Automation components and wiring

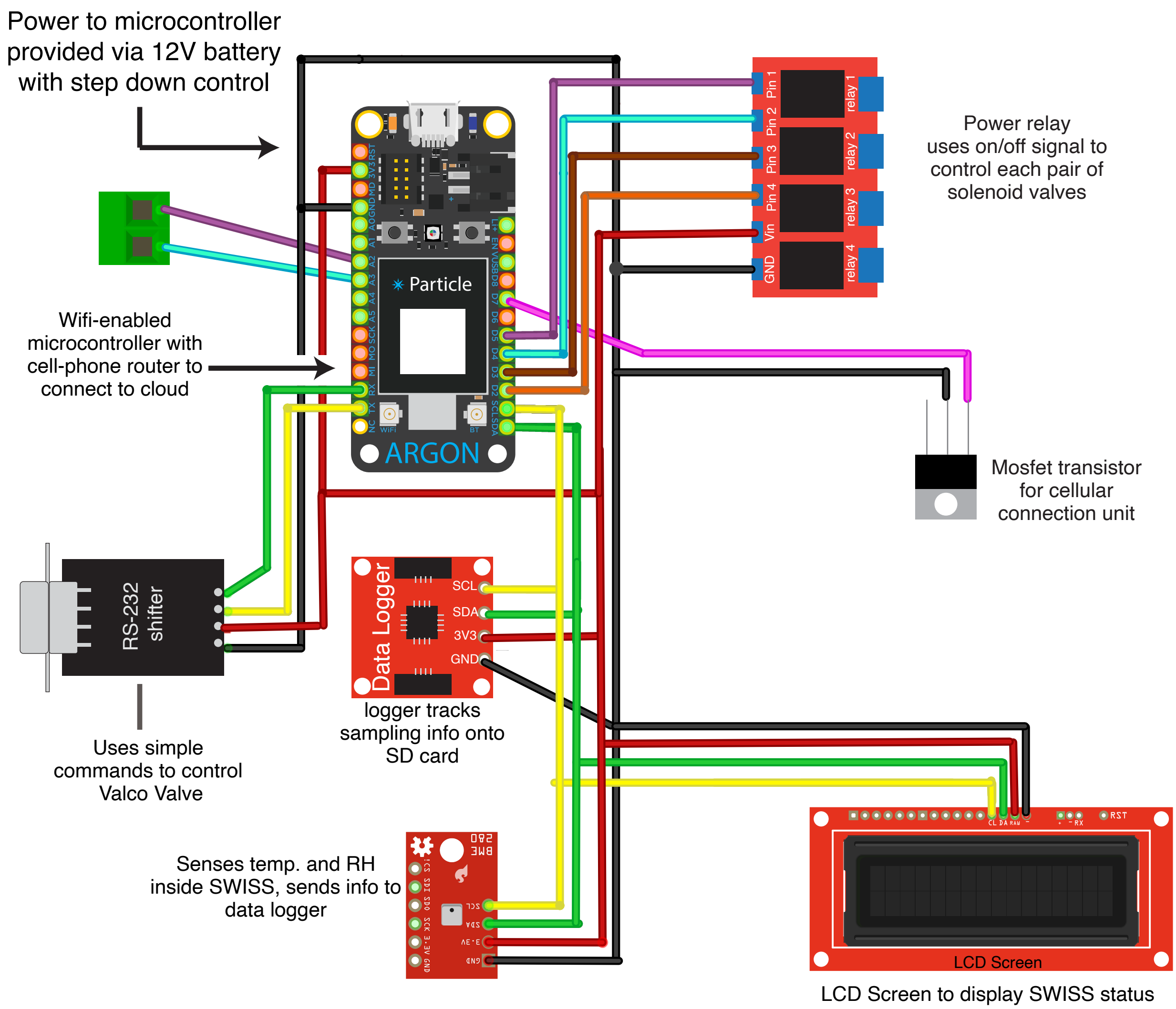


Figure SI 1. Wiring diagram for the components used to automate the SWISS. All of the components can be optimized for each user's needs.

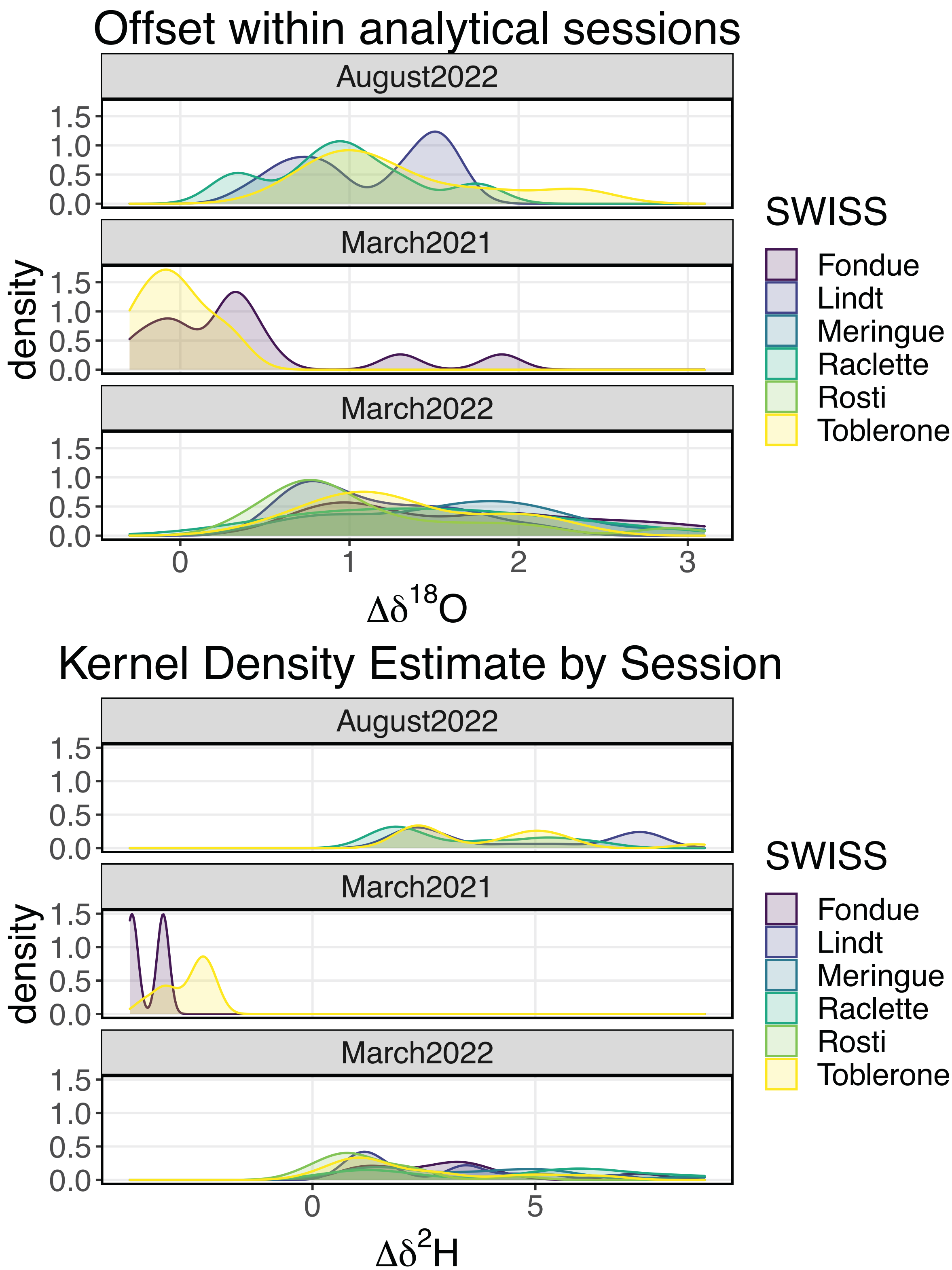


Figure SI 2. Kernel density estimate of the difference between the starting and final δ18O and δ2H values, separated by analytical session.

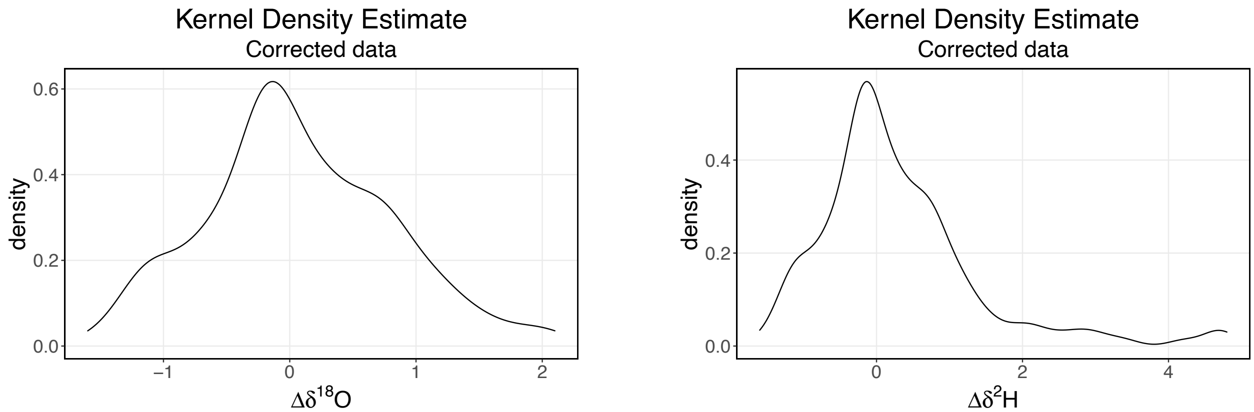


Figure SI 3. Kernel density estimate of the difference between the starting and final δ18O and δ2H values after the offset correction is applied to each dataset.

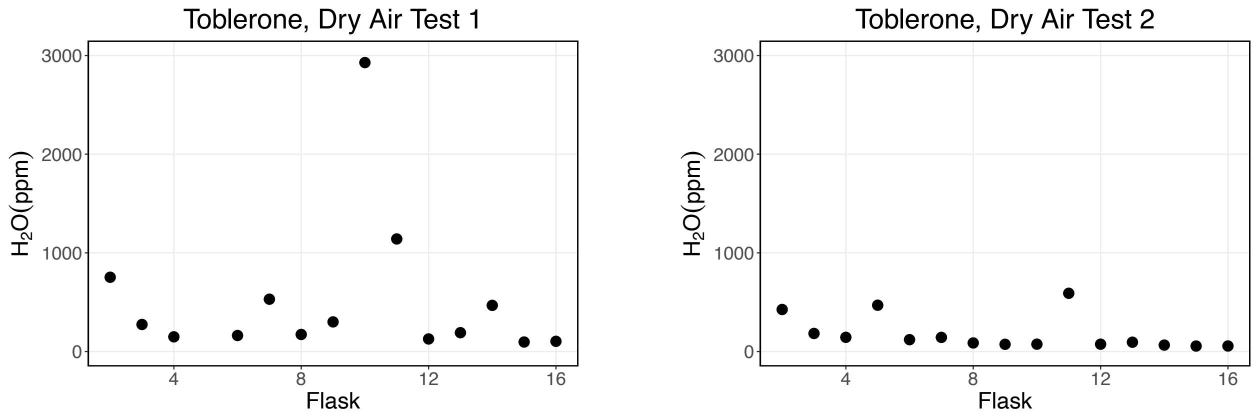


Figure SI 4. The results of two successive dry air tests where we show that tightening of the fittings can significantly improve a flask's resistance to leaking. The dry air test is a time efficient test to find and fix problematic flasks

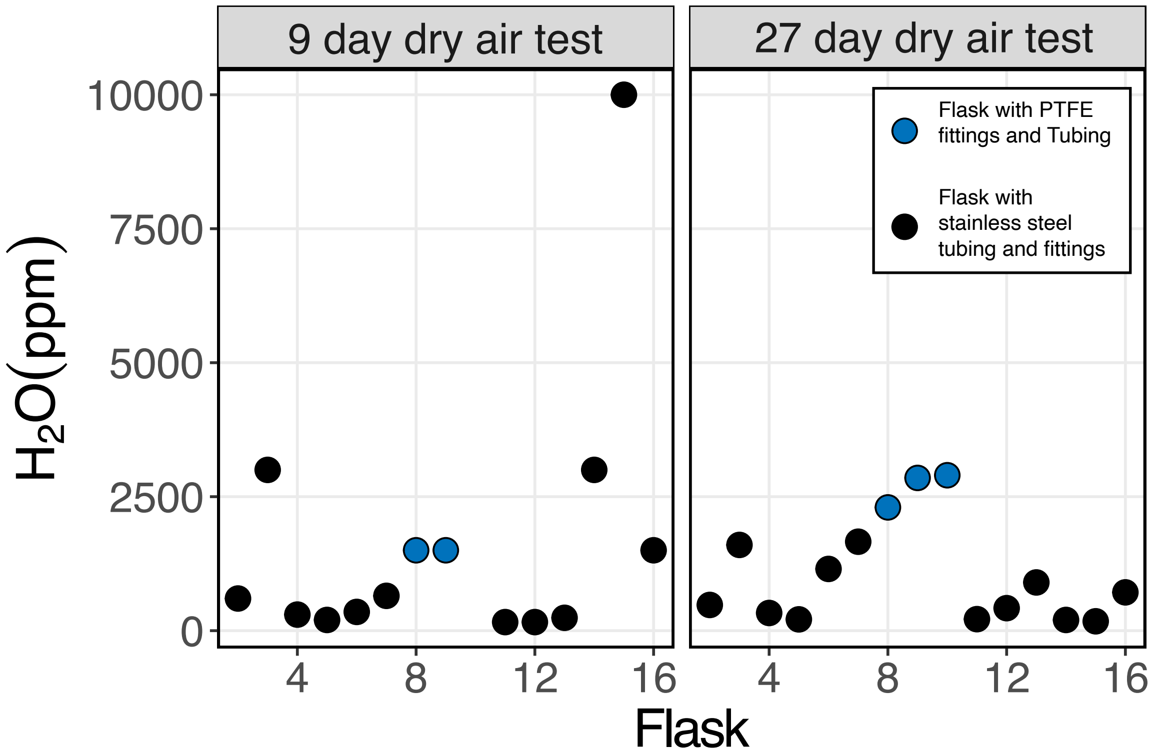


Figure SI 5. The results of a seven day and 27 day dry air test. Flasks 8, 9, and 10 were all fitted with Swagelok PTFE unions and ⅛" PTFE tubing. On a seven-day timescale, the PTFE fittings performed similarly to the stainless steel tubing, but over 27 days, the PTFE fittings performed worse than the other fittings.

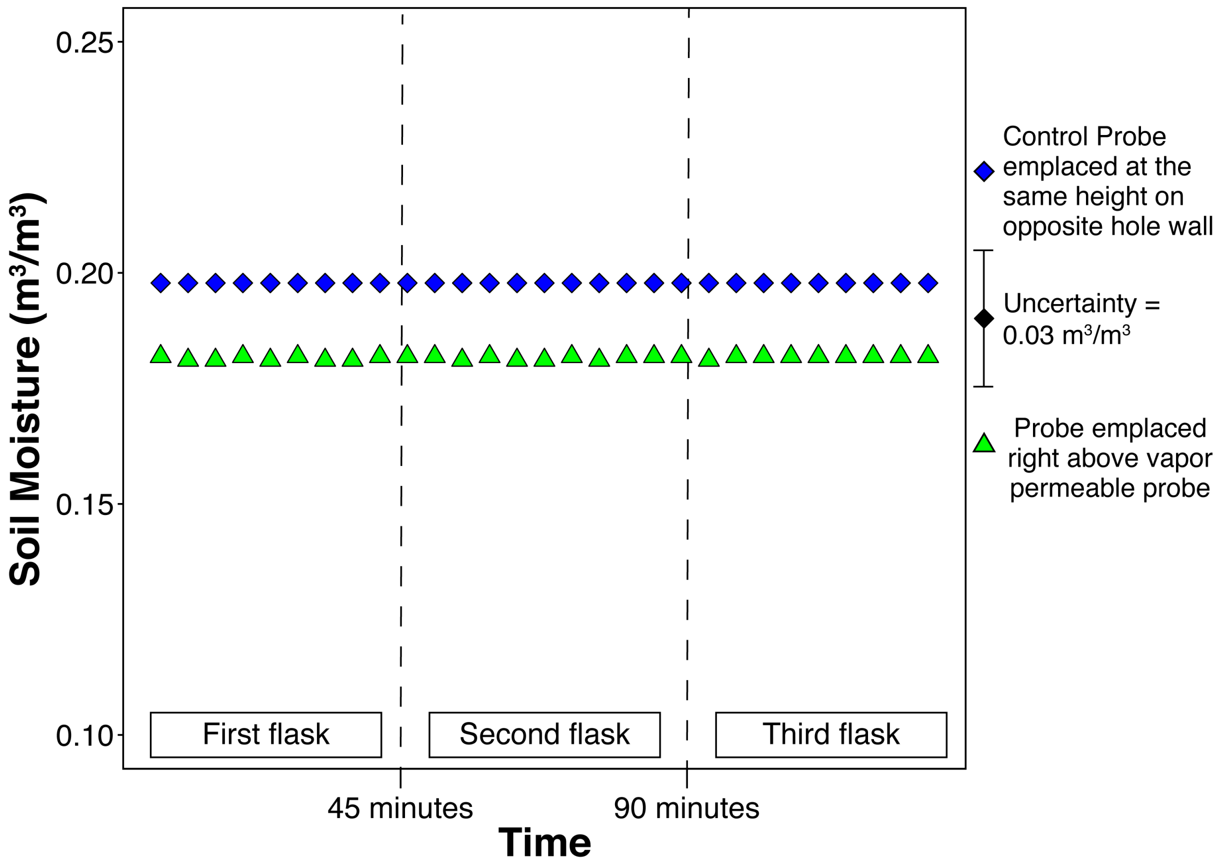


Figure SI 6. Soil moisture test results. Soil moisture was measured every 5 minutes during three consecutive sample collection phases to fill flasks with water vapor. Green triangles indicate the soil moisture measured directly above (< 2 cm away) the vapor permeable membrane probe, blue diamonds represent soil moisture measured at the same height on the opposite wall of the hole. Uncertainty, based on manufacturer specifications, on all measurements is 0.03 m3/m3.

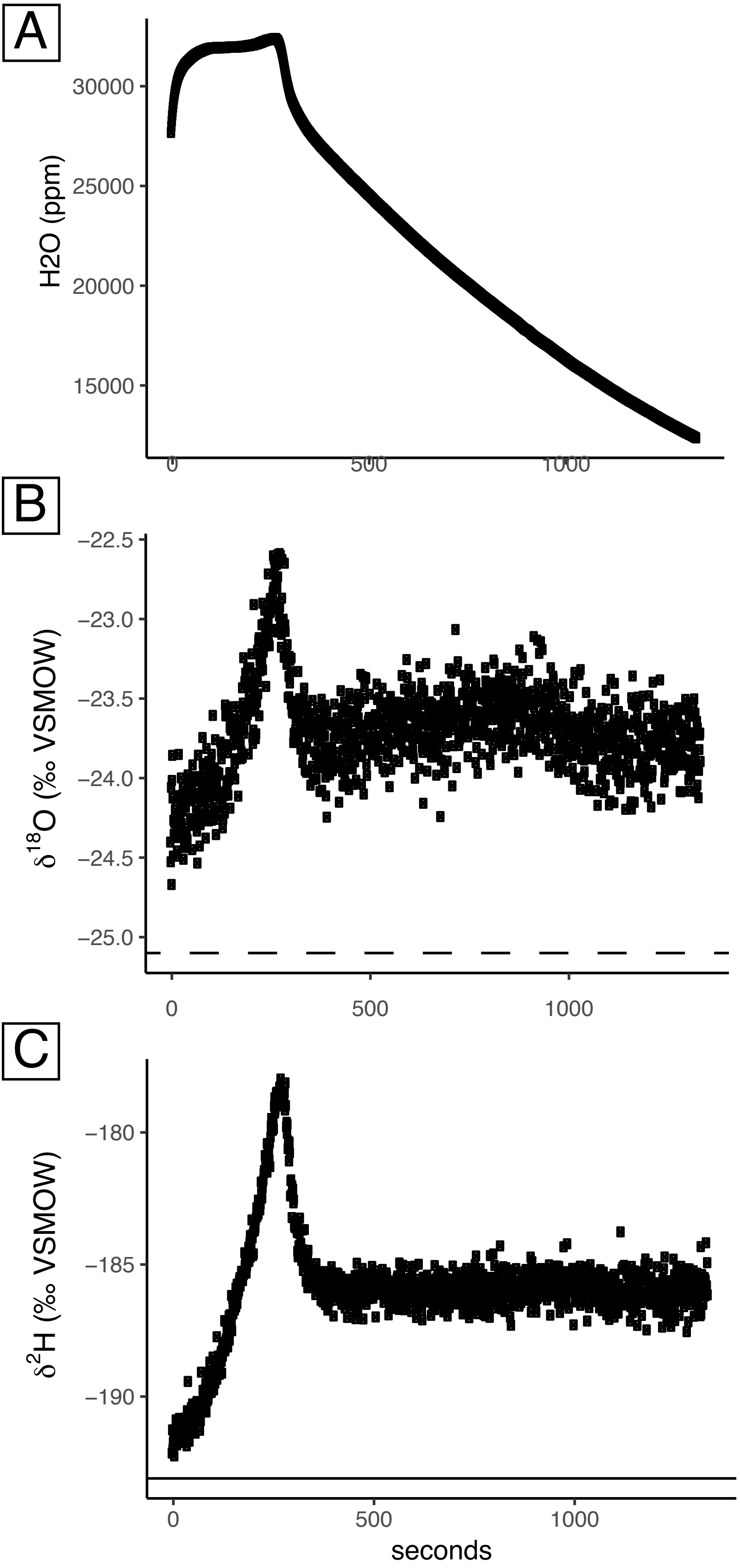


Figure SI 7. A) Plot of water concentration vs. time during the measurement of a flask where there is condensation in the stainless steel tubing between the flask and valco valve. B) and C) are plots δ18O and δ2H, respectively through the same measurement period.

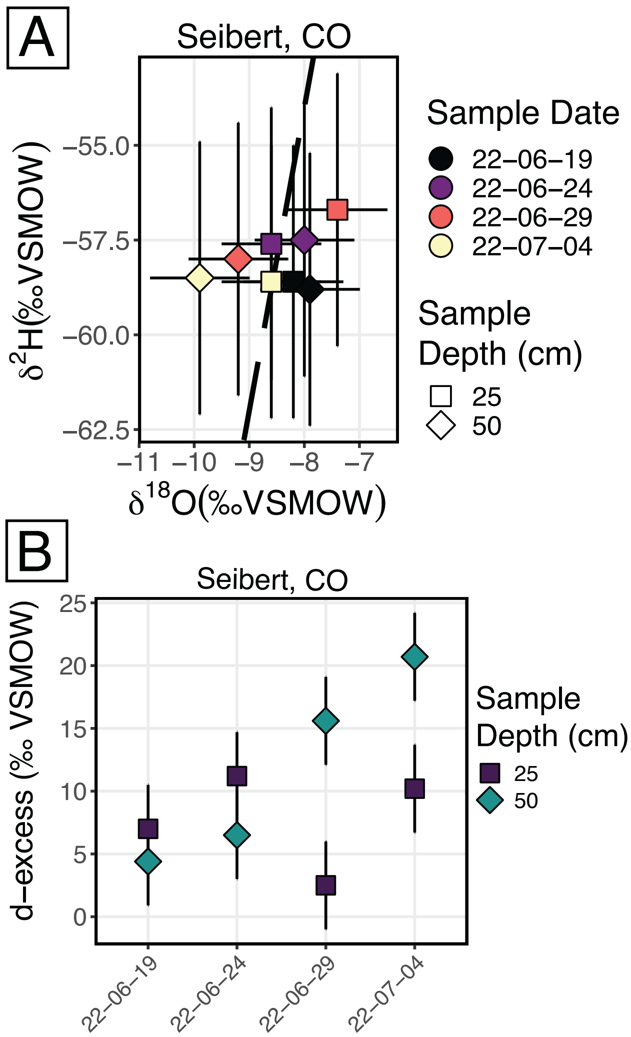
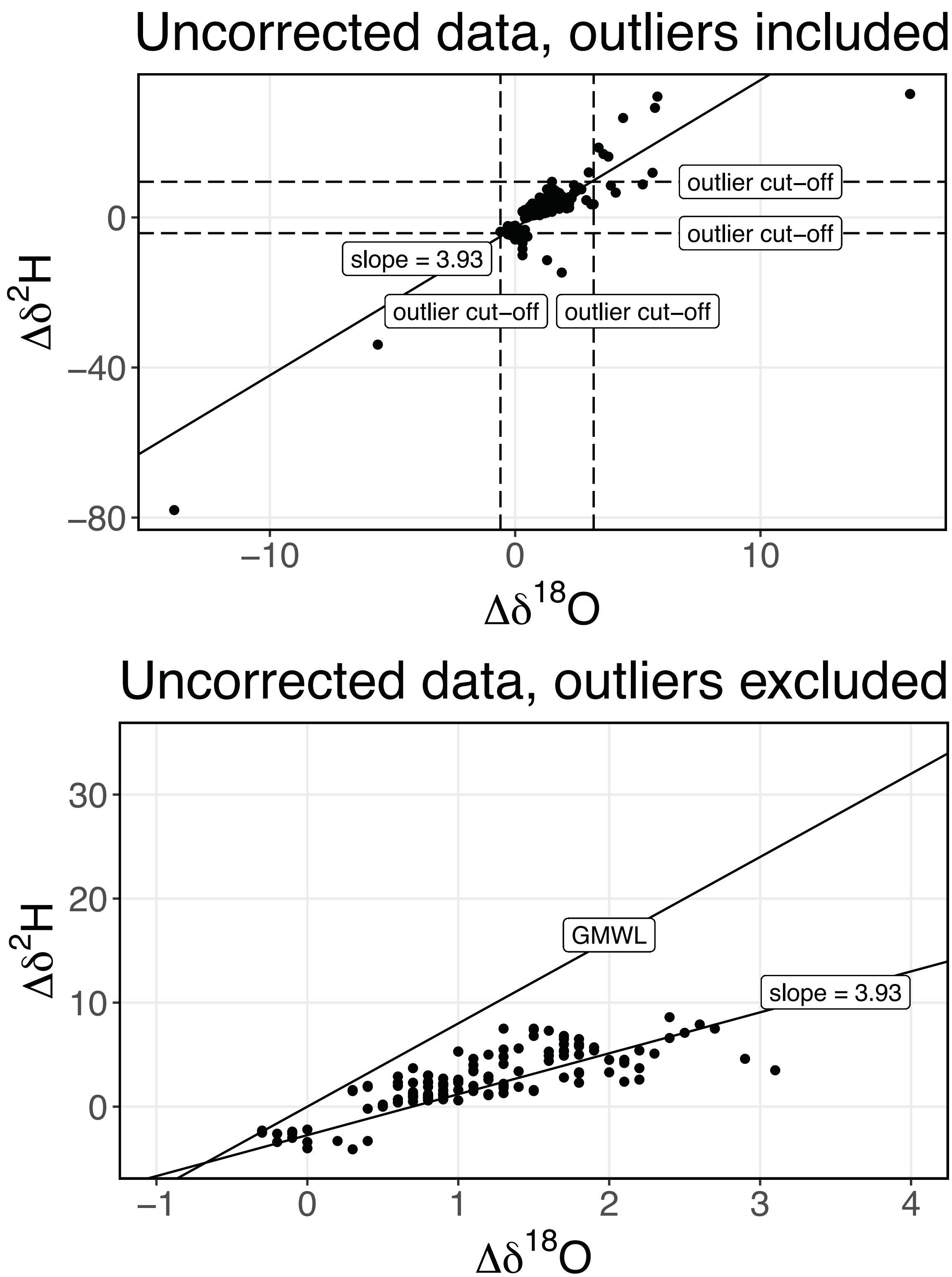


Figure SI 8. The difference between the start and end of the water vapor isotopes during the water vapor tests. The top plot includes all data, and the outlier cutoffs are marked with dashed lines. The line is a calculated linear regression across all of the data. The bottom plot excludes outliers, and also includes the global meteoric water line as a reference slope.



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Supplemental Figure 8

SWISS Hardware			
Item	Source and/or Distributor	Location	Potential Adaptions
650 ml Flasks	Precision Glass Blowing Inc.,	Englewood, Colorado, USA	flask size and dimensions (especially if there are weight concerns)
Valco Multiselector Valve with RS-232 communication	Valco Instruments Co. Inc.,	Houston, Texas, USA	Number of selectable ports ranges from 2 - 16; communication style (e.g. RS-232) can be done in multiple ways
1/8th inch stainless steel tubing	Swagelok	Ohio, USA	
1/4" - 1/8" union fittings	Swagelok	Ohio, USA	
1/4" - 1/4" union fittings	Swagelok	Ohio, USA	
1/4" PTFE Fittings	Ohio Valley Specialty Co.	Marietta, Ohio, USA	
Waterproof, insulated case (61 cm x 61 cm x 61 cm with Pick n' Pluck foam)	Pelican Products Inc.	Torrance, CA, USA	Case size and internal configuration
1/4" push to fit bulkhead fittings	McMaster Carr		
Mass Flow Controller	200 SCCM Flow Controller	Alicat Scientific	Tuscon, Arizona, USA

Vapor Probes			
Item	Part Number	Soure and/or Distributor	Loacation
Vapor Permeable Tubing	ACCURELL PP V8/2HF	3M	Germany
Vapor impermeable tubing	Bev-A-Line® IV Transfer Pump Tubing	Cole-Parmer	Vernon Hills, Illinois, USA
Soil temperature logger	HOBO MX2201	Onset Computer Corporation	Bourne, Massachusets, USA
Soil moisture Logger	S-SMD-M005	Onset Computer Corporation	Bourne, Massachusets, USA
Logging microstation for soil moisture	H21-USB	Onset Computer Corporation	Bourne, Massachusets, USA

Remote Power	
12V Deep Cycle Battery	ECO-WORTHY 12V Lithium Battery, 30Ah Rechargeable LiFePO4 Lithium Ion Phosphate Deep Cycle Battery
12 V, 100 Watt Solar Panel	Renogy 100W 12V Monocrystalline Solar Starter Kit w/Wanderer 30A Charge Controller
DC to AC Power Inverter	Renogy 1000 W 12V Pure Sine Wave Inverter

Table SI 1: A list of parts required to build a SWISS and sample a soil.

Item	Part (where applicable)	Source and/or Distributor	Location	Notes and Potential Adaptions
Microcontroller	Photon Wifi Development Board	Particle Industries Inc.	San Francisco, California, USA	Many microcontrollers are commercially available, and all have their strengths and weaknesses
Normally Closed 2 port Solenoid Valves with 1/4" push to fit fittings	VVX214BO4B, VX2A0AZ1EH, KQ2H07-36NS, KQ2H07-35NS	SMC Corporation of America		Voltage, push to fit fitting size, number of ports available (aka # of sampling depths)
VDC Power relay				Should be able to step either 3.3 V or 5V up to 12 V, multiple options can be found on Amazon
VAC Power Relay	IoT Power Relay II	Digital Loggers	Santa Clara, California, USA	This can be bypassed if the mass flow controller and Valco valve can be directly powered by direct current
RS-232 Shifter				Multiple options can be found on Amazon
Coin Cell Battery holder	Lilypad Coincell Battery holder	Sparkfun	Boulder, Colorado, USA	
Data Logger	Sparkfun QWICC OpenLog	Sparkfun	Boulder, Colorado, USA	

Table SI 2: A list of example parts that can be used to replicate our automation system

SWISS	Days	H2O (ppm)	H2O Standard Dev. (ppm)	SWISS	Days	H2O (ppm)	H2O Standard Dev. (ppm)
Lindt	7	680	43	Fondue	43 Days	695	61
Lindt	7	371	9	Fondue	43 Days	1051	7
Lindt	7	351	7	Fondue	43 Days	262	22
Lindt	7	291	7	Fondue	43 Days	255	15
Lindt	7	278	9	Fondue	43 Days	222	12
Lindt	7	364	13	Fondue	43 Days	291	6
Lindt	7	288	7	Fondue	43 Days	248	9
Lindt	7	292	9	Fondue	43 Days	207	2
Lindt	7	277	8	Fondue	43 Days	408	25
Lindt	7	309	5	Fondue	43 Days	231	10
Lindt	7	464	20	Fondue	43 Days	383	18
Lindt	7	363	6	Fondue	43 Days	1084	14
Lindt	7	376	10	Rosti	34 Days	650	
Lindt	7	460	10	Rosti	34 Days	290	
Lindt	7	351	11	Rosti	34 Days	272	
Raclette	7	534		Rosti	34 Days	260	
Raclette	7	352		Rosti	34 Days	290	
Raclette	7	310		Rosti	34 Days	1600	
Raclette	7	371		Rosti	34 Days	810	
Raclette	7	310		Rosti	34 Days	800	
Raclette	7	305		Rosti	34 Days	290	
Raclette	7	374		Rosti	34 Days	270	
Raclette	7	292		Rosti	34 Days	365	
Raclette	7	321		Rosti	34 Days	355	
Raclette	7	523		Rosti	34 Days	320	
Raclette	7	428		Rosti	34 Days	515	
Raclette	7	267		Rosti	34 Days	420	
Raclette	7	265		Toblerone	52 Days	2123	57
Raclette	7	269		Toblerone	52 Days	2535	422
Raclette	7	261		Toblerone	52 Days	1728	452
Toblerone	7	546	10	Toblerone	52 Days	554	13
Toblerone	7	336	2	Toblerone	52 Days	1981	438
Toblerone	7	311	7	Toblerone	52 Days	500	75
Toblerone	7	275	6	Toblerone	52 Days	2207	460
Toblerone	7	258	9	Toblerone	52 Days	1189	401
Toblerone	7	259	6	Toblerone	52 Days	1212	413
Toblerone	7	248	9	Toblerone	52 Days	1509	458
Toblerone	7	211	5	Toblerone	52 Days	483	17
Toblerone	7	207	6	Toblerone	52 Days	623	11
Toblerone	7	225	7	Toblerone	52 Days	410	8
Toblerone	7	190	7	Toblerone	52 Days	328	7
Toblerone	7	225	7	Toblerone	52 Days	423	9
Toblerone	7	181	5				
Toblerone	7	173	6				
Toblerone	7	171	7				

Table SI 3: Results of the dry air tests

SWISS	Days	Session	Δ $\delta^{18}O$ (‰)	Δ $\delta^{2}H$ (‰)
Lindt	14	Aug-22	0.6	1.8
Lindt	14	Aug-22	0.5	6.9
Lindt	14	Aug-22	-0.4	0.3
Lindt	14	Aug-22	0.5	4.8
Lindt	14	Aug-22	0.6	4.7
Lindt	14	Aug-22	-0.1	-0.4
Lindt	14	Aug-22	-0.3	-0.3
Lindt	14	Aug-22	-0.1	-0.4
Lindt	14	Aug-22	-0.6	-0.6
Lindt	14	Aug-22	0.5	4.9
Lindt	14	Aug-22	0.5	4.2
Lindt	14	Aug-22	-0.4	-0.3
Lindt	14	Aug-22	-0.2	0.4
Lindt	14	Aug-22	0.3	2.9
Lindt	14	Aug-22	0.3	4.9
Raclette	14	Aug-22	0.7	3.4
Raclette	14	Aug-22	0.0	2.7
Raclette	14	Aug-22	0.0	2.7
Raclette	14	Aug-22	0.0	-1.0
Raclette	14	Aug-22	0.3	-0.6
Raclette	14	Aug-22	-0.2	-0.3
Raclette	14	Aug-22	0.1	1.4
Raclette	14	Aug-22	0.3	2.2
Raclette	14	Aug-22	0.8	3.9
Raclette	14	Aug-22	-0.6	-0.7
Raclette	14	Aug-22	-0.7	-1.0
Raclette	14	Aug-22	-0.3	1.1
Raclette	14	Aug-22	-0.2	-0.7
Raclette	14	Aug-22	-0.7	-1.1
Raclette	14	Aug-22	-0.1	0.1
Toblerone	14	Aug-22	-0.2	-0.2
Toblerone	14	Aug-22	1.4	6.0
Toblerone	14	Aug-22	0.3	1.5
Toblerone	14	Aug-22	-0.4	-0.6
Toblerone	14	Aug-22	0.9	3.1
Toblerone	14	Aug-22	-0.1	-0.4
Toblerone	14	Aug-22	1.3	2.5
Toblerone	14	Aug-22	0.1	2.0
Toblerone	14	Aug-22	0.0	0.0
Toblerone	14	Aug-22	0.0	-0.3
Toblerone	14	Aug-22	0.2	2.4
Toblerone	14	Aug-22	0.4	3.0
Toblerone	14	Aug-22	0.7	2.3
Toblerone	14	Aug-22	0.0	-0.2
Toblerone	14	Aug-22	-0.2	0.4

Table SI4: Results of the water vapor tests

Supplement Section 1: Detailed Build-Out description

This supplement describes how to build a SWISS as we have built ours. There are many places where the system could be modified or adjusted based on a user's needs.

Step 1: Prepare the storage case

To prep the case for the build out the two main tasks are:

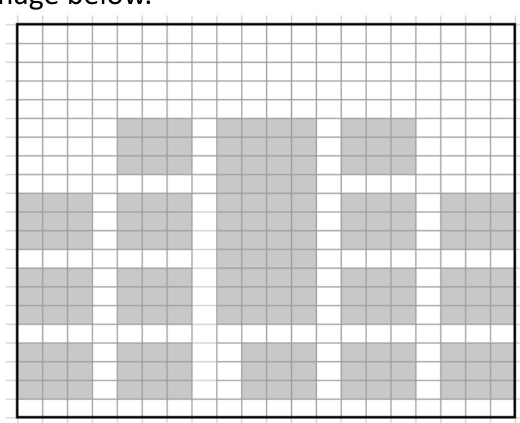
1. Pluck the foam so you can place the Valco stands & flasks
2. Drill the holes that you'll put the air and power cords through. I like to put the holes in the back (the one side without latches) so its easiest to route cords without having to go over the flasks later on.

Materials and tools needed for step 1:

- Pelican 0370 Protector Cube Case with Pluck n' Peel foam
- ¼" Push-to-fit Bulkhead Fittings (e.g. **5779K677**) (2 per sampling depth + 1 for the dry air inlet)
- Cordless drill

Plucking foam:
Inside your pelican case there are 7 pieces of foam: one base piece, 4 layers of Pluck N' Peel (we'll work with the top three) & two lid pieces. Each pluckable piece is 1" x 1" x 4" (l x w x h). For each flask we need to pull out a zone that is 3" x 3" X 12".

Working from the top piece of pluckable foam, pull out 15 3x3 holes for the flasks and one section that is 4" wide and 11" long. My preferred layout is to have the Valco valve hole in the center of the box, a row of 5 flask holes along the front, and 5 flasks arranged on either side of the valco valve, like in the image below.



Pull out the same pattern from the second and third pieces of foam. Note: the pieces are not all the exact same size and so they won't align perfectly.

Holes:

While there aren't breakable glass flasks in the box it can be nice to drill the holes you'll eventually feed power and sample air through. Drill one hole for each push to fit bulkhead fitting you will need, making the hole as small as allowable. I prefer to drill these holes on the back of the box so that my tubing can efficiently run out the box, and won't interfere with the valco at all. You will also want to eventually drill one hole for the power cords, but that one can be done later once power is all worked out. I tend to drill this hole on the side of the box to make cord management easier.

Step 2: Mount Valco valve vertically

Materials and tools:

- Wood
- Wood screws
- 6 X 1/8" diameter, 2" long machine with nuts and washers
- Valco valve and associated cords
- Hand drill

We used scrap 2x4's to build stands to mount the valco valve so that the head of the valco valve is positioned up. We used a 12" vertical piece, attached to an 11" horizontal piece of wood with screws. The Valco valve was then mounted onto the wood with 1/8" diameter, 2" long machine screws so that there was a 4" gap below the back of the valco valve so that cords can be plugged in/unplugged as needed.

** Note: it is very advantageous to attach all of the necessary cords (RS-232, power, display) at this step - it is very tricky once it is placed inside the box.

Step 3: Prep stainless steel tubing

Materials and tools:

- 316 Stainless Steel 1/8” OD tubing
- Tube cutter
- De-burring tool
- Optional: aluminum ⅛” OD tubing for mocking up tubes and string
- Valco valve fittings
- ⅜” wrench
- Valco valve

With a flask placed in each spot in the case, and the valco valve mounted and placed in the correct location, use aluminum tubing to create a mock-up tube that goes from the correct Valco valve port to the desired flask location. As you mock the tubing up make sure to have the tubing that attaches to the valco valve be completely vertical for 1 - 1.5” so that as you tighten the swagelok fittings there is no angular force. Don’t forget to make a jumper loop on port 1 of the valco valve, as well as an inlet and outlet tube!

Then use string to measure the length of each mock-up. Cut the ⅛” stainless steel tubing to the correct length. Be sure to thoroughly de-bur and clean the tubing after cutting. Any small pieces of stainless steel tubing that make its way into the Valco valve can scratch and wear down the valco valve, making it leaky.

Then, once all of the tubing has been cut and de-burred, use the mounted Valco valve to attach the fittings to one side. Make sure that the ferrule is clamped down and can no longer slide around.

Step 4: Prep glass flasks

I find it easiest to put the Swagelok fittings onto the glass flasks prior to putting them into the box.

Materials and tools:

- Glass flasks
- ¼” to ⅛” reducing union fittings from Swagelok
- PTFE ferrules
- ½” and 9/16” wrenches

I like to take a piece from the lid and the topmost plucked foam piece and to put all the flasks out into their spots. I then take all of the ¼”-1/8” (32) reducing unions from the box, and remove the stainless steel ferrule from the ¼” side. I take a spare piece of bev-a-line or other flexible ¼” tubing, and put the stainless steel ferrules onto the flexible tubing to save for other uses. They’re good to save because each ferrule set is about $2.50. I then put the ¼” caps on all the flasks, followed by a ¼” teflon ferrule from ohio valley. I typically buy about 20 extra teflon ferrules per SWISS box because you will inevitably break a few flasks as you go through the building process, and they’re nice to just have on hand. Then tighten the rest of the union fitting onto the glass flask.

Step 5: Bend the stainless steel tubing

<u>Materials and tools:</u>

- Tube bender
- Mounted valco valve
- Prepped stainless steel tubing
- Prepped flasks placed in case

Bend the stainless steel tubes attached to the valco valve so that they easily slide in and out of the swagelok fittings.

Pro-tips:

1. I position all of the flasks to start so that the center tube (the long one that goes to the bottom) is on the left side – and I attach the bottom Valco fitting to the center tube. I've done this so that is my inlet side and so air gets pushed down to the bottom and then you flush out the top.
2. While I'm tube bending, sometimes I flip the position of the flask – but still make sure the bottom goes to the center tube. Particularly for the flasks on the far right side of the box, it can be helpful to twist them around so you have a lot more room to fit wrenches in.
3. You should aim to have the portion of the tube that attaches to the flask to be completely vertical for 1 - 1.5" because the Swagelok fitting has to perfectly line up, otherwise you'll snap the tube in the tightening process.
4. As much as possible don't have tubes crossed – it makes your life a pain later if you need to replace something.

Step 6: Tighten Swagelok fittings

Materials and tools:

- Wrenches

Use an extra union fitting to tighten the swagelok ferrules onto the stainless steel tubing. Then, attach and tight the stainless steel tubing to the union fittings. This is the most common step where flasks break. Go slowly and patiently through this step.

Supplement Section 2: Detailed Protocols for QA/QC

Terminology:

- Dry air fill: Flush flasks with dry air for a period of time such that the air in the flask is fully turned over 10 times.
- Water vapor fill: Flash flasks with water vapor of either known or unknown composition such that the gas in the flask is fully turned over at least 5 times.
- Dry air test: A short (e.g. 7 day) test where dry air is put into the flasks, allowed to sit for a period of time, and then the water vapor molar fraction is measured at the end of the test. The goal is for flasks to maintain a low water vapor mole fraction.
- Dead end pull measurement: There is no input of dry-air into the flasks during a measurement period. A cap is placed over the inlet tube on the Valco valve. During the dead-end pull method, there is no supply of a carrier gas and the picarro intakes gas at a rate of approximately 29 - 31 ml/min.
- Carrier gas measurement: Dry-air or dry-N_2 is supplied to the inlet of the Valco valve at a rate of 30 ml/min during the measurement phase. It is expected that fractionation would occur as pressure decreases, and so using a carrier gas prevents large pressure changes that might induce fractionation.

Dry Air Test Protocol:

Fill: We used air filtered through drierite (100 - 300 ppm), flowing at a rate of 2 L/min to flush each flask for 5 minutes. At this rate, the air in each 650 ml flask turned over 15 times. At the time of filling the flasks, we noted the molar fraction of water vapor in both the ambient atmosphere and the dry-air.

Hold period: We recommend at least 7 days, however, shorter timescales could be used

Measure: Use a *dead end pull measurement* style to measure flasks for 5 minutes. Do not use a carrier gas, because it will dilute the signal.

Data Processing: To determine the water concentration in each flask, we marked the time the flask opened using the ‘outlet valve’ value from the Picarro. For each new flask we saw the pressure wave as a peak in the Outlet Valve value. The advantage of using this method is that it is also easy to identify flasks that are likely leaking based on an outlet valve value that is lower and more similar to an ambient pressure value. After marking the start of each flask, we then removed the first 90 seconds of that measurement to discard any memory effects in either the tubing from the swiss to the picarro or the picarro itself. We then averaged the concentration across the subsequent 180 seconds. The code for this process is available via github.

How to ‘pass’ this protocol: Maintain a water vapor mixing ratio of less than 500 ppm.

Water Vapor Test Protocol:

Fill: Flush flasks with water vapor of known composition produced using the vapor permeable probes at a rate of 150 ml / min for 30 minutes. For a 650 ml flask, this is approximately 6 full turnovers of the water vapor in the flask. We found that 5 full turnovers was the minimum number required to get water vapor molar fraction values that were stable within ± 100 ppm for the final three minutes of the measurement period.

Hold period: We recommend at least 14 days. If the desired storage time is longer than one month, we recommend testing your system with a longer storage period.

Measure: Prior to the start of measuring each flask, we ran dry air via the flask bypass loop for 5 minutes to sufficiently dry and remove memory effects in the impermeable tubing that runs between the SWISS. During that five minute period, lightly warm the flasks and tubing. The goal is to make sure that everything is uniformly warmed to just at or above room temperature so that there is no condensation. This is especially important for the valco valve and stainless steel tubing. Using the *carrier gas measurement* method, measure each flask for 10 minutes. Closely monitor each flask for signs of condensation (i.e. increasing water vapor mole fraction through the measurement, associated with increasing isotope values). Also closely monitor the water concentration right after switching back to the bypass loop, if the water concentration stays the same or increases with a marked increase in isotope values, mark that flask as problematic.

Data Processing: To mark the start of each flask, we used the rapid increase in water vapor mole fraction as the start time. We then discarded the first three minutes of measurement, and averaged the next 3 minutes (see supplemental figure).

How to 'pass' this protocol: After applying an offset correction, flasks should be evenly distributed about 0, and ideally within the uncertainty of the vapor permeable probes ± 0.5 ‰ and ± 2.4‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively (Oerter et al., 2017).