



Supplement of

A versatile water vapor generation module for vapor isotope calibration and liquid isotope measurements

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Supplementary text:

V1_x are manifold-mounted three way solenoid valves (SMC, VO307-6DZ1-Q, VV307-01-043-01N-F)

V2_x, V3_x, V4_x are manifold-mounted solenoid valves (SMC, VDW23-6W-1-G-Q, VV2DW2-G0401N-F-Q)

Humidity sensor is obtained by combining temperature sensor (Analog Devices, AD22100STZ) and relative humidity (Honeywell, HHH-4000-004).

MFC1 and MFC2 are mass flow controllers for air (Aalborg, model GFC17A)

Dual-valve electronic pressure controller is ALICAT model PCD-5PSIG

Vacuum pump is KNF membrane pump model NMP830KPDC

PID control is achieved by LabVIEW software.

Supplementary Tables:

Name	δD (‰)	$\delta^{17}O$ (‰)	$\delta^{18}O$ (‰)	d-excess (‰)	$\Delta^{17}O$ (per meg)
FL0	6.47	-	0.56	2	-
BER	-2.10 ± 0.17	-0.05 ± 0.02	-0.25 ± 0.02	4	82
SW	-75.63 ± 0.17	-5.5558	-10.56 ± 0.02	9	34
FL1	-81.1	-	-11.65	12	-
WW	-268.30 ± 0.31	-17.9710	-33.881 ± 0.03	2	26
FL2	-308.14	-	-40.06	12	-
SP	-435.31	-29.6497	-55.39	8	-11
AW	-	-	-		17

Table S1: Standards used in this study. Precision (\pm) is the standard error.

Name	SW (g)	WW (g)	Ratio	$\Delta^{17}O$ (ppm)
M20	15.85	3.99	0.2011	21 ± 13
M50	9.93	9.93	0.5000	12 ± 13
M85	16.96	2.98	0.8506	18 ± 13

Table S2: Samples used to perform $\Delta^{17}O$ tests. M20 - M85 resulted from a mixture of SW and WW. Ratio is $WW_{mass}/(SW_{mass}+WW_{mass})$.

Name	Start (Oct. 2022)	Stop (Oct. 2022)	Holder #	Duration (hours)	H₂O mean	H₂O std	n
SP	10 16:18	10 20:18	1	4	17353	118	13790
BER-01	10 20:18	11 04:18	2	8	17296	215	27634
BER-02	11 04:18	11 12:18	3	8	17163	410	27652
BER-03	11 12:18	11 19:18	4	7	17143	571	24202
BER-04	11 19:18	12 02:18	2	7	17067	310	24215
BER-05	12 02:18	12 09:18	3	7	17177	120	24223
BER-06	12 09:18	12 16:18	4	7	17186	560	24224
BER-07	12 16:18	12 23:18	2	7	17265	168	24228
BER-08	12 23:18	13 06:18	3	7	17232	349	24243
BER-09	13 06:18	13 13:18	4	7	17239	318	24222
BER-10	13 13:18	13 20:18	2	7	17242	146	24208
BER-11	13 21:00	14 04:42	3	7	17256	353	26609
BER-12	14 04:42	14 11:42	4	7	17380	113	24189
BER-13	14 11:42	14 12:24	2	<1	17460	204	2418

Table S3: Sequence of standard injected for the long term stability test.

H₂O avg. (ppmv)	H₂O 1σ_{1-sec} (ppmv)	RSD (%)	ΔH₂O/Δt (ppmv/h)	Duration (h)
584	44	7.5	2	6.1
995	30	3.0	11	4.9
2421	101	4.2	29	5.8
4538	18	0.4	10	4.5
7026	82	1.2	24	7.3
8902	44	0.5	10	5.0
11001	47	0.4	-1	6.9
11584	63	0.5	-5	3.5
13856	54	0.4	24	5.6
16047	89	0.6	-1	8.7
17902	89	0.5	-18	3.8
19616	110	0.6	-24	5.4

Table S4: Humidity levels selected to test the short term performances of the vapor generation module. H₂O 1 σ _{1-s} is one standard deviation calculated at standard sampling rate (~1 Hz). RSD stands for relative standard deviation.

For panels (a) and (b)

Data	off	a	b	R²
δ¹⁸O FL0	0.0327 ± 0.0167	-9.3335 ± 4.5600	-0.0054 ± 0.0009	0.9782
δ¹⁸O FL1	0.0292 ± 0.0316	-1.8082 ± 0.454	-0.0016 ± 0.0004	0.9718
δ¹⁸O FL2	-0.0141 ± 0.0610	-4.4829 ± 0.6220	-0.0019 ± 0.0003	0.9965
δD FL0	0.2708 ± 0.2230	15.4957 ± 2.5800	-0.0020 ± 0.0003	0.9805
δD FL1	-0.1496 ± 0.0859	17.3759 ± 8.4800	-0.0031 ± 0.0007	0.9587
δD FL2	0.0391 ± 0.0859	-14.3201 ± 1.3100	-0.0022 ± 0.0002	0.9953

For panels (c) and (d)

Data	off	a	b	R²
δ¹⁸O SD	0.4171 ± 0.0179	3.7372 ± 0.2340	-0.0019 ± 0.0001	0.9943
δD SD	1.2720 ± 0.1060	13.8565 ± 0.9990	-0.0017 ± 0.0001	0.9778

Table S5: Results of the best fits are reported in Figure 6 of the manuscript. Coefficients reported with standard error. H₂O is the mixing ratio in ppmv measured by the CRDS analyzer against the best fit equation: off+a*expb*H₂O

Supplementary Figures

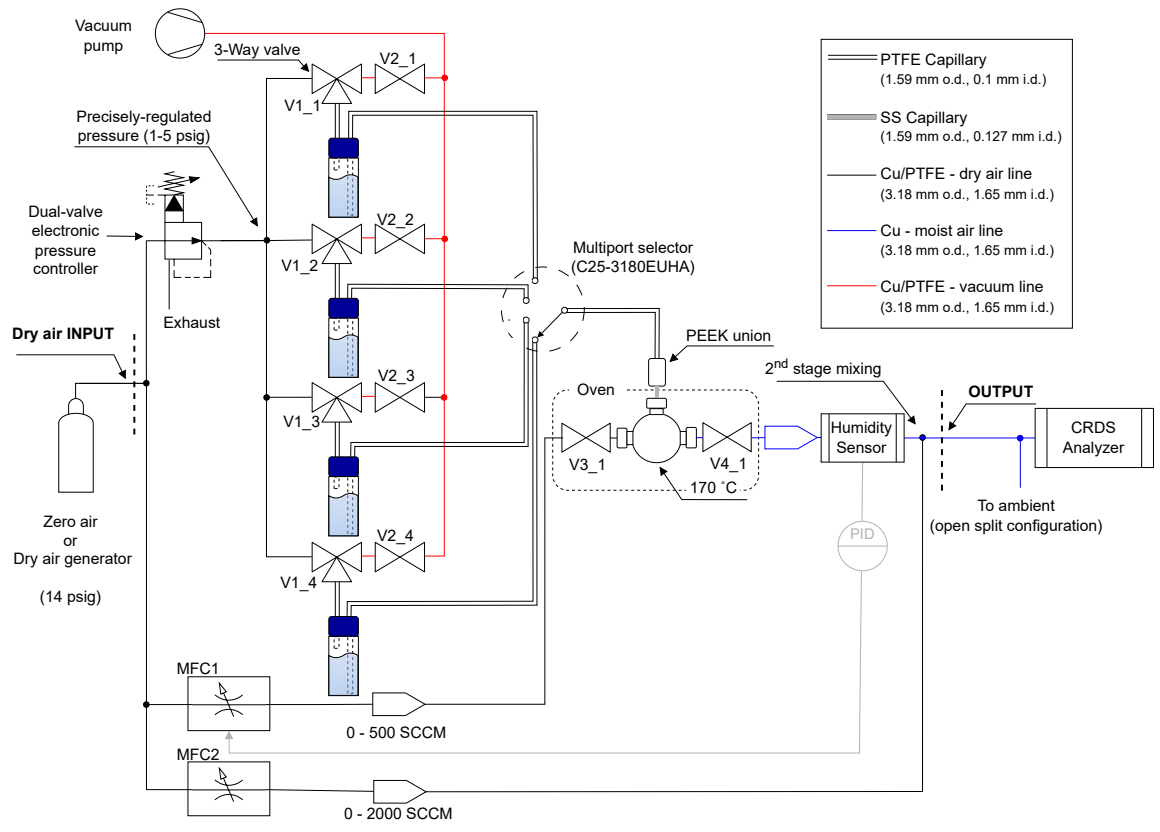


Figure S1: Sketch of the vapor generation module equipped with single oven using Multiport selector.

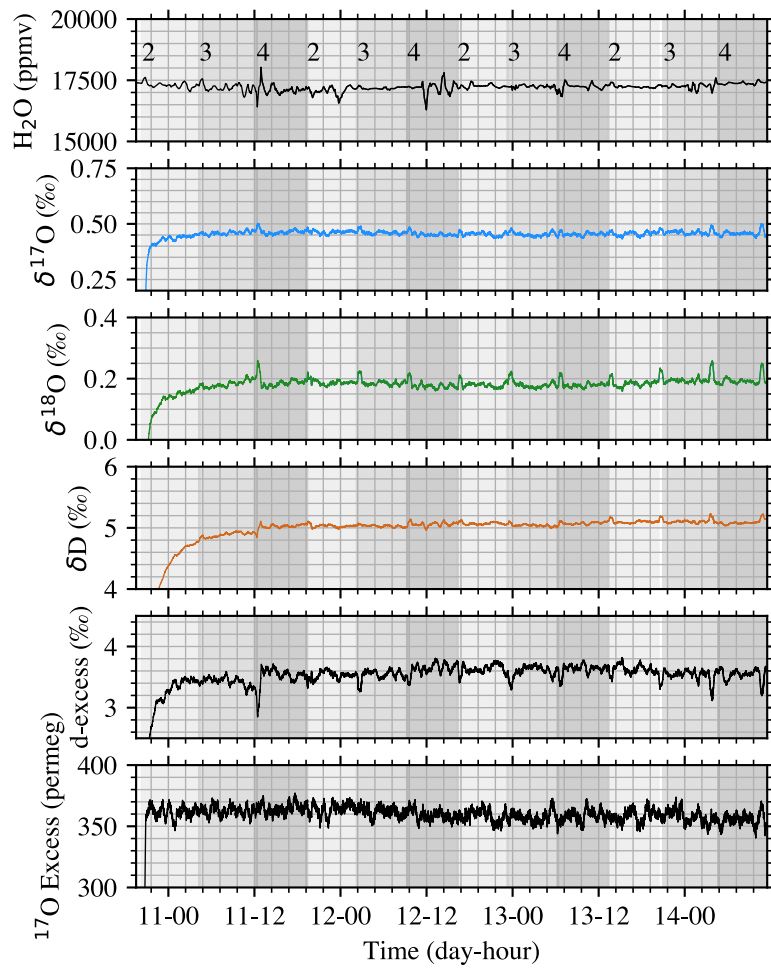


Figure S2: The temporal evolution in the different parameters (Humidity, d¹⁷O, d¹⁸O, dD, d-excess, ¹⁷O-excess) used to generate the Allan Deviation Figure 3 when applied a rolling averaging window of 1800 s.

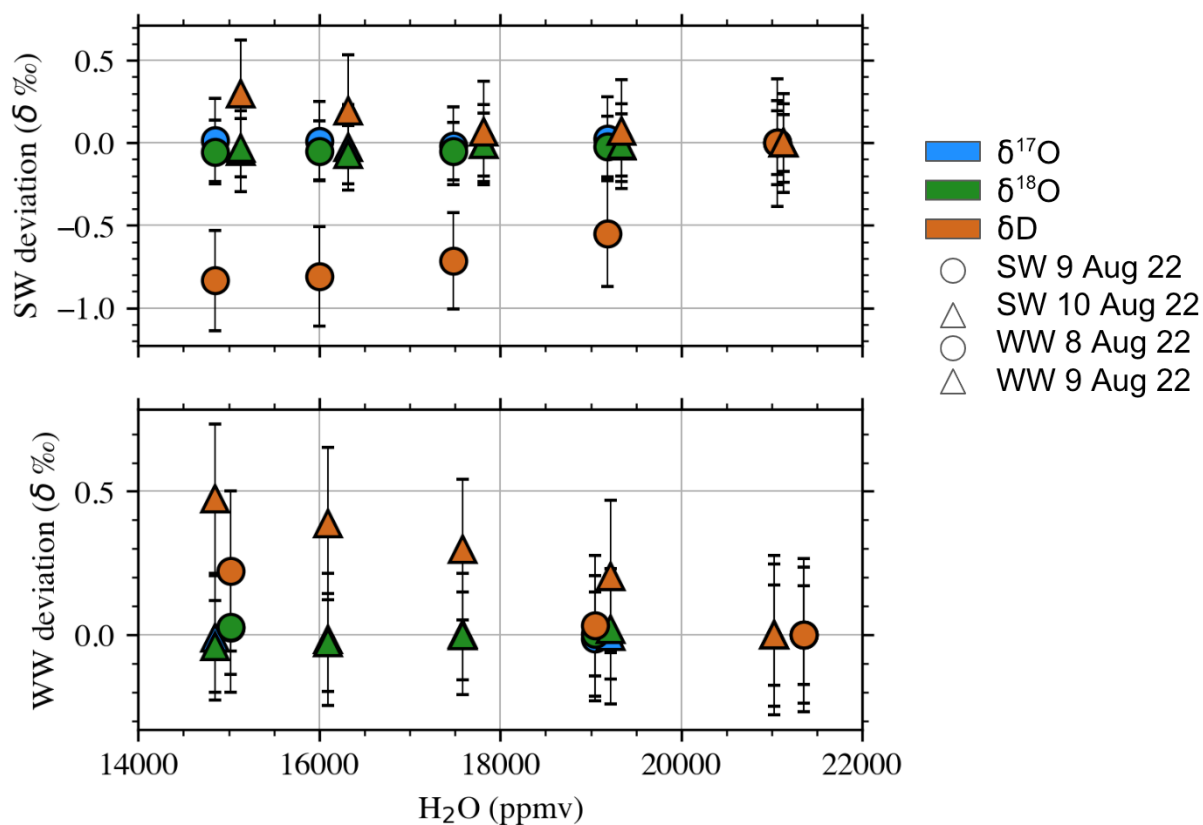


Figure S3: Humidity - Isotope response for SW and WW standards. The humidity-isotope response was investigated for SW and WW standards between 15000 - 22000 ppmv. The figure shows the deviation of the raw isotopic signal for each standard at different humidity levels. The deviation was calculated against the highest humidity value for each run. Different symbols represent different runs (8 - 9 Aug for WW, 9-10 Aug for SW). Error bars are the standard deviation of the raw signal for each level, as measured at 1 second resolution.

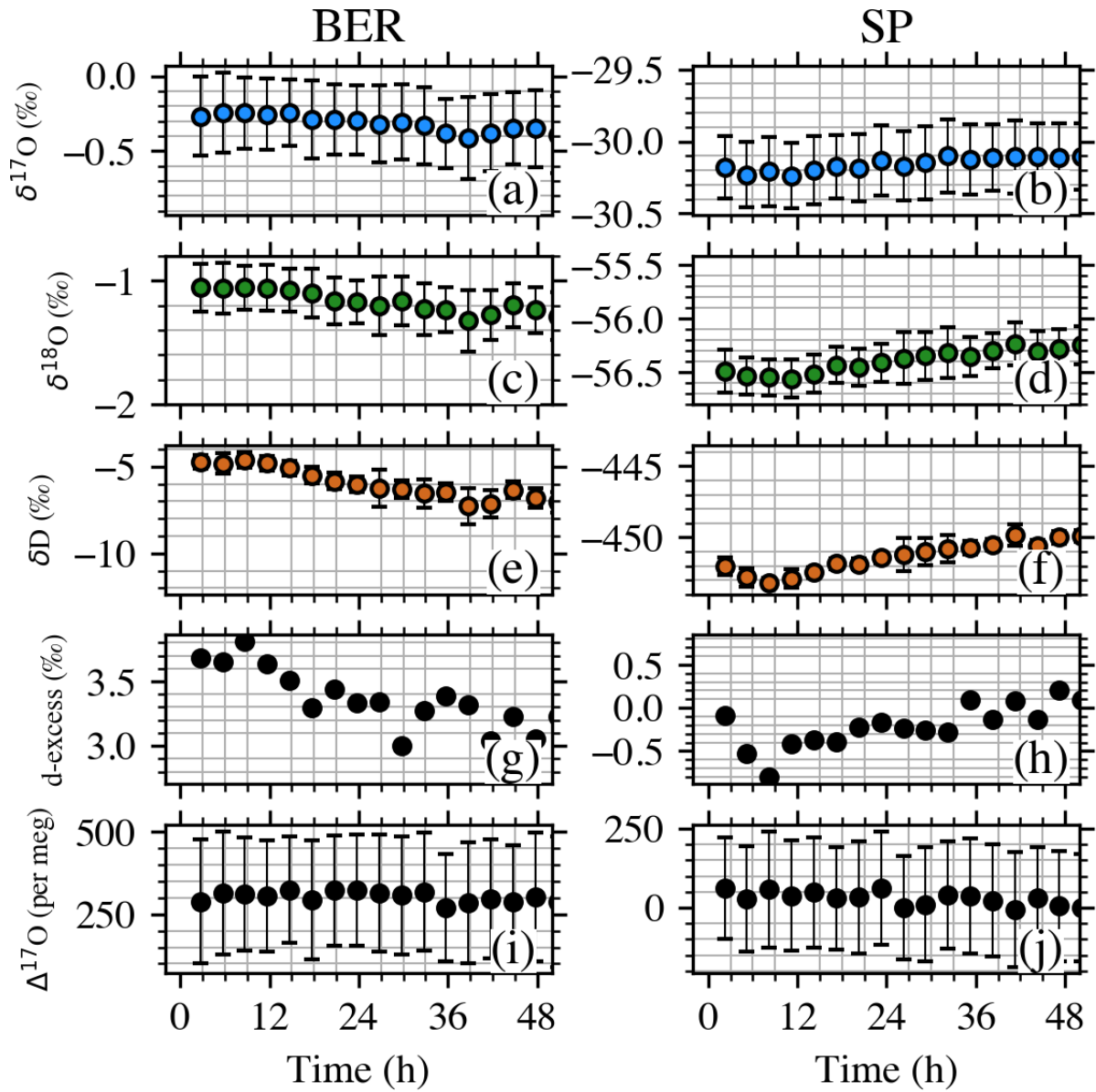


Figure S4: Pulse train test performed with a single oven and a four position selector. Similarly to Figure 8 in the manuscript, results reported as average \pm standard error calculated for the last 5 minutes of $\delta^{17}\text{O}$ (a and b), $\delta^{18}\text{O}$ (c and d), δD (e and f), d-excess (g and h) and $\Delta^{17}\text{O}$ (i and j) signals.

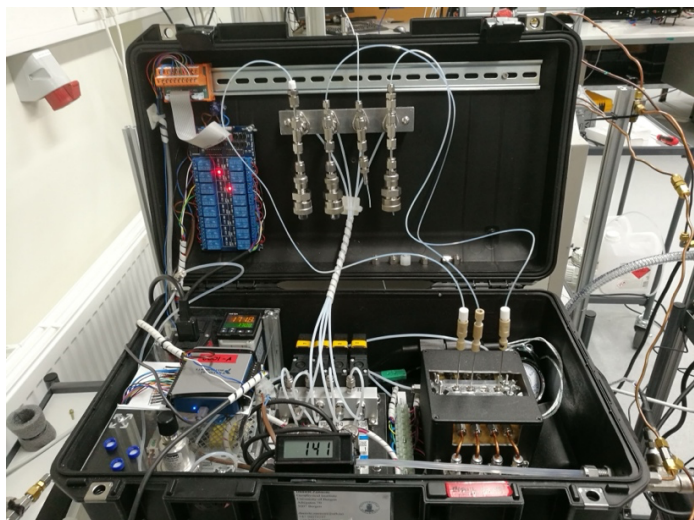


Figure S5: Photo of the vapor generation module as rack mountable version (top) and travel version in a pelican case (bottom) allowing it to go be checked-in as regular luggage.