	22 May 2022 to 23 May 2022	15 May 2022 to 16 May 2022	16 May 2022 to 17 May 2022	17 May 2022 to 18 May 2022	26 May 2022 to 27 May 2022	04 May 2022 to 05 May 2022	23 May 2022 to 24 May 2022	27 May 2022
Temperature (℃)	~20 ℃	~60 ℃	~20 ℃	~60 ℃	~20 ℃	~60 ℃	~20 ℃	~60 ℃	~20 ℃	~60 ℃	~20 ℃	~60 ℃	~20 ℃	~20 ℃	~20 ℃	~20 ℃
Analyzer air flow speed (L min^{-1})	~0.1	~0.1	~0.1	~0.1	~0.1	~0.1	~0.1	~0.1	~0.1	~0.1	~0.1	~0.1	~0.1	~0.1	~0.1	~0.1
Replicates (# of enriched-to-depleted δ switches)	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Run Length (sec)	3825	3825	3825	3825	3825	3825	3825	3825	3825	3825	3825	3825	3825	3825	3825	3825
WVISS δD vapor (‰)	-33.26	-34.37	-33.14	-33.58	-36.80	-38.97	-32.91	-32.45	-34.13	-34.31	-36.49	-37.47	-31.17	-31.63	-31.17	-30.94
WVISS $\delta^{18}O$ vapor (‰)	-4.186	-4.014	-4.172	-3.345	-3.178	-3.157	-3.326	-2.783	-3.899	-4.565	-4.283	-3.456	-2.863	-3.882	-3.225	-4.310
WVISS D-excess vapor (‰)	1.234	-1.418	0.952	-6.459	-8.934	-10.706	-6.286	-8.731	-1.355	3.069	-1.551	-6.839	-8.278	1.386	-2.055	5.121
WVISS mV	3.78	3.9	3.9	3.9	4	4.2	3.9	3.9	4.05	3.97	4	4	3.85	3.6	4.04	3.95
WVISS H_2O average (ppm)	9149	8866	8859	8835	8745	8569	8825	9000	8723	8827	8721	8811	9294	9472	8826	9274
DPG δD vapor (‰)	-171.16	-165.77	-171.58	-168.36	-171.37	-168.94	-169.28	-169.13	-174.34	-171.72	-172.90	-172.95	-169.12	-170.62	-168.30	-166.20
DPG $\delta^{18}O$ vapor (‰)	-21.785	-21.006	-21.984	-20.678	-20.660	-20.123	-20.968	-20.424	-22.482	-22.669	-22.008	-21.200	-20.202	-21.273	-21.155	-21.554
DPG D-excess (‰)	1.579	0.374	1.899	-4.067	-7.369	-9.718	-3.519	-7.740	3.583	8.056	1.003	-5.148	-8.918	-2.697	-0.277	4.870
DPG H_2O average (ppm)	8888	8888	8911	8915	8429	8390	8862	8828	8965	8938	8625	8549	9029	8843	8949	9175

Table S1 continued.

Tubing Type	Teflon (PTFE) short	Teflon (PTFE) long	Copper
Tubing Information	Advanced Technology Products $^{3}/_{16}$ inch ID x $^{1}/_{4}$ inch (PTFE-0304X100)	Advanced Technology Products $^{3}/_{16}$ inch ID x $^{1}/_{4}$ inch OD 100 foot length (PTFE-0304X100)	McMaster-Carr cleaned and capped $^{1}/_{8}$ inch Tube Size, $^{1}/_{4}$ inch OD, 0.03 inch Wall Thickness (5174K21)
Date ran	20 Sept 2022 to 21 Sept 2022	21 Sept 2022	03 Oct 2022
Temperature (℃)	~21 ℃	~21 ℃	~21 ℃
Analyzer air flow speed (L min^{-1})	0.2–0.3	0.2–0.3	0.2–0.3
Replicates (# of enriched-to-depleted δ switches)	4	5	5
Run Length (sec)	3825	3825	3825
WVISS δD vapor (‰)	-27.44	-27.58	-27.28
WVISS $\delta^{18}O$ vapor (‰)	-3.465	-4.180	-1.515
WVISS D-excess vapor (‰)	1.095	5.384	-14.934
WVISS mV	3.90	3.91	3.85
WVISS H_2O average (ppm)	9394	9553	8824
DPG δD vapor (‰)	-180.09	-181.02	-175.29
DPG $\delta^{18}O$ vapor (‰)	-22.813	-23.184	-20.293
DPG D-excess (‰)	2.473	4.883	-11.798
DPG H_2O average (ppm)	9249	9201	9016

S2. Allan variation for averaging interval determination

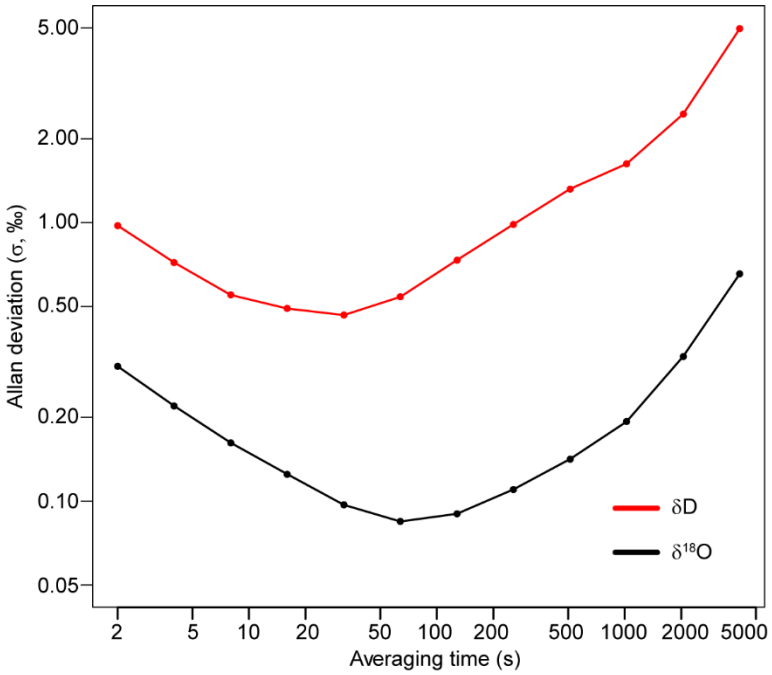

Figure S1. Example Allan deviation (σ) plot for slow analyzer air flow indicates 32 s for δD and 64 s for $\delta^{18}O$ as the optimal averaging times over 4.5 hours of unchanging DPG-produced vapor for δD (red) and $\delta^{18}O$ (black). While a longer averaging time is optimal to reduce noise, we chose 20 s averages as a way to reduce noise without excessively smoothing signal changes. Allan variance was calculated using R's "avar" package (Guerrier et al., 2020).

S3. Switching test results

While Aemisegger (2012) indicated desorption of enriched isotopes takes longer than desorption of depleted isotopes, our results for both the enriched-to-depleted and depleted-to-enriched switches were similar after accounting for a WVISS purge cycle in the depleted-to-enriched transition.

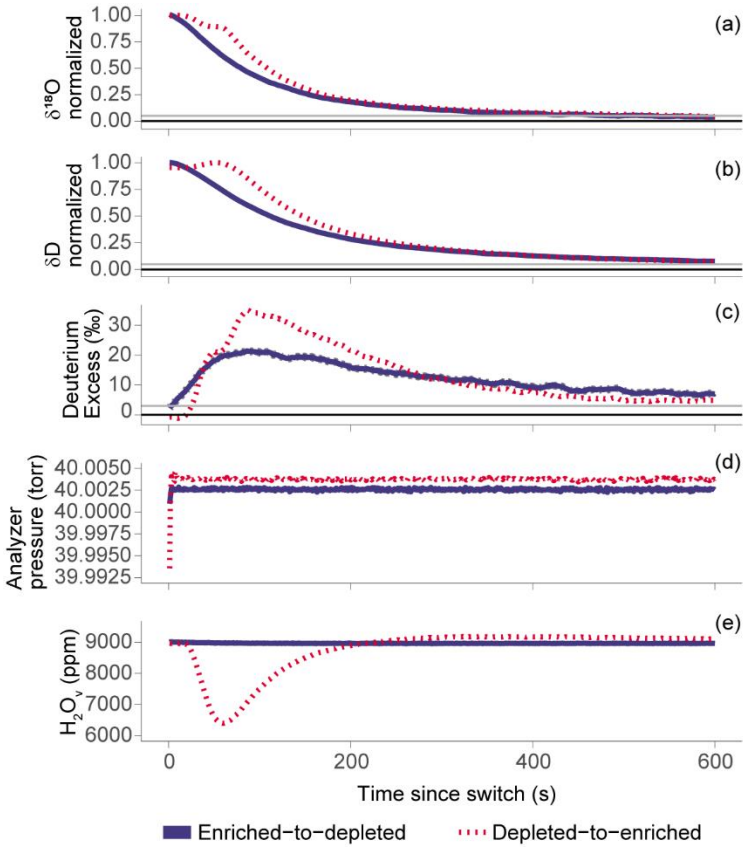

Figure S2. Averaged enriched-to-depleted and depleted-to-enriched transition results for short, thin-walled PTFE for $\delta^{18}O$ (a), δD (b), D-excess (c), analyzer pressure in torr (d), and water concentration (e) plotted as time since switch. Solid lines indicate the enriched-to-depleted switch, while the dotted-dashed lines indicate the depleted-to-enriched switch. D-excess is adjusted to end at 0‰ for each experiment, and δD and $\delta^{18}O$ are normalized from 0–1. Horizontal lines indicate thresholds of y=95% completion for δD and $\delta^{18}O$, and 3‰ for D-excess. There is an isotopic signal artifact created due to a purge cycle when the WVISS initiates, while the transition from the WVISS to the DPG was uninterrupted. Both directions of isotopic switches are similar in terms of δD, $\delta^{18}O$, and D-excess metrics. Lag has not been subtracted from these results.

S4. Thin- and thick-walled tubing test results

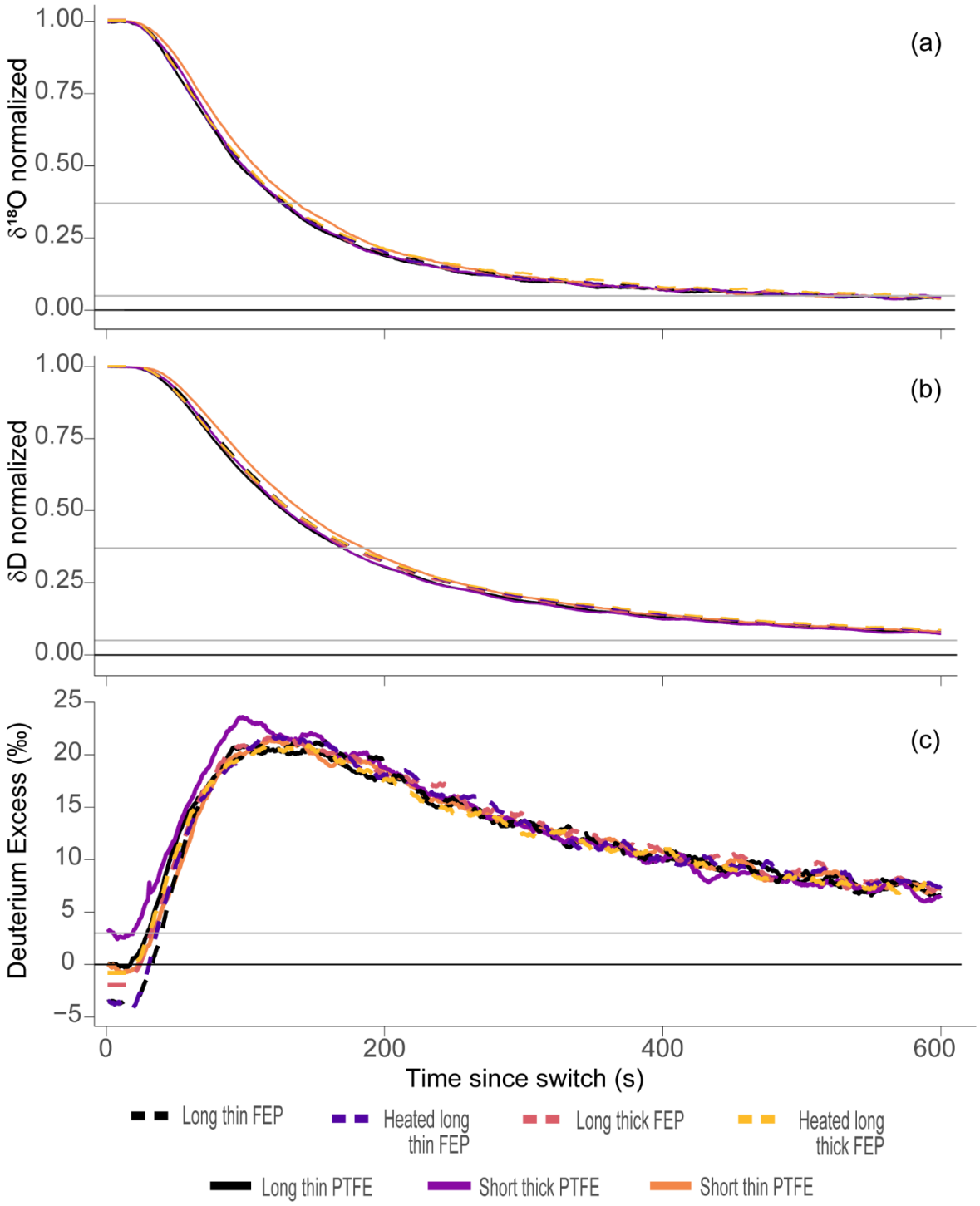

Figure S3. Mean attenuation curves for enriched-to-depleted transitions comparing thin- and thick-walled tubing for $\delta^{18}O$ (a), δD (b), and D-excess (c) plotted over the first 600 s after source switch. Solid lines indicate PTFE tubing, while dotted indicate FEP. The thin-walled long tubing types are black in color. To compensate for small differences in isotopic values between experiments, δD and $\delta^{18}O$ are normalized from 0–1 with zero at the start of the source

switch and 1 at the final value after 1 hour, and D-excess is adjusted to end at 0‰ for each experiment. Gray horizontal lines indicate thresholds of 95% and 63% transition completion for δD and δ^{18}O, and 3‰ for D-excess, while a black line indicates 100% completion for all isotopes. Short and/or thick-walled tubing lengths have been lag adjusted to their long and/or thin-walled counterparts. The rate of isotopic equilibrium appears insensitive to the length of the tubing or the surface area to volume ratio under these conditions.

S5. Non-replicated switching test with and without Omega mass flow meter

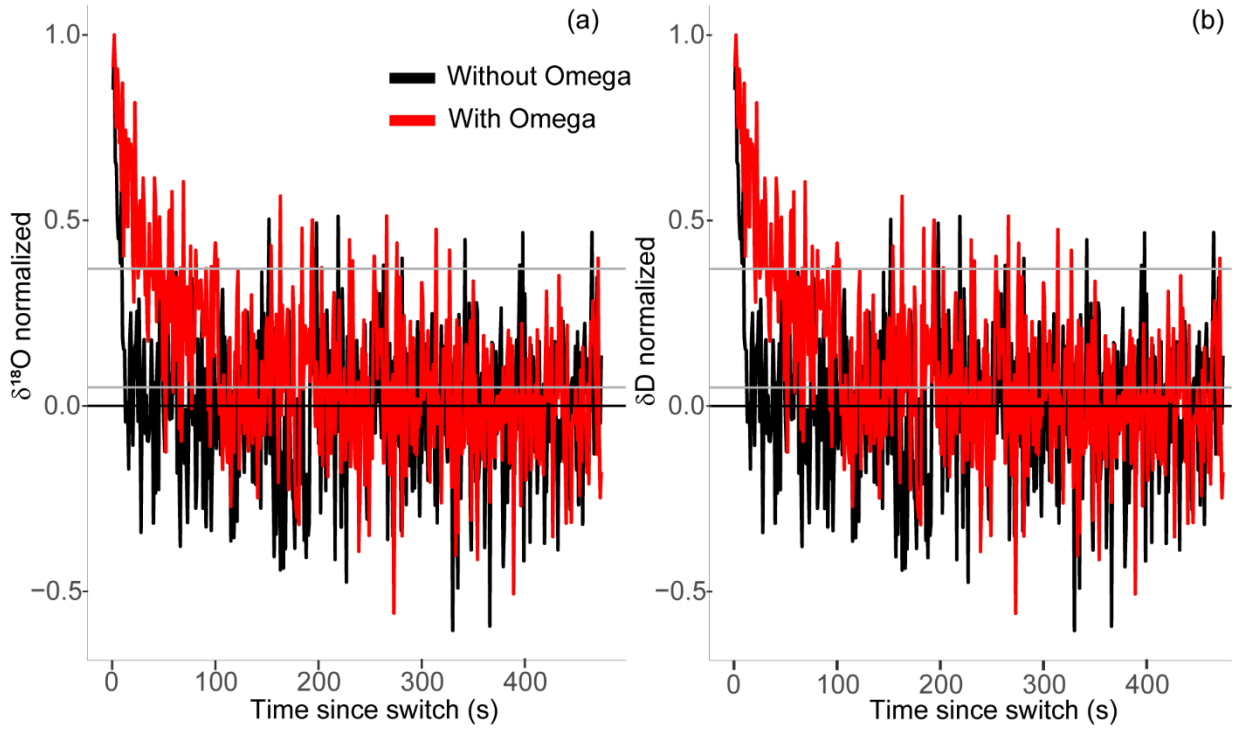

Figure S4. Enriched-to-depleted transition for one replicate with (red lines) and without (black lines) the Omega mass flow meter for δ^{18}O (a) and δD (b) plotted as time after inclusion/removal of the meter. Data workup was similar to all other experiments, except using 1 Hz data with no running mean, the maximum delta value, and the average minimum delta of 400–474 seconds. The Omega slows the total sweepout time.